

Short communication

# Thermodynamic properties of direct methanol polymer electrolyte fuel cell

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## Abstract

A new semi-empirical model is established to describe the cell voltage of a direct methanol fuel cell (DMFC) as a function of current density. The model equation is validated experimental data over a wide range of a methanol concentration and temperatures. A number of existing models are semi-empirical. They, however, have a serious mathematical defect. When the current density,  $j$ , becomes zero, the equation should reduce to the open circuit voltage,  $E_0$ . These models, however, do not meet the mathematical boundary condition. The proposed model focuses on very unfavorable conditions for the cell operation, i.e. low methanol solution concentrations and relatively low cell temperatures. A newly developed semi-empirical equation with reasonable boundary conditions includes the methanol crossover effect that plays a major role in determining the cell voltage of DMFC. Also, it contains methanol activity based on thermodynamic functions to represent methanol crossover effect.

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**Keywords:** DMFC; Cell voltage; Current density; Methanol crossover

## 1. Introduction

Characterization of the fuel cell (FC) frequently uses large and complex computer models, based on minute details of cell component design (physical dimensions, materials, etc.) along with chemical and physical considerations (transport phenomena, electro-chemical kinetics, electrode kinetics, etc.) The codes, often proprietary, needed in the design and development of fuel cells are cumbersome and time-consuming for use in system analysis models. Simpler approaches are normally used for system studies. Another approach, which is not time and cost efficient would be to conduct appropriate tests at every condition expected to be analyzed in the system. Alternatively, it is prudent to develop

correlations based on the thermodynamic model, which describe cell performance according to operating conditions such as temperature and pressure [1].

In the development of model equations to describe the performance of polymer electrolyte fuel cells, a number of approaches using empirical models have been attempted [2–7]. In many cases a fairly good agreement between the model and experimental data is achieved by adjusting appropriate coefficient/parameters in the model equations. Srinivasan et al. [2] showed that it is possible to use a simple equation to describe the cell voltage vs. current density behavior for PEMFCs. This earliest approach tried to elucidate the behavior of such a complex system, and was solely based on the electro-chemical considerations, which formulated an empirical equation to describe the polarization curve. This empirical equation can replicate the polarization curve reasonably well at low and intermediate current density, but failed at high current density. Kim et al. [3] improved the empirical

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**Nomenclature**

- b* Tafel slope
- E* cell voltage
- E<sub>r</sub>* reversible cell potential
- E<sub>0</sub>* open circuit voltage
- E<sub>0</sub><sup>\*</sup>* appropriate open circuit voltage (OCV)
- F* Faraday’s constant
- J* current density (*i*)
- J<sub>0</sub>* exchange current density (*i<sub>0</sub>*)
- n* number of electrons involved in a reaction
- R<sub>e</sub>* ohmic resistance of the cell

*Greek letters*

- $\alpha$  transfer coefficient
- $\delta$  methanol crossover effect coefficient
- $\lambda_d$  effective coefficient in diffusion overpotential for mass transport limitation

equation for better replication of the cell performance at high current density. Squadrito et al. [7] reformed the Kim’s equation with addition of two extra terms to improve the prediction of the mass transfer related resistance. Argyropoulos et al. [8] corrected the equation that coefficients follow specific trends with fuel cell operating variables and allow any physically real interpretation of the model.

Methanol is an attractive fuel because its energy density is much higher than that of hydrogen, and it is an inexpensive liquid and easy to handle, store and transport. However, in practice, DMFC has a much lower open circuit voltage (OCV). One of the major reasons is that methanol can cross through the proton exchange membrane (PEM), such as Nafion<sup>®</sup>, to reach the cathode side via physical diffusion and electro-osmotic drag (by protons). Such crossover not only results in a waste of fuel, but also lowers the cell performance. The effect of methanol crossover in the DMFC has attracted attention worldwide and its impact on cathode operation and system efficiency.

