Oxygen Transfer Model in Cathode GDL of PEM Fuel Cell for Estimation of Cathode Overpotential

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Abstract

The mathematical model involving kinetics and mass transfer in a PEM fuel cell cathode is developed in two dimensions assuming only diffusion transport in oxygen mass transfer. The model calculates oxygen concentration profile which provides current density. At each current density along with experimentally obtained parameters, *i.e.*, cathode transfer coefficient, and exchange current density, the cathode overpotential can be estimated. The cell potential can also be estimated from the calculated overpotential in combination with Ohmic resistance obtained from the experimental data. The cell potential predicted from the model give a good fit in verification with the experimental data.

Keywords

gas diffusion layer, cathode overpotential, polarization curve, oxygen transfer

Introduction

A proton exchange membrane fuel cell, PEMFC, converts chemical energy to electricity without emission. The products are electricity, heat, and water. It operates at low temperature with quick start-up. It is made of a solid polymer without moving part. It has a membrane electrode assembly, MEA, which is sandwiched between two graphite plates, current collectors, and end plates. An MEA comprises two gas diffusion layers, GDLs, two catalyst layers, and a membrane layer in the middle. Although the GDL is seemingly a minor component in a fuel cell, it has been shown that a GDL can lead to more improvements on the performance of the cell [1]. Thus this paper focuses on mass transfer within GDLs. The duty of the GDL is to distribute the reactant gas uniformly on the catalyst layer, conduct the electrons from the anode to the external circuit and entering to the cathode. It is also a passage of water during the operation of the fuel cell. Therefore a GDL directly affects the over potential and performance of the PEMFC. The literature usually worked on modeling of oxygen transfer in a PEMFC by assuming constant cathode activation overpotential, *i.e.*, the work of Jeng and coauthors [2]. They studied a simple two-dimensional model of oxygen mass transfer with in a GDL to investigate the effect of current collector ribs with a constant cathode activation overpotential assumption. However, cathode activation loss can vary with current density and therefore this work models oxygen transfer in a PEMFC with emphasis on variation of cathode activation overpotential. Usually, the cell performance can be shown by a polarization curve. The cell potential is plotted at various current densities.

Nomenclature

A_S catalyst surface area per unit mass of catalyst (cm^2/g)
A_V specific reaction surface per volume of catalyst (m^2/m^3, cm^2/cm^3)
C total concentration of gas mixture (mol/m^3)
C_{O_2} oxygen concentration (mol/m^3)
$C_{O_2}\text{-}_{ref}$ reference oxygen concentration (mol/m^3)
C_{H_2} hydrogen concentration (mol/m^3)
$D_{O_2\text{-}H_2O}$ effective diffusivity (m^2/s, cm^2/s)
E_{cell} cell voltage (volt)
E_{Nernst} theoretical voltage (volt)
E_{oc} open circuit voltage (volt)
E^0_{rev} reversible cell voltage (volt)
F Faraday constant (96,487 C/mol)
i_0 exchange current density (A/m^2, mA/cm^2)
i local current density (A/m^2, mA/cm^2)
I current density (A/m^2, mA/cm^2)
k lumped factor containing the kinetic constant (m/s)
k' lumped factor containing k
k_{rxn} kinetic constant
m_P catalyst mass loading per unit area of cathode (mg/cm^2)
N_{O_2} molar flux of oxygen (mol/m^2s)
P cell operating pressure (1atm)
R universal gas constant (8314 J /mol- K)
T temperature (K)
T_C thickness of catalyst layer (m)
T_{GDL} thickness of gas diffusion layer (m)
w_C width of flow channel (m)
w_r width of flow channel rip (m)
x mole fraction of gas
y dimension acress the flow channel
z dimension across the gas diffusion layer

Greek symbols

a transfer coefficient
a_C cathode transfer coefficient
η_{act} activation loss of reaction (volt)
η_C cathode over potential (volt)
$\Re$ cell electrical resistance (Ωcm^2)

Subscripst and Superscripts

act activation
c cathode
l order of reaction, number not specified
mixed electron crossover loss and others
oc open circuit
rxn chemical reaction *cl*catalyst layer

Under ordinary operation without mass transport loss, it is known to be obtained by,

$$E_{cell} = E_{Nernst} - \eta_{act} - I\Re \quad (1)$$

where E_{cell} is the cell voltage, E_{Nernst} the theoretical voltage obtained from thermo dynamics, η_{act} activation loss of reaction, I the cell current density, and $\Re$ the cell electrical resistance. Figure 1 shows a typical polarization curve for a PEM fuel cell. The anode overpotential has less effect in comparison to the cathode overpotential [3] and can be neglected. In this way the cathode overpotential is the activation loss.

