

New Model of seven layers in PEMFC

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ABSTRACT

This model is an isothermal, isobar, one-dimensional and steady-state model for a polymer electrolyte fuel cell with a 117 Nafion membrane. In former years, Springer and colleagues presented the model for five-layer, in which the anode and cathode catalyst layer regardless available. On the other hand, Chen and Chang presented another the five-layer model that was ignoring the input anode and cathode channel, while this model has studied seven layers of fuel cell. Model results show that with increasing current density, concentration of water in the cathode electrode is increased and water vapor may be a serious problem for the hole blocking gas diffusion layer and catalyst layer and reduce the amount of oxygen transport. Therefore, if the relative humidity reduce to about 80%, membrane can be kept in the suitable moisture and flooding of water is controllable. On the other hand, less membrane resistance will be created at high hydrogen stoichiometry and thin cell membrane thickness which voltage is also more. But this increases the risk of flooding in the cathode.

Keywords: fuel cell, seven layers, water transport, one-dimensional, steady-state, modeling.

1. Introduction

One of the most promising alternatives to the burning of fossil fuel in the production of electric power is the Proton Exchange Membrane (PEM) Fuel Cell. The PEM fuel cell has many advantages to the current internal combustion engine. Since it is not limited by the Carnot cycle, it can achieve much higher efficiencies than a combustion cycle. The PEM fuel cell is also environmentally friendly. When operated on hydrogen, the PEM fuel cell is a zero emission power source. Even when operated on reformat hydrogen (hydrogen evolved from hydrocarbon fuel sources); the emissions are lower than in a standard combustion engine. Other advantages of this fuel cell system include the simplicity of design, low noise operation and economic independence. It will help developing countries that lack the power grid infrastructure by using fuel cells for localized electric power stations. Fuel cells can eliminate

the need for large, noisy power plant hundreds of miles from the eventually usage location. Furthermore, by localizing power generation the power loss due to transmission through long distance power lines is eliminated [1].

PEMFC is an electrochemical energy conversion device that converts hydrogen and oxygen into water and, in the process, it produces heat and electricity. The oxygen required for a fuel cell comes from the air pumped into the cathode. However, hydrogen has some limitations that make it impractical for use in most applications. One of the most critical aspects of a PEMFC is the water management. There is a delicate balance between the membrane hydration and avoiding cathode from flooding. Cathode flooding occurs when the water produced exceeds the water removal rate. Flooding in the cathode reduces the oxygen transport to the reaction sites and decreases the effective catalyst area. In modern fuel cells, the cathode (or the anode) consists of: a catalyst layer, gas diffusion layer (GDL) and bipolar plates. The GDL is a porous medium electrically conductor. Liquid water that builds up at a fuel cell cathode decreases the performances and inhibits robust operation [2].

Water is one of the most important factors in the PEMFC operation because the performance of a PEMFC depends strongly on the water balance within the cell. As it is well known, electro-osmotic drag and back diffusion in the membrane affect the water distribution in the PEMFC competitively [3].

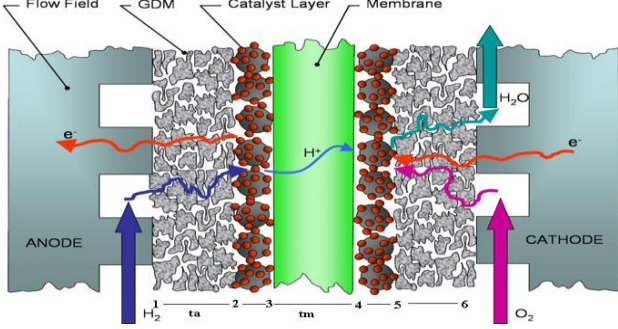
A study from 1991 to 2008 to develop a theoretical model to describe the phenomenon of water in the PEMFC is performed most reliable conditions for this model have been expressed [4].