In this study, we develop a new semi-empirical model for the cell voltage as a function of current density response of the DMFC, which is based on methanol activity with thermodynamic function, diffusion overpotential to represent methanol crossover contribution and mass transport limitation which affects significantly the performance of DMFC.

**2. Model development**

Srinivasan et al. [2] showed that it is possible to use a simple model equation to describe the cell voltage (*E*) versus current density (*j*) behavior for PEMFCs in the activation and ohmic controlled current density region:

$$E = E_0 - b \log j - R_e j \tag{1}$$

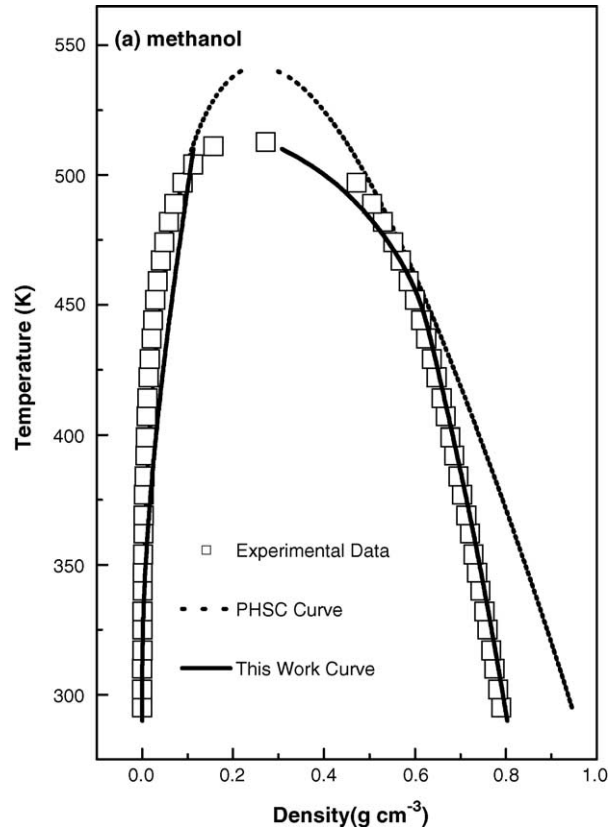


Fig. 1. Vapor/liquid equilibrium experimental data for water. The solid lines are calculated from this work. The dotted lines are calculated from the PHSC model. Open squares are experimental data [11].

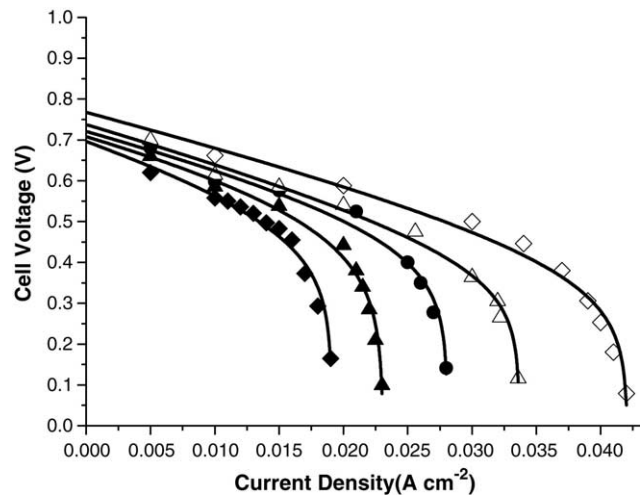


Fig. 2. Comparison between experimental data [8] and empirical equation based prediction for a cell operated with 0.125 M methanol solution. For a cell operated with each 0.125, 0.25 0.5 M methanol solution supplied at a rate of 1.12 cm<sup>3</sup> min<sup>-1</sup> with air fed cathodes pressurized at 2 bar. Catalysts consisted of 35 wt.% Pt–15 wt.% Ru (2 mg cm<sup>-2</sup> metal loading) and membrane type is Nafion 117 membrane of 0.3 mm thickness (cell temperatures: (◆) 343.15 K; (▲) 348.15 K; (○) 353.15 K; (△) 358.15 K; (◇) 363.15 K).