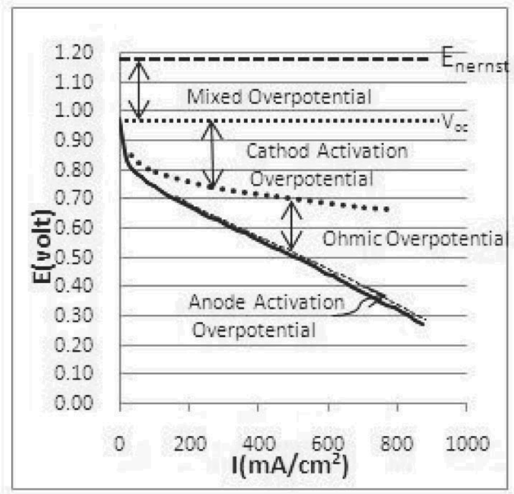

Figure 1 : Typical polarization curve for PEM fuel cells, showing the cathode overpotential, anode overpotential, Ohmic overpotential, and mixed electrode potential.

The electrochemical reaction rate at the cathode side is lower than that at the anode side about 100 times [4]. Therefore, the cathode reaction controls the overall performance in a fuel cell. Thus,

$$\eta_{act} = \eta_C$$

where η_C is cathode overpotential. Moreover, in an actual fuel cell, the open circuit voltage, E_{oc} at zero current density is related to E_{Nernst} by[5],

$$E_{oc} = E_{Nernst} - E_{mixed} \quad (2)$$

where E_{mixed} is a mix potential at the electrodes resulting from electron crossover loss and others.

The cathode overpotential, η_C, is a function of current density and can be estimated from oxygen mass transfer modeling. In this way, a convenient method for estimation of cathode overpotential and cell electrical resistance is obtained.

The oxygen transport phenomena through the cathode GDL

An exploded view of cathode GDL element for two-dimensional modeling is shown in Figure 2. It is bounded by the lines L_1 and L_2 corresponding to centerlines of adjacent rib and channel, respectively, with a thickness of T_{GDL}.

The gas flows into the cathode side consist of oxygen and water vapor. The water in the cathode side comes from electrochemical reaction and moisture in feeding oxygen. The molar flux of oxygen, N_{O_2}, in GDL on the cathode side, obtained from Fick's first law, is shown below [6].

$$N_{O_2} = x_{O_2} \sum_{i=O_2,H_2O} N_i - CD_{O_2-H_2O} \nabla x_{O_2} \quad (3)$$

where $x_{O_2} = \frac{C_{O_2}}{C}$ is oxygen mole fraction, C the total concentration of gas mixture, and C_{O_2} the oxygen concentration.

The first term on the right hand side of Eq. (3) is the convective transport, and the second term is the diffusion transport. The gas mixture flows through GDL porous layer very slowly. Thus, it can be assumed that the gas transport within GDL is by diffusion only resulting in constant concentration of gas mixture due to neglible pressure drop. Here, the effective diffusivity, $D_{O_2-H_2O}$, of binary gas mixture with Bruggeman's correlation is applied.The oxygen molar flux is:

$$N_{O_2} = -\varepsilon^{3/2} D_{O_2-H_2O} \nabla C_{O_2} \qquad (4)$$

where, ε is the porosity.

The molar flux of the oxygen at steady state depends on local current density, i, as

$$N_{O_2} = \frac{i}{4F} \qquad (5)$$

where F is the Faraday's constant of 96,487 C/mol.

At steady state, the oxygen molar flux is constant. Considering a two dimensional oxygen mass transport within a cathode GDL, the Laplace's equation can be obtained to explain the oxygen concentration distribution within the GDL :

$$\nabla^2 C_{O_2} = \frac{\partial^2 C_{O_2}}{\partial y^2} + \frac{\partial^2 C_{O_2}}{\partial z^2} = 0 \qquad (6)$$

Boundary conditions of system can be specified as shown in Figure 2. Symmetrical boundary conditions on both the upper and lower boundaries of the GDL element are used.

The molar flux across the GDL/rib interface is zero, and the oxygen concentration at the boundary facing the channel is C_{O_20}.

At the interface of gas diffusion layer and catalyst layer, the flux is equal to reaction rate.