2. Mathematical Model

In former years, Springer and colleagues presented a five-layer model that considered the anode and cathode catalyst layers very thin. On the other hand, Chen and Chang presented another five-layer model that ignored the anode and cathode channels input. While the proposed mathematical model is a one dimensional, steady state, isothermal and isobar model to describe the water transport

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phenomena in a PEMFC with a seven-layer structure, in which consists of anode and cathode inlet channels, anode and cathode gas diffusion layer (GDL), catalyst layers (CLs) and the proton exchange membrane. The seven layer polymer fuel cell in the form (2-1) is shown.



(2-1): seven layers studied in polymer fuel cell.

2.1 Anode and cathode inlet channels [5]

Consumption hydrogen molar flux through the anode in steady state condition is:

$$J = I/2F \quad (\text{mol/cm}^2\text{s}) \quad (1)$$

I : Current density (A/cm^2)

F : Faraday constant (96484 C/mol)

The fluid composition in the anode and cathode flow channel is assumed to be uniform.

From flow balance, the anode inlet water flow less the exit water flow is the flow crossing interface 1:

$$N_{WA}^I - N_{WA}^L = N_{WA} \quad (2)$$

$$\frac{v_H x_{WA}^I}{1-x_{WA}^I} J - \frac{(v_H-1)x_{W1}}{1-x_{W1}} J = \alpha J \quad (3)$$

$$v_H : \text{stoichiometric coefficient} = \frac{N_{H_2}^I}{N_{H_2,1}}$$

On the cathode side there are three species. The inlet dry gas mole fraction of oxygen, X_{ON} , is known. The inlet O_2 mole fraction of the saturated gas is $X_{O}^I = (1-X_{WC}^I)X_{ON}$.

The three species inlet flow rates and exit flow rates expressed proportional to I are:

$$N_{WC}^I = \frac{v_O x_{WC}^I}{2(1-x_{WC}^I)x_{ON}} J$$

$$N_{O}^I = \frac{v_O}{2} J, \quad N_{N}^I = \frac{v_O(1-x_{ON})}{2x_{ON}} J \quad (4)$$

$$N_{WC}^L = N_{WC}^I + (1+\alpha)J, \quad N_{O}^L = \frac{(v_O-1)}{2} J$$

$$N_{N}^L = \frac{v_O(1-x_{ON})}{2x_{ON}} J \quad (5)$$

By summing the three flows in Eq. (5), the total cathode exhaust flow is:

$$N_{total,C}^L = \left(\frac{v_O}{2(1-x_{WC}^I)x_{ON}} + \alpha + \frac{1}{2} \right) J \quad (6)$$

The mole fraction of water and oxygen at interface 4 and throughout the cathode flow channel is the ratio of the water or oxygen flow to the total flow through interface 4. Thus:

$$x_{W6} = \frac{x_{WC}^I v_O + 2(1+\alpha)(1-x_{WC}^I)x_{ON}}{v_O + (2\alpha+1)(1-x_{WC}^I)x_{ON}} \quad (7)$$

$$x_{O6} = \frac{(v_O-1)(1-x_{WC}^I)x_{ON}}{v_O + (2\alpha+1)(1-x_{WC}^I)x_{ON}} \quad (8)$$

Thus, the mole fraction of water at interface 1:

$$x_{W1} = \frac{x_{WA}^I v_H - \alpha(1-x_{WA}^I)}{x_{WA}^I - \alpha(1-x_{WA}^I) + v_H - 1} \quad (9)$$

2-2. Gas diffusion in the electrodes [5]