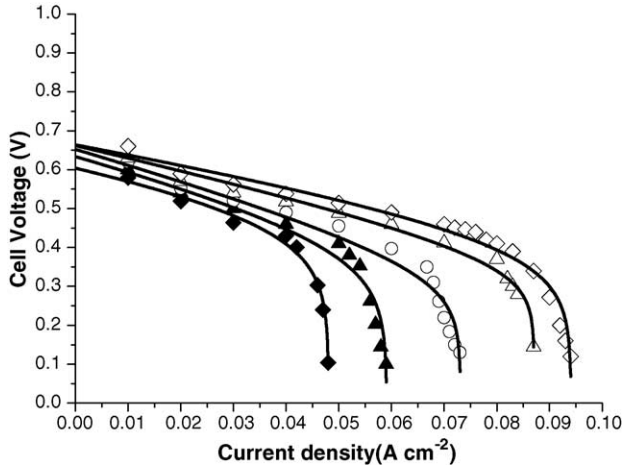


Fig. 3. Comparison between experimental data [8] and empirical equation based prediction for a cell operated with 0.25 M methanol solution. For a cell operated with each 0.125, 0.25, 0.5 M methanol solution supplied at a rate of  $1.12 \text{ cm}^3 \text{ min}^{-1}$  with air fed cathodes pressurized at 2 bar. Catalysts consisted of 35 wt.% Pt–15 wt.% Ru ( $2 \text{ mg cm}^{-2}$  metal loading) and membrane type is Nafion 117 membrane of 0.3 mm thickness (cell temperatures: (◆) 343.15 K; (▲) 348.15 K; (○) 353.15 K; (△) 358.15 K; (◇) 363.15 K).

with

$$E_0 = E_r + b \log j_0 \quad (2)$$

where  $E_r$  is the reversible cell potential,  $b$  the Tafel slope for oxygen reduction and  $R$  the ohmic resistance of the cell.

Using Eq. (1), with the appropriate coefficients, it was shown that as current density increased the predicted cell potential decreased much less rapidly than observed [2]. To increase the reliability of the aforementioned equation, Kim

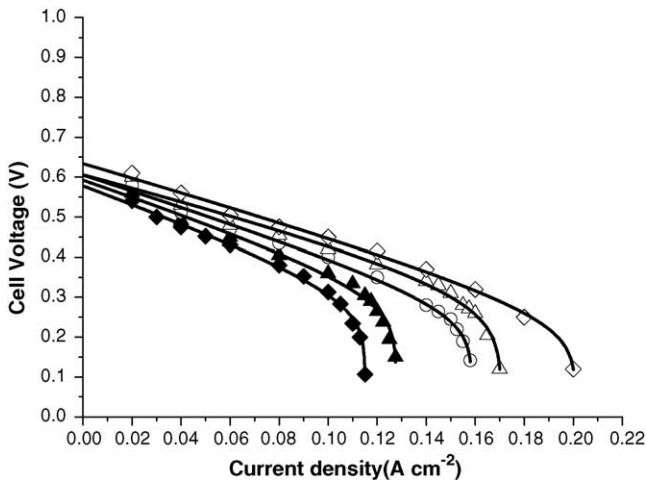


Fig. 4. Comparison between experimental data [8] and empirical equation based prediction for a cell operated with 0.5 M methanol solution. For a cell operated with each 0.125, 0.25, 0.5 M methanol solution supplied at a rate of  $1.12 \text{ cm}^3 \text{ min}^{-1}$  with air fed cathodes pressurized at 2 bar. Catalysts consisted of 35 wt.% Pt–15 wt.% Ru ( $2 \text{ mg cm}^{-2}$  metal loading) and membrane type is Nafion 117 membrane of 0.3 mm thickness (cell temperatures: (◆) 343.15 K; (▲) 348.15 K; (○) 353.15 K; (△) 358.15 K; (◇) 363.15 K).

et al. [3] suggested

$$E = E_0 - b \log j - R_e j - m e^{nj} \quad (3)$$

where  $m$  and  $n$  are the parameters that account for the “mass transport overpotential” as a function of current density.