The boundary conditions for the GDL element are summarized as:

$$\frac{\partial C_{O_2}}{\partial z} = -\frac{k C_{O_2}}{\varepsilon^{3/2} D_{O_2-mix}} = -k' C_{O_2}$$

$$for\ 0 \le y \le \frac{w_r + w_c}{2}, and\ z = T_{GDL} \qquad (7)$$

$$\frac{\partial C_{O_2}}{\partial y} = 0\ for\ y = \frac{w_r + w_c}{2}, and\ 0 \le z \le T_{GDL} \qquad (8)$$

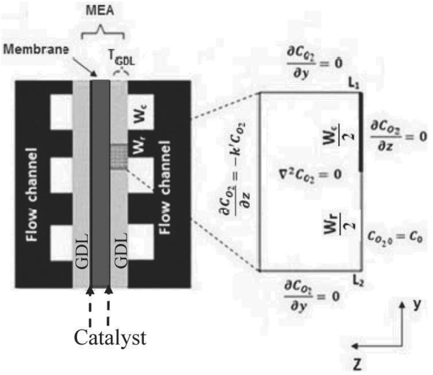

Figure 2 : Schematic diagram of a PEM fuel cell and an enlarge gas diffusion layer element.

$$\frac{\partial C_{O_2}}{\partial y} = 0\ for\ \frac{w_c}{2} \le y \le \frac{w_r + w_c}{2}, and\ z = 0 \qquad (9)$$

$$C_{O_20} = C_0\ for\ 0 \le y < \frac{w_c}{2}, and\ z = 0 \qquad (10)$$

$$\frac{\partial C_{O_2}}{\partial y} = 0\ for\ y = 0, and\ 0 \le z \le T_{GDL} \qquad (11)$$

The catalyst layer is assumed to be an infinitely thin film. The electrochemical reaction rate within the catalyst layer can be described by using Butler–Volmer rate expression [7, 8] with simplification to a Tafel type equation as

$$i = i_O \begin{Bmatrix} f_I\ (\theta, \theta_0)\exp(\frac{aF\eta}{RT}) \\ -f_2\ (\theta, \theta_0)\exp(-(1-a)\frac{F\eta}{RT}) \end{Bmatrix} \qquad (12)$$

where i_O the exchange current density, a the transfer coefficient.

From homogenous reaction in Eq.(12), the $f_l\ (\theta, \theta_0)$ the parameters commonly take the form of ratios such as θ/θ_0 or$(1-\theta)/(1-\theta_0)$ which can be written as $C_i\ /\ C_{i\text{-}ref}$ .The second term on the right-hand side with anode overpotential has small effect and can be neglected. Thus it can be applied to heterogeneous reaction with [2].

$$A_vT_c = A_sm_{pl} \tag{13}$$

Therefore, combination of Eq.(12) and Eq.(13) gives a Butler-Volmer equation in Tafel type form as

$$i = i_O A_sm_{pl} \frac{C_{O_2}(y,T_{GDL})}{C_{O_2}} exp(\frac{a_cF\eta_c}{RT}) \tag{14}$$

where A_v is the specific reaction surface, T_c the catalyst layer thickness, A_s the catalyst surface area per unit mass of catalyst, m_{pl} the catalyst mass loading per unit area of cathode, $C_{O_2}(y,T_{GDL})$ the oxygen concentration on the GDL/catalyst layer interface, $C_{O_{2\text{-}ref}}$ the reference oxygen concentration, a_c the cathode transfer coefficient, and η_c the cathode over potential. Both local current density and oxygen concentration at the GDL/catalyst layer interface vary along$y$ direction. Under the steady-state condition, a linear reduction of channel C_{O_2} from C_{O_20} at inlet to C_{O_2} final at fuel cell outlet is assumed with negligible reactant crossover.

The current density is determined from the oxygen diffusion rate at the GDL/catalyst layer interface. This indicates that :

$$N_{O_2}\Big|_{z=T_{GDL}} = \frac{i}{4F} = k_{rxn}C_{O_2}C^l_{H_2}\Big|_{z=T_{GDL}} \tag{15}$$

where l is the reaction order.

The value of $i$in Eq. (15) can be obtained from Eq. (14). After rearranging, Eq. (15) becomes.

$$\begin{aligned} N_{O_2} &= \frac{A_sm_{pl}i_O}{4FC_{O_{2\text{-}ref}}} exp(\frac{a_cF\eta_c}{RT})C_{O_2}(y,T_{GDL}) \qquad (16) \\ &= kC_{O_2}(y,T_{GDL}) \end{aligned}$$

where

$$k = \frac{A_sm_{pl}i_O\ exp(\ a_cF\eta_c \,\big|\, RT\ \ )}{4FC_{O_{2\text{-}ref}}} \tag{17}$$

and

$$k = k_{rxn}C^l_{H_2} \tag{18}$$

Parameter k is a lumped factor containing the kinetic constant, k_{rxn}, hydrogen concentration, C_{H_2}, reaction order, l , and can be estimated from a_c, i_0, and η_c .