Anode and cathode gas mixtures with water vapor act as ideal gases. Let z increase in the direction of reactant flow. The Stefan-Maxwell equation for multi-component diffusion defines the gradient in mole fraction of the components:

$$\frac{dx_i}{dz} = RT \sum_j \frac{x_i N_j - x_j N_i}{P D_{ij}} \quad (10)$$

From Eq. (10), for mole fraction of water in anode (x_{WA}) and mole fraction of oxygen and water in cathode (x_{OC}, x_{WC}), it is:

$$\frac{dx_{WA}}{dz} = \frac{RTJ}{P_A D_{WH}} (x_{WA} (1+\alpha) - \alpha) \quad (11)$$

$$\frac{dx_O}{dz} = \frac{RTJ}{P_C} \left(\frac{x_O(1+\alpha) - 0.5 x_{WC}}{D_{WO}} + \frac{(1-x_{WC}-x_{ON})(-0.5)}{D_{ON}} \right) \quad (12)$$

$$\frac{dx_{WC}}{dz} = - \frac{RTJ}{P_C} \left(\frac{(1-x_{WC}-x_O)(1+\alpha)}{D_{WN}} + \frac{(-0.5 x_{WC}) + x_O(1+\alpha)}{D_{WO}} \right) \quad (13)$$

Equation (11) can be integrated across the anode thickness, so:

$$x_{W2} = \left(x_{W1} - \frac{\alpha}{1+\alpha} \right) \exp\left(\frac{RTJ t_a}{P_A D_{WH}} \right) + \frac{\alpha}{1+\alpha} \quad (14)$$

Eq. (12) and (13) can be integrated during at interface 5 to obtain x_{W5} .

2-3. Catalyst layers [6]

The catalyst layer contains voids and electrolyte phase. Hence, three mechanisms may contribute to water transport in CLs. In voids the water vapor is transported by Knudsen diffusion, while in the electrolyte phase the water transport is mainly due to diffusion and drag. we can assume the water transport is primarily in vapor form through the voids due to Knudsen diffusion. Accordingly, at the anode CL. It is:

$$J_2 = -D_{cl} \left(\frac{\partial C_2}{\partial z} \right) \quad (15)$$

D_{cl} is the Knudsen diffusion coefficient of water vapor in the voids. The Knudsen diffusion coefficient is assumed to 0/0012 (cm²/s) [7].

From the mass conservation equation, we have:

$$-\frac{\partial J_2}{\partial z} = 0 \quad (16)$$

The boundary conditions at interface 2 are:

$$C_1 = C_2 \quad (17)$$

$$D_{gl} \left(\frac{\partial C_1}{\partial z} \right) = D_{cl} \left(\frac{\partial C_2}{\partial z} \right) \quad (18)$$

Above equations can be solved during at interface 2 to obtain x_{W3} .

Also for cathode we have:

$$0 = -\frac{\partial J_4}{\partial z} + \frac{S_W Q}{n F} \quad (19)$$

$$J_4 = -D_{cl} \left(\frac{\partial C_4}{\partial z} \right) \quad (20)$$

The boundary conditions at interface 5 are:

$$C_4 = C_5 \quad (21)$$

$$D_{gl} \left(\frac{\partial C_4}{\partial z} \right) = D_{cl} \left(\frac{\partial C_5}{\partial z} \right) \quad (22)$$

Above equations can be solved during at interface 5 to obtain x_{W4} .

2-4. Water transport in membrane [5]

λ , is given as the ratio of the number of water molecules to the number of charge (SO₃H⁺) sites. A fit of the experimental relationship of λ vs. water vapor activity, a , used in the model is:

$$\lambda = 0.043 + 17.81 a - 39.85 a^2 + 36 a^3 \quad (23)$$

For $0 < a \leq 1$

$$\lambda = 14 + 1.4 (a - 1) \quad \text{for } 1 \leq a \leq 3 \quad (24)$$

Water transport in membrane has two dominant mechanisms. One of that is electro-osmotic drag and another is back diffusion transport. So, water flux through the membrane in effect of electro-osmotic drag (mol/cm²s) is:

$$N_{W,drag} = 2J \cdot n_{drag}, n_{drag} = n_{drag}^{sat} \lambda / 22 \quad (25)$$