Squadrito et al. [7] used Eq. (3) as a starting point to analyze the different contributions to the mass transport limitation and produced an equation in the form:

$$E = E_0 - b \log j - R_e j + a j^k \ln(1 - \beta j) \quad (4)$$

where  $a$ ,  $k$  and  $\beta$  are the parameters.

The term  $\ln(1 - \beta j)$  introduces a limit to the available current density. For  $k=1$ ,  $a$  has the same dimension as  $R_e$  and can be interpreted as an additional resistance term due to the overall mass transport limitation.

Argyropoulos et al. [8] showed the applicability of Kim’s and Squadrito’s equations for predicting voltage response of the DMFC:

$$E_{\text{cell}} = E_0 - b \log j - R_e j + C_1 \ln(1 - C_2 j) \quad (5)$$

i.e. in the Squadrito equation  $k=0$ .

Number of models introduced here are semi-empirical. All models are based on Srinivasan et al.’s model, Eq. (1). It, however, has a serious mathematical defect. When the current density,  $j$ , becomes zero, the equation should reduce to the voltage,  $E_0$ . These models, however, do not meet the mathematical boundary condition.

We propose a new semi-empirical cell voltage model:

$$E_{\text{cell}} = E^* - \kappa_R j + \lambda_d \ln \left( \frac{1 - 1 - j}{j_{\text{lim}}} \right) \quad (6)$$

with

$$E_0^* = E_0 = \delta a_{\text{MeOH}} \quad (7)$$

The derivations are shown in Appendix A. We employed methanol activity term ( $\delta a_{\text{MeOH}}$ ) to take into account the methanol crossover effect account [9] and  $\delta$  is an effective coefficient. To describe methanol activity of DMFC, we employed an equation of state (EOS) based on the modified perturbed hard-sphere-chain (PHSC) model. It considers a new perturbation equation that is obtained from the generalized Lennard–Jones potential function based on statistical–mechanical relationship [10]:

$$\ln a = \left[ \frac{3 \frac{BE}{F} \eta^3 - \left( \frac{E^3}{F^2} + \frac{BE}{F} \right) \eta^2 + \left( \frac{E^3}{F^2} + 6 \frac{BE}{F} \right) \eta - \frac{E^3}{F^2}}{(1 + \eta)^2} + \frac{\frac{E^3}{F^2} (1 + \eta)}{(1 - \eta)^3} + \left( \frac{E^3}{F^2} - 1 \right) \ln(1 - \eta) - \left( \frac{E^3}{F^2} - 1 \right) \frac{\eta}{(1 - \eta)} \right] + \sum_{i,j=1}^m \phi_i \phi_j \left[ \left( \frac{24\eta}{\tilde{T}} \right) \left\{ -\frac{8}{3A^3} - \frac{1}{A} \left( \frac{\ln(A\lambda - 1)}{A^2} + \frac{\lambda^2}{2} + \frac{\lambda}{A} - \frac{4}{A^2} \right) + \frac{1}{3} \right\} \right] \quad (8)$$

Table 1  
Calculated values for the this semi-empirical equation coefficients for DMFCs operated with methanol solution

Cell temperature (K)	MeOH solution concentration (M)	Calculated values				
		$E_0$ (V)	$\delta$ (V)	$\kappa_R$ (V j <sup>-1</sup> )	$\lambda_d$ (V)	Limiting current
363.15	0.125	1.3175	2.6557	6.8525	0.07097	0.0421
358.15	0.125	1.2876	2.6328	7.5806	0.06451	0.0337
353.15	0.125	1.2708	2.6103	6.4519	0.07327	0.0282
348.15	0.125	1.2579	2.5882	5.5692	0.09211	0.0230
343.15	0.125	1.2460	2.5665	7.6569	0.07663	0.0191
363.15	0.25	1.2238	2.3657	1.9491	0.06022	0.0939
358.15	0.25	1.2136	2.3244	2.9761	0.02846	0.0870
353.15	0.25	1.2021	2.2832	3.6132	0.04775	0.0731
348.15	0.25	1.1934	2.2412	3.1202	0.06307	0.0591
343.15	0.25	1.1538	2.2008	1.8737	0.06749	0.0482
363.15	0.5	1.1886	2.1041	1.8067	0.02090	0.2001
358.15	0.5	1.1662	2.0832	1.7101	0.02849	0.1702
353.15	0.5	1.1650	2.0598	1.7872	0.03399	0.1581
348.15	0.5	1.1423	2.0357	1.8624	0.03591	0.1278
343.15	0.5	1.1278	2.0125	2.0314	0.03451	0.1152