Oxygen molar flux of Eq. (4) is constant in GDL z-direction but varies in GDL y-direction, thus Eq. (4) becomes

$$N_{O_2} = -\varepsilon^{3/2} D_{O_2\,H_2O} \frac{\partial C_{O_2}}{\partial z}\Big|_{z=T_{GDL}} \tag{19}$$

Eqs. (16) and (19) give the concentration gradient as,

$$\begin{aligned} \frac{\partial C_{O_2}}{\partial z}\Big|_{z=T_{GDL}} &= \frac{k}{\varepsilon^{3/2} D_{O_2\,H_2O}} C_{O_2}(y,T_{GDL}) \qquad (20) \\ k' &= C_{O_2}(y,T_{GDL}) \end{aligned}$$

where

$$k' = \frac{k}{\varepsilon^{3/2} D_{O\text{ - }H_2O}} \tag{21}$$

The reference oxygen concentration, $C_{O_{2\text{-}ref}}$ is taken as the inlet oxygen concentration to the cell, C_{O_20} , and can be estimated from ideal gas.

i_0 and η_c can be calculated by Tafel equation and experimental data [9]. i_0 can be estimated from the intercept of a straight line from Tafel plot at Nernst potential. E_{Nernst} is obtained from the Nernst equation at T [10],

$$E_{Nernst} = E^{0}_{rev} + \frac{RT}{nF} ln\left[\frac{x_{H_2}x_{O_2}^{0.5}}{x_{H_2O}}\right] + \frac{RT}{2nF}\ln P \quad (22)$$

where E^{0}_{rev} is reversible cell voltage of 1.229 volts obtained at the thermodynamic equilibrium, n the number of moles of electrons in the cell reaction(n =2), P the cell operating pressure (1atm), x_{H_2}, x_{O_2} and x_{H_2O} mole fractions of hydrogen, oxygen, and water vapor, respectively. E_{Nernst} is obtained at cell temperature of 353.15 and atmospheric pressure as 1.18 volts.

Binary gas is saturated with water vapor at the GDL and catalyst interface. The fraction of water vapor at saturation is obtained from Dalton's law.

The actual measured fuel cell voltage is calculated from Eqs. (1) and (2)

$$E_{cell,actual} = E_{cell} - E_{mixed} \quad (23\ a)$$

$$E_{cell,actual} = E_{oc} - \eta_c - I\Re \quad (23\ b)$$

Methodology

Experimental data is obtained from Kaewchada's work [10] which is sumarized as follow.

A fuel cell with 5 cm^2 active surface area was tested on a load box (Scribner 890 CL) at 353.15 K. The cell was comprised of Nafion® 115 Dupont, at a platinum loading of 0.2 mg/cm^2, 40% Pt on carbon black Hispec™4000 Alfa Aesar, the catalyst surface area per unit mass of catalyst of 6,000 cm^2/g, with carbon paper GDL (Sigracet 10BA) of 0.88 in porosity and 0.4 mm in thickness.

Hydrogen was fed to the anode side with a flow rate of 0.2 liter/min and pure oxygen in the cathode side with a flow rate of 0.13 liter/min. The calculation was fitted from Kaewchada's experimental data obtained from averaging three experiments.

Solution procedure

The cathode transfer coefficient, a_c, and exchange current density, i_O, are obtained from Tafel's slope of Kaewchada's experimental data for calculating cathode overpotential and used in mathematical model. Tefel's slope can be estimated from low current region because the activation loss or cathode overpotential dominates cell performance, while both ohmic and transports loses are minimal. The oxygen concentration and the oxygen molar flux distribution within the GDL can be estimated by the two-dimensional Laplace's equation, Eq.(6), with corresponding boundary conditions, Eqs. (7) to (11).Varying parameter k, which is a function of the hydrogen concentration, C_{H_2}, in the cathode, the Laplace mass transfer is solved by a computer program. The oxygen molar flux at the GDL/catalyst layer interface, $N_{O_2}\big|_{z=T_{GDL}}$,is estimated by averaging oxygen molar flux throughout entire y distance of the fuel cell active surface area.The cathode overpotential, η_c, can be calculated from Eq. (17). The cell Ohmic resistance ($\Re$) can be estimated by differentiating Eq. (23b) with the current density and experimental data from literature. Then predicted E_{cell} at various current density can be calculated from Eq. (23b) and verified against experimental polarization curve.