$$n_{drag}^{sat} = 0.2 \pm 2.5 \quad (26)$$

Eq. (27) shows the water molar flux through the membrane in effect of back diffusion. In order to eliminate tracking the membrane swelling in the model, we convert to the equivalent water concentration in a dry membrane ($\lambda \rho_{dry} / M_m$). To account for membrane swelling, dry membrane thickness dimensions are expanded by the factor $(1+s\lambda)$ [8]. So:

$$N_{w,diff} = -D' c_w \frac{d(\ln a)}{d\lambda} \frac{d\lambda}{dz} = -D' \left(\frac{\lambda \rho_{dry}}{M_m} \frac{\lambda da}{(1+s\lambda)^2 a d\lambda} \right) \frac{d\lambda}{dz} = -\frac{\rho_{dry}}{M_m} D_\lambda \frac{d\lambda}{dz} \quad (27)$$

$$D_\lambda = 10^{-6} \exp \left[2416 \left(\frac{1}{203} - \frac{1}{273+T_{cell}} \right) \right] (2.563 - 0.333\lambda + 0.0264\lambda^2 - 0.000671\lambda^3) \quad (28)$$

So, the net water flux through the membrane is:

$$N_w = n_{drag}^{sat} \frac{\lambda}{22} (2J) - \frac{\rho_{dry}}{M_m} D_\lambda \frac{d\lambda}{dz} = \alpha J \quad (29)$$

$$\frac{d\lambda}{dz} = \left[2n_{drag}^{sat} \frac{\lambda}{22} - \alpha \right] \frac{J M_m}{\rho_{dry} D_\lambda} \quad (30)$$

Now we can calculate a new α and check this value to old value. If new α is closer to old α , our calculation is correct.

The key to solving the water transport through the PEFC, we must apply in iteration to determine the proper value of α . We guess a value for α and calculate all mole fractions, and then we distinguish new α which is obtained following the integration of Eq. (30). These two values will be equal when the proper value of is used.

3. Result and Discussion.

The set of model parameters used for our base case is listed in Table 1. And the computed variables of model and Springer model are listed in Table 2.

Input Parameters		
I	A/cm ²	0.5
j_0	A/cm ²	0.01
P_A, P_C	atm	3
t_{mem}	cm	0.0175
t_a, t_c	cm	0.0365
t_{cat}	cm	0.0020
T_{cell}	K	353.115

Table 1: The base-case input parameters for a cell with Nation 117 membrane.

computed variables	model	Springer model
V_{cell} (Volt)	0.6795	0.6680
R_{mem} ($\Omega\text{-cm}^2$)	0.2699	0.2850
x_{W1}	0.1024	0.1015
x_{W2}	0.1010	0.1013
x_{W3}	0.1	0.2327
x_{W4}	0.2347	0.2264
x_{W5}	0.2242	
x_{W6}	0.2239	
x_{O5}	0.1405	
x_{O3}		0.1329
x_{O6}	0.1408	
x_{O4}		0.1403

Table 2: The computed variables of model and Springer model.

Results show that resistance in this model is lower than Springer model resistance, which voltage is also more.

Figure 2 – shows the profiles of water concentration ratio C/C_{sat} in anodic side, Figure 3 – shows the water content λ in the membrane And Figure 4 – shows the profiles of water concentration ratio C/C_{sat} in cathodic side. Both anode and cathode reactant gases are humidified with 100% saturated water vapor. (First line is this model and second line is Chen and Chang model with hydrogen and oxygen stoichiometry of 1)

As shown in Figure 2, the water vapor is transported from the anode gas channel to the membrane through the GDL and CL for the four assigned values of current density $J = 0.25, 0.5, 0.75, 1 \text{ A/cm}^2$. It is found that all these curves decrease gradually. At this model, each current density at channels interface with anode gas diffusion layer has different relative humidity. Because it seems more logical that the different current densities need different moisture for electrochemical reaction.