The first term of Eq. (6),  $E_0$  is the voltage without methanol crossover. In Eq. (7),  $E_0^*$  is defined as an appropriate open circuit voltage (OCV). In this study, when the current density becomes zero, all terms should be zero except  $E_0^*$  term. In Eqs. (1), (3)–(5), the term,  $\log j$ , however, goes to infinity. It is not possible to have infinity at  $j = 0$ . The third term,  $\kappa_R j$  presents the ohmic resistance and electrode–electrolyte overpotential of the cell. To take into account rapid voltage drop at high current density, we employ diffusion overpotential in last term.

The above equation describes the methanol crossover contribution and diffusion contribution for mass transfer limitation region. In general, the methanol crossover effect plays a major role in determining the open circuit voltage of DMFC.  $\delta$  and  $\lambda_d$  represent the methanol crossover effect coefficient and effective coefficient in diffusion overpotential for mass transport limitation, respectively. Also value of  $j_{lim}$  is value of  $j$  when  $\eta \rightarrow -\infty$ .

Confirmed in Eq. (6), as the value of the current density approaches zero, the cell voltage becomes the appropriate open circuit voltage (OCV),  $E_0^*$  containing methanol crossover.

### 3. Result and discussion

We propose a new semi-empirical model to predict the cell voltage as a function of a current density for a liquid feed direct methanol fuel cell (DMFC). The performance of the DMFC, at higher current densities has been shown to be limited by a mass transport process, which mainly occurs, by diffusion.

In Fig. 1, the solid and dotted lines are calculated from the proposed model and MPHSC equation, respectively [11]. In the entire density region, MPHSC EOS shows slight deviations from the experimental data [11], however our model shows good agreement with the data. The obtained charac-

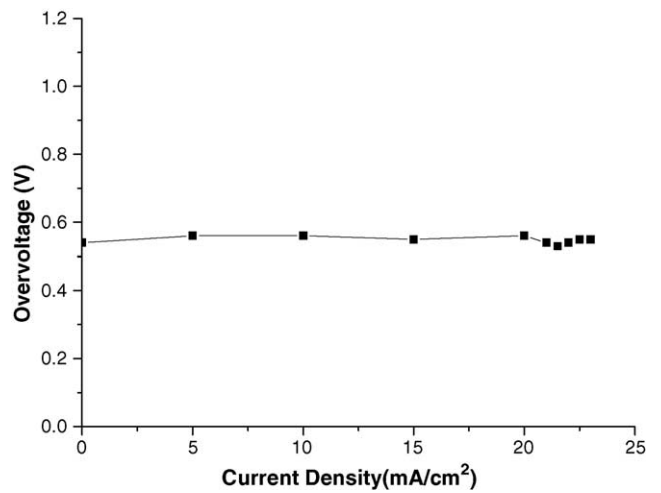


Fig. 5. Experimental overvoltage values of only methanol crossover [9] (temperature: 348 K, pressure: 2.0 bar air, methanol concentration: 0.125 M).

