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Temperature Effect on Proton Exchange Membrane Fuel Cell Performance Part I: Modelling and Validation

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Abstract

The aim of this part 1 of this paper is to present the mathematical modeling and validation of the temperature effect on PEM fuel cell by different assumptions. The Tafel equation has been used to find the electrochemistry relation that combined with mass transfer parameters. The final models are then compared and validated with experimental data. Results show that both anodic and cathodic over-potential have significant effect on modeling results but the effect of anode over-potential is much less than its cathode.

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1. PEM fuel cell modeling

The electrochemical reactions occurring on electrodes of a PEM fuel cell can be described as follows. The first and second equation show the anode and cathode side reaction respectively and the third equation show the overall electrochemical reaction [1].



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During the processes of electrochemical reactions and electron transfer, an electromotive force is generated between the two electrodes. The output voltage of a single cell can be written as

$$V_{cell} = V^{oc} - \eta_{act} - \eta_{ohm} \quad (4)$$

Where η_{act} being the sum of the polarization over-potentials or activation over-potentials due to kinetic losses at the anode and cathode, η_{ohm} the over-potential due to ohmic losses and V^{oc} is the open-circuit-voltage of PEM fuel cell [2]. Activation losses are associated with overcoming reaction energy barriers at the electrode-electrolyte interfaces. Ohmic losses are associated with electron and ion conduction processes occurring in the electrodes, electrolyte, and interconnects, as well as the contact resistances across each material interface [3]. The activation over-potentials and ohmic losses parameters can be expressed as equations 5-6.

$$\eta_{act} = \eta_a + \eta_c \quad (5)$$

$$\eta_{ohm} = I.R_m \quad (6)$$

where η_a and η_c are the over-potential in anode and cathode respectively and can be calculated by the Butler-Volmer equation as follow [4]

$$I_i = i_i^0 \left[\exp\left(\frac{\alpha_i n_i F \eta_i}{RT}\right) - \exp\left(-\frac{(1-\alpha_i) n_i F \eta_i}{RT}\right) \right] \quad (7)$$

where I , i^0 , α , n , F , R and T are current density, apparent exchange current density (AECD), transfer coefficient, electron transfer number, faraday number, gas constant and temperature, respectively and the notation i can be a and c represent anode and cathode. The above form of Butler-Volmer equation just use to find activation over-potential but there is another loss in PEM fuel cell called concentration or mass transfer over-potential. The following form of Butler-Volmer equation can be used to find the relation of activation loss and current density and enter the concentration over-potential [5].

$$I_i = i_i^0 \left[\left(1 - \frac{I_i}{I_{di}^f}\right) \exp\left(\frac{\alpha_i n_i F \eta_i}{RT}\right) - \left(1 - \frac{I_i}{I_{di}^b}\right) \exp\left(-\frac{(1-\alpha_i) n_i F \eta_i}{RT}\right) \right] \quad (8)$$

where I_{di}^f and I_{di}^b are the apparent diffusion limiting current densities for the cathodic/anodic forward and backward reactions, respectively. Actually, the second term of above equations is much less than first term and usually omitted. On the other hand, the concentration activation loss in low polarization range is much less than activation over-potential and therefore can also be omitted [6]. There are two approximations of Butler-Volmer equation, which are at low (equation 9) and high polarization (equation 10). This equation can be expressed as follow respectively for anode and cathode of PEM fuel cell [7]

$$\eta_i = \frac{RT}{n_i F i_i^0} I_i \quad (9)$$

$$\eta_i = -\frac{RT}{n_i \alpha_i F} \ln(i_i^0) + \frac{RT}{n_i \alpha_i F} \ln(I_i) \quad (10)$$

The output voltage of cell (equation 4) can be rewritten in the following equation at low and high polarization, respectively. If the anode over-potential is insignificant due to large exchange current density, the cell voltage can be expressed as equation 13 [5, 6].

$$V_{cell} = V^{oc} - \frac{RT}{n_c F i_c^0} I_{cell} - I_{cell} R_m \quad (11)$$

$$V_{cell} = V^{oc} + \frac{RT}{n_a \alpha_a F} \ln(i_a^0) + \frac{RT}{n_c \alpha_c F} \ln(i_c^0) - \frac{RT}{n_a \alpha_a F} \ln\left(\frac{I_{cell} \cdot I_{da}^f}{I_{da}^f - I_{cell}}\right) - \frac{RT}{n_c \alpha_c F} \ln\left(\frac{I_{cell} \cdot I_{dc}^f}{I_{dc}^f - I_{cell}}\right) - I_{cell} R_m \quad (12)$$

$$V_{cell} = V^{oc} + \frac{RT}{n_c \alpha_c F} \ln(i_c^0) - \frac{RT}{n_c \alpha_c F} \ln\left(\frac{I_{cell} \cdot I_{dc}^f}{I_{dc}^f - I_{cell}}\right) - I_{cell} R_m \quad (13)$$

The open circuit voltage of PEM fuel cell can be expressed as equation 14, where E_c^r and E_a^r can be expressed by Nernst equation according to anode and cathode reaction as shown in equations 15-16. E_a^0 is zero at any temperature and E_c^0 is a temperature dependence constant illustrated in equation 17. Therefore, by combination of equations 14-17, the final theoretical equation for open circuit voltage achieved can be expressed equation 18 [8].