In the membrane as shown in Figure 3, the maximum of water content occurs at the cathode boundary because of the generation of water there, and then λ decreases gradually toward the anode side. At low current density conditions, ($J = 0.25 \text{ A/cm}^2$) the water content is relatively lower at the cathode boundary while decreases slowly to the anode side resulting in a higher average water content in the membrane. In contrast to this case, at high current density ($J = 1.0 \text{ A/cm}^2$) the water content is higher at the right interface but descends quickly to the left side causing a lower average water content in the membrane. Obviously, when the cell operates at higher current densities, the effect of electro-osmotic drag becomes significant and reduces the water content at the anode boundary distinctly.

As indicated by Figure 4, because of the generation of water vapor inside the CL, the water concentration always appears to have a maximum at the membrane/CL interface and then decreases gradually toward the cathode gas channel for all cases considered. In the case $J = 0.25 \text{ A/cm}^2$, the water concentration in the CL is only slightly higher than that of the intake saturated air, which indicates that the flooding phenomena should be limited. However, as the current density increases to $J = 1.0 \text{ A/cm}^2$, the water concentrations in the CL and GDL rise rapidly and the high supersaturated concentration implies that the condensation of water vapor may become a severe problem to block the pores of the CL and GDL, and reduce the amount of oxygen transport. It seems that, the water concentration profile for Chen and Chang model decreases gradually toward the cathode gas diffusion for all cases considered. So it seems that extra vapour has returned to the cathode gas diffusion. If for any current density of model, moisture is different at the channel/cathode gas diffusion interface. In addition to changes in water concentration profile model at gas diffusion layer is very low. Since, at the gas diffusion layer does not accept the electrochemical reaction; it seems logically that the slope in this section is not sharpness than Chen and Chang's diagram. So it seems the proposed model is closer to reality.

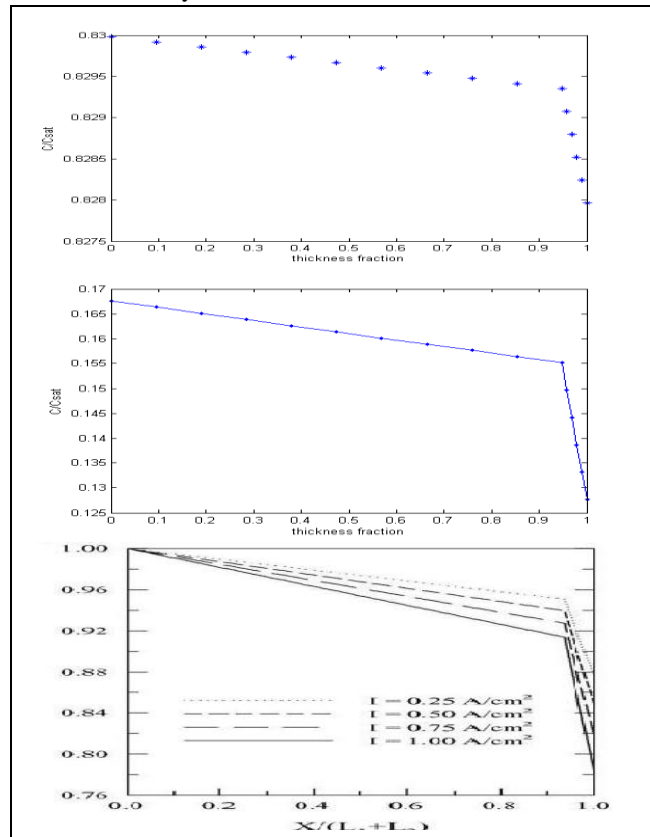


Figure 2 – the water concentration profile in the cathode electrode. At base case. (first line: $J = 0.25 \text{ A/cm}^2$, second line: $J = 1 \text{ A/cm}^2$)

