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A Finite Difference Scheme for the Modeling of a Direct Methanol Fuel Cell

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***Abstract*— *A one dimensional (1-D), isothermal model for a direct methanol fuel cell (DMFC) is introduced and solved numerically by a simple finite difference scheme. By using numerical calculation, the model model can be extended to more complicated situation which can not be solved analytically. The model considers the kinetics of the multi-step methanol oxidation reaction at the anode. Diffusion and crossover of methanol are taken into account and the reduced potential of the cell due to the crossover is then estimated. The calculated results are compared to the experimental data from literature. This finite difference scheme can be rapidly solved with high accuracy and it is suitable for the extension of the model to more detail or to higher dimension.*

I. INTRODUCTION

Direct Methanol Fuel Cells (DMFCs) are recently being attracted as an alternative power source to batteries for portable applications since they potentially provide better energy densities. However, there are two key constraints limiting the effectiveness of DMFC systems: crossover of methanol from anode to cathode and the sluggish kinetics of the electrochemical oxidation of methanol at the anode.

The crossover of methanol lessen the system efficiency and decreases cell potential due to corrosion at the cathode. The electrochemistry and transport processes in DMFCs are shown in Fig.1. Methanol is oxidized electrochemically at both the anode and cathode, however the corrosion current at the cathode does not create any useful work. A number of experimental and computational investigations have reported methanol crossover in DMFCs [1-4].

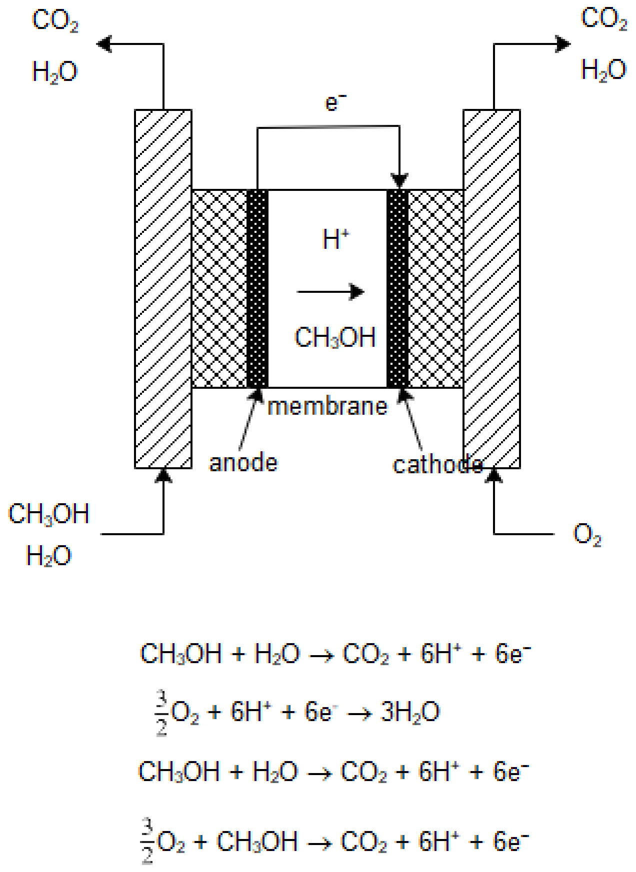

Fig.1 Schematic illustration of a DMFC.

There are several models have developed to predict the behaviour of direct methanol fuel cells, which is important in the design, operation and control. Among them, 1D model show the advantage of simple and fast calculation, which is suitable for real time simulation. García et al. [5] presented a one dimensional, isothermal model of a DMFC to rapidly predict the polarization curve and goes insight into mass transfer happening inside the cell. The model was solved analytically. However, analytical methods have some drawbacks such as the limitation to some specific cases and difficulty to extend to more complicated situation. Therefore, in this current study, instead of using analytical method, the model is solved numerically using a simple finite difference scheme.

One-dimension mathematical modeling of direct methanol fuel cell

The model which was developed in [5] is used in this study. The details are briefly discussed as follows.

Assumptions. The model considers the 1D variation of methanol concentration across the fuel cell which includes anode backing layer (ABL), anode catalyst layer (ACL), and membrane. The schematic diagram of the layers considered in the model and several assumption illustration were presented in . The assumptions are detailed as follows

1) Steady-state and isothermal operation.

2) Variables are lumped along the flow direction

3) Convection of methanol is neglected.

4) Isothermal conditions.

5) All physical properties, anodic and cathodic overpotentials are considered constant.

6) Local equilibrium at interfaces between layers can be described by a partition function.

7) All the reaction are considered as homogeneous reactions.

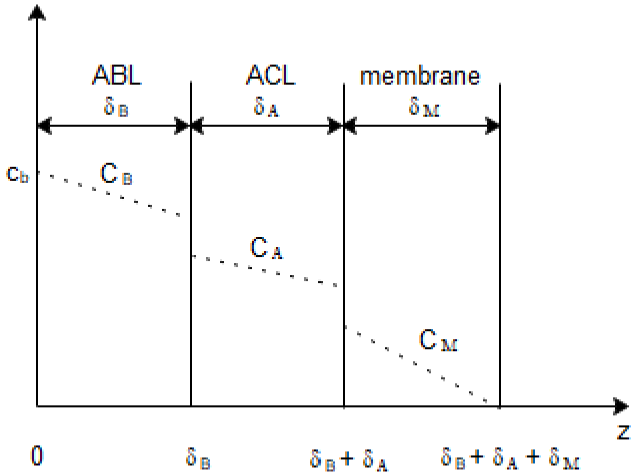

Fig.2 Schematic diagram and concentration distribution of the DMFC layers

The voltage of the cell is calculated as

$$V_{cell} = U^{O_2} - U^{MeOH} - \eta_C - \eta_A - \frac{\delta_M I_{Cell}}{\kappa}$$

(1)

in which,

U_{O_2} and UMeOH are the thermodynamic equilibrium potential of oxygen reduction and methanol oxidation respectively

η_C and η_A are the cathode and anode overpotentials, respectively

$\frac{\delta_M I_{Cell}}{\kappa}$ represents the ohmic drop across the membrane.

Anode backing layer