Result and discussion

Kaewchada's experiment data can provide i_O and Tefel's slope. Tefel slope of logarithmic plot of experimental data, Figure 3 is

$$\frac{RT}{a_c F}\log e = \frac{0.70 - 0.83}{\log 100 - \log 10} \qquad (24)$$

$$= -0.13\,Volt/dec$$

Then, a_c can be calculated from Eq.(24) as 0.539. i_O can also be obtained. It is 0.0203 mA/cm^{2}at E_{Nernst} of 1.18 volts for 353.15 K.

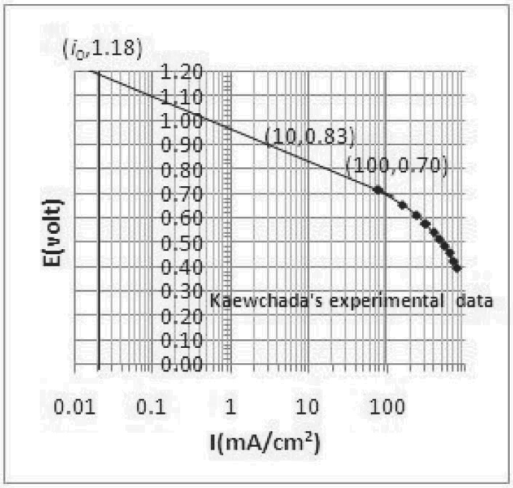

Figure 3 : Tafel's slope of Kaewchada's experimental data

The cathode overpotential, η_c, can be obtained from Eq.(17) shown in Figure 4 for each current density.

The cathode over potential variation with cell current density, I, can be obtained from Figure 4, and written as

$$\eta_c = 0.063 I^{0.248} \qquad (25)$$

The cell Ohmic resistance can be estimated from differentiation of Eq. (23 b) with current density.

$$\frac{dE_{cell}}{dI} = \frac{d\eta_c}{dI} = -\Re \qquad (26)$$

where $\left[\frac{dE_{cell}}{dI}\right]$ is the slope of experimental polarization curve.

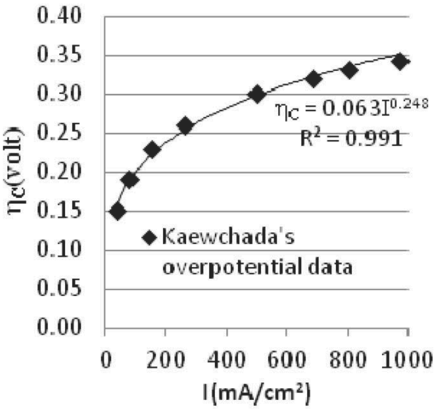

Figure4 : Calculated cathode activation overpotential at various current densities

Eq. (26) along with Eq. (25) can provide the average experimental cell resistance, $\Re$, at 353K which is equal to 0.302 Ωcm^2. The predicted E_{cell} from the mathematical model, Eq. (23b) and is shown in Figure 5, in which E_{oc} is obtained from Kaewchada's experimental data. The estimated mix potential, in Eq. (23a), is 0.216 volt. The open circuit potential is 0.964 volt. The predicted results are compared to experimental data as shown in Figure 5.

The mathematical model is in good fit with Kaewchada's experimental data.

Conclusions

The mathematical model developed in two dimensional with simplified concepts of kinetic and mass transfer processes in the PEM fuel cell cathode is developed to calculated oxygen concentration profile giving current density. The cathode overpotential is estimated. The cell potential was obtained and compared satisfactorily with Kaewchada's experimental data.

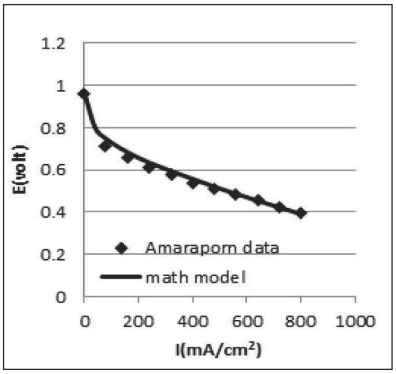

Figure 5 : Polarization curve from mathematical model verification with Kaewchada's experimental data.

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