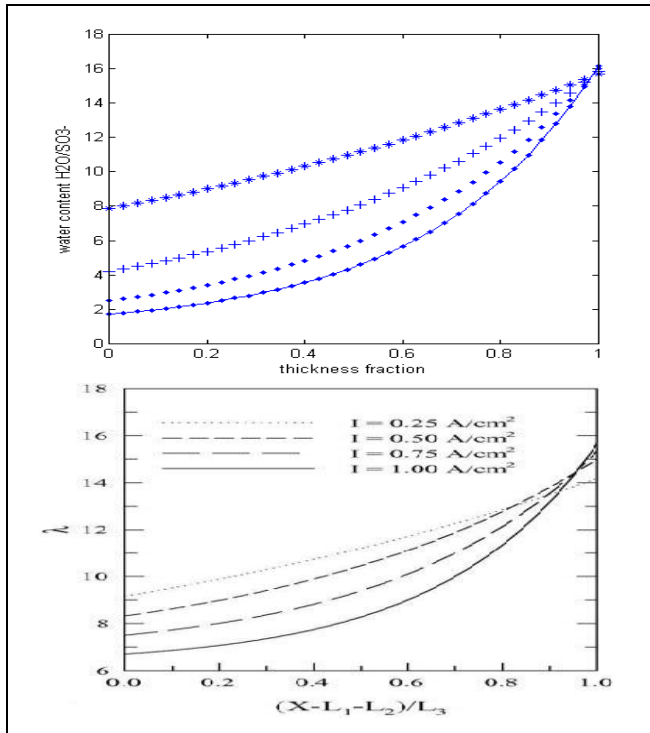


Figure 3 – the water content profile in the membrane. At base case.

* J=0.25 A/cm²
 + J=0.5
 • J=0.75
 — J=1

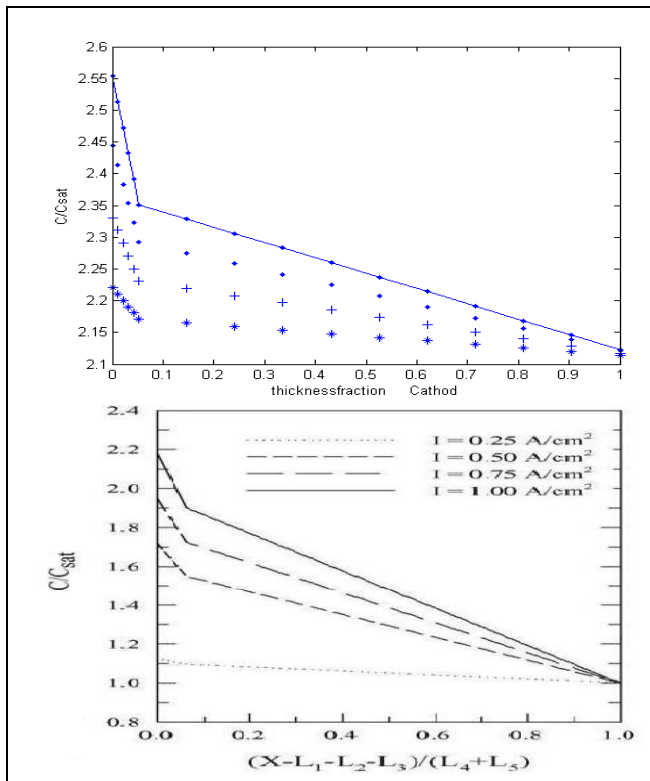


Figure 4 – the water concentration profile in the anode electrode. At base case.

Other results indicate that with increasing current density, concentration of water in the cathode electrode is increased and water vapor may be a serious problem for the hole blocking gas diffusion layer and catalyst layer and reduce the amount of oxygen transport. Also with high porosity of gas diffusion layer and reduce relative humidity in both anode and cathode reactant gases (about 80%) reduce flooding. On the other hand, with thin cell membrane thickness (about 50 μm) and with high hydrogen Stoichiometry, the performance will increase, but this increases the risk of flooding in the cathode. Therefore it is not suitable for water management and is not recommended.

So, with cathode input relative humidity about 60% and anode input relative humidity about 80%, also with hydrogen Stoichiometry of 4 and oxygen Stoichiometry of 6, water management and performance of fuel cell is improved.

4. REFERENCES

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