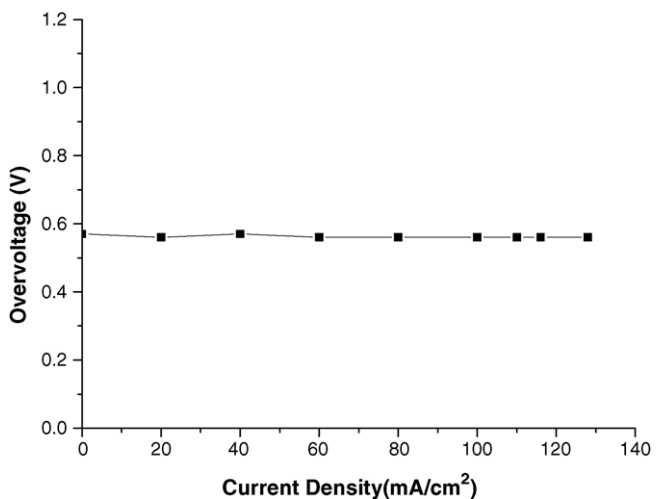


Fig. 6. Experimental overvoltage values of only methanol crossover [9] (temperature: 348 K, pressure: 2.0 bar air, methanol concentration: 0.5 M).

teristic parameters for water are  $r_{\text{MeOH}} = 2.9$ ,  $\sigma_{\text{MeOH}} = 2.95$ ,  $\varepsilon_{\text{MeOH}}/k = 550.2$ .

In Figs. 2–4, calculated cell voltages are presented for three different aqueous methanol solution concentrations (0.125, 0.25 and 0.5 M) at a various range of cell operating temperatures. Model parameters are listed in Table 1. The model equation proposed in this study is able to express the cell voltage in the entire current density region. The existing models, however, do not satisfy the mathematical boundary condition, that is, when the current density goes to zero, the open circuit voltage (OCV) diverges to the infinity. However our calculated  $E_0^*$  values are reasonable with temperature as shown in Table 1. In practical, the value of OCV decreases with increasing methanol concentration [9]. As shown in these figures, the cell voltage decreases with increasing current density. Especially, at the high current density region, the cell voltage decreases radically. It is because the diffusion affects the performance of total cell voltage. Thus, we employ these two contributions in the proposed model.

Undoubtedly, the methanol crossover is not the only issue in DMFC. One must also consider aspects such as the pressure effect and fuel flow rate. In fuel cells, membranes operate under the significant mechanical pressure that acts in opposition to the osmotic pressure and fuel flow rate is involved in a methanol crossover.

#### 4. Conclusion

We have established a new semi-empirical model to describe the cell voltage of a direct methanol fuel cell (DMFC) as a function of current density. The model presented here includes an accurate open circuit voltage (OCV), methanol crossover from methanol activity and diffusion effect that takes into account rapid voltage drop at high current density. Its advantage follows from its simplicity; a simple algebraic form with a few adjustable model parameters appears to be suitable for representing the appropriate open circuit voltage for the given systems.

#### Acknowledgement

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#### Appendix A

The total cell voltage is given:

$$E_{\text{cell}} = E_{\text{OCV}} - E_{\text{methanol\_crossover}} - \eta_{\text{electrode-electrolyte}} - \eta_{\text{ohmic\_resistance}} - \eta_{\text{diffusion}} \quad (\text{A1})$$

where  $E_{\text{OCV}}$  is the open circuit voltage,  $E_{\text{methanol\_crossover}}$  the methanol crossover effect,  $\eta_{\text{electrode-electrolyte}}$  the electrode–electrolyte overpotential,  $\eta_{\text{ohmic\_resistance}}$  the ohmic resistance,  $\eta_{\text{diffusion}}$  the diffusion overpotential.

##### A.1. Methanol crossover

The methanol crossover effect is expressed by methanol activity equation.

As shown in Figs. 5 and 6, the methanol crossover can be represented by:

$$E_{\text{methanol\_crossover}} = \delta a_{\text{MeOH}} \quad (\text{A2})$$

##### A.2. Electrode–electrolyte overpotential

Butler–Volmer equation is as follows:

$$i = i_0 \left[ \exp \left( \frac{n(1-\alpha)F\eta}{RT} \right) - \exp \left( \frac{-n\alpha F\eta}{RT} \right) \right] \quad (\text{A3})$$

where  $i$  is the current density (it has same meaning of  $j$ ),  $i_0$  the exchange current density ( $j_0$ ),  $\alpha$  the transfer coefficient,  $n$  the number of electrons involved in a reaction and  $F$  the Faraday’s constant.