$$V^{oc} = E_c^r - E_a^r \quad (14)$$

$$E_c^r = E_c^0 + \frac{RT}{4F} \ln(P_{O_2} [H^+]^4) \quad (15)$$

$$E_a^r = E_a^0 + \frac{RT}{2F} \ln\left(\frac{[H^+]^2}{P_{H_2}}\right) \quad (16)$$

$$E_c^0 = 1.229 - 0.000846(T - 298.15) \quad (17)$$

$$V^{oc} = 1.229 - 0.000846(T - 298.15) + \frac{RT}{4F} \ln(P_{O_2} P_{H_2}^2) \quad (18)$$

where $[H^+]$ is the molar concentration of protons. P_{H_2} and P_{O_2} are partial pressure of reactants at anode and cathode, respectively. The cathode transfer coefficient is also temperature dependence and can be calculated by using equation 19, but the anode transfer coefficient usually approximated to 0.5 [6].

$$\alpha_c = 0.001678T \quad (19)$$

2. Electrochemical impedance spectroscopy

Two important unknown factors in equations 11-13 are apparent exchange current density and membrane resistance. One of the best methods to find these parameters is by using electrochemical impedance spectroscopy (EIS). EIS is a suitable diagnostic testing method for fuel cell because it is non-destructive, able to distinguish the individual contributions of the interfacial charge transfer and the mass transport resistances in the catalyst layer and diffusion layer. The membrane resistance (R_m) and charge transfer resistance (R_{ct}) can be achieved by EIS. The charge transfer resistance also equal to differential of activation over-potential by current density as follow [9, 10]

$$R_{ct} = \frac{\partial \eta_{act}}{\partial I_{cell}} \quad (20)$$

By combination of equations 11-13 and 20, the apparent current density at cathode can be obtained as follow (equations 21-23). At high polarization, equations are more complicated and the apparent current density and diffusion limiting current density at cathode should be calculated using experimental data.

$$R_{ct} = \frac{\partial \eta_{act}}{\partial I_{cell}} = \frac{RT}{n_c F i_c^0} \quad (21)$$

$$R_{ct} = \frac{\partial \eta_{act}}{\partial I_{cell}} = \frac{RT}{n_c \alpha_c F} \cdot \frac{1}{I_{cell}} + \frac{RT}{n_c \alpha_c F} \cdot \frac{1}{I_{cell}} - \frac{RT}{n_c \alpha_c F} \cdot \frac{I_{dc}^f}{I_{cell} (I_{dc}^f - I_{cell})} - \frac{RT}{n_c \alpha_c F} \cdot \frac{I_{dc}^f}{I_{cell} (I_{dc}^f - I_{cell})} \quad (22)$$

$$R_{ct} = \frac{\partial \eta_{act}}{\partial I_{cell}} = \frac{RT}{n_c \alpha_c F} \cdot \frac{1}{I_{cell}} - \frac{RT}{n_c \alpha_c F} \cdot \frac{I_{dc}^f}{I_{cell} (I_{dc}^f - I_{cell})} \quad (23)$$

Although some previous research suggested using equation 11 in low current density, but it can only valid to small range of current density [3]. Since this research is only focused on high and wide range of current density, therefore the Tafel equations has been used in this research.

3. Result and discussion

Figure 1 illustrates the results of the modeling conducted using equations 12-13 against the experimental data collected from literature [5]. The experiments have been done at 23°C, 3 atm and 100% relative humidity. Although the equation 13 has a good agreement with experiment data at the low current density but the local error at the high current density is significant. On the other hand, equation 12 covered the experiment normally in all range of current density and there is no significant error in special range or zone.

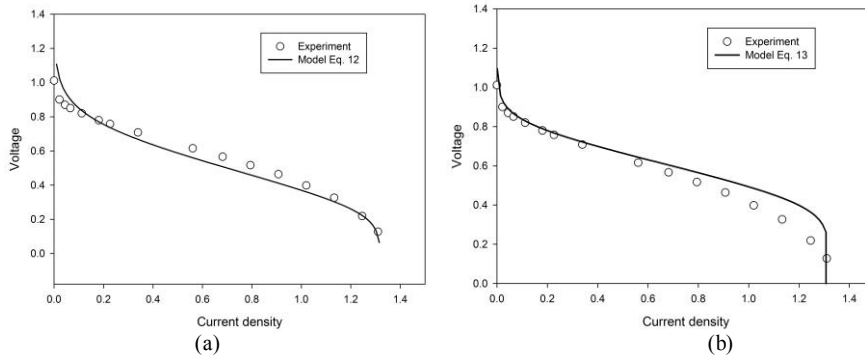


Fig. 1. (a) Validation of equation 12 by experiments; (b) Validation of equation 13 by experiments

4. Conclusion

In this paper a mathematical modeling of PEM fuel cell has been investigated. The Tafel equation has been used to find the electrochemistry relation that combined with mass transfer parameters. Validation results have clearly showed that anode over-potential has significant effect and cannot be omitted in the PEM fuel cell. The parametric study of cell based on equation 12 has been conducted and presented in the second part of this paper.

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Biography

Hamid Kazemi Esfeh is PhD candidate in Universiti Teknologi Malaysia. I worked in Islamic Azad University, Mahshahr Branch as scientific board member of chemical engineering faculty since 2009. My research interest is on fuel cell modeling.