Taylor expansion gives:

$$\begin{aligned} j &= j_0 \left\{ \left[ 1 + \frac{n(1-\alpha)F}{RT} \eta + \left( \frac{n(1-\alpha)F}{RT} \right)^2 \eta^2 + \dots \right] \right. \\ &\quad \left. - \left[ 1 + \frac{-n\alpha F}{RT} \eta + \left( \frac{-n\alpha F}{RT} \right)^2 \eta^2 + \dots \right] \right\} \\ &= j_0 \left[ \left\{ \frac{n(1-\alpha)F}{RT} - \frac{-n\alpha F}{RT} \right\} \eta \right. \\ &\quad \left. + \left\{ \left( \frac{n(1-\alpha)F}{RT} \right)^2 - \left( \frac{-n\alpha F}{RT} \right)^2 \right\} \eta^2 + \dots \right] \quad (\text{A4}) \end{aligned}$$

We take first order approximation due to  $\eta \ll 1$ :

$$\eta_{\text{electrode-electrolyte}} = \frac{RT}{nFj_0} j \quad (\text{A5})$$

##### A.3. Ohmic resistance

Ohmic resistance is:

$$\eta_{\text{ohmic\_resistance}} = R_e j \quad (\text{A6})$$

where  $R_e$  is the ohmic resistance of the solid polymer electrolyte.

##### A.4. Diffusion overpotential

Nernst diffusion layer equation is:

$$E = E^0 + \frac{RT}{nF} \ln a_0 \quad (\text{A7})$$

Above equation can represent current density:

$$E_i = E^0 + \frac{RT}{nF} \ln a \quad (\text{A8})$$

Diffusion overpotential is difference of two overpotential:

$$\eta = E_j - E = \frac{RT}{nF} \ln \frac{a}{a_0} \quad (\text{A9})$$

The activity can be represented concentration ratio:

$$\frac{C}{C_0} = \frac{r_0}{r} \exp\left(\frac{nF\eta}{RT}\right) \quad (\text{A10})$$

Current density can be expressed combining Fick's law about diffusion and Faraday's law:

$$\frac{j}{nF} = -D \frac{C_0 - C}{l} \quad (\text{A11})$$

Combining (A10) and (A11), current density is:

$$\begin{aligned} j &= -\frac{nFDC_0}{l} \left(1 - \frac{r_0}{r} \exp\left(\frac{nF\eta}{RT}\right)\right) \\ &= -\frac{nFDC_0}{l} \left(1 - \exp\left(\frac{nF\eta}{RT}\right)\right) \\ &= j_{\text{lim}} \left(1 - \exp\left(\frac{nF\eta}{RT}\right)\right) \end{aligned} \quad (\text{A12})$$

where as  $j_{\text{lim}}$  is limiting current density, it is value that  $\eta \rightarrow -\infty$ .

Therefore, diffusion overpotential can be derived as follows:

$$\eta_{\text{diffusion}} = \frac{RT}{nF} \ln \left(\frac{1-j}{j_{\text{lim}}}\right) = \lambda_d \ln \left(\frac{1-j}{j_{\text{lim}}}\right) \quad (\text{A13})$$

By combining Eqs. (A1), (A2), (A5), (A6) and (A13):

$$E_{\text{cell}} = E_0^* - \kappa_R j + \lambda_d \ln \left(\frac{1-j}{j_{\text{lim}}}\right) \quad (\text{A14})$$

with

$$E_0^* = E_0 - \delta a_{\text{MeOH}} \quad (\text{A15})$$

$$\kappa_R j = \left(\frac{RT}{nFj_0} + R_e\right) j \quad (\text{A16})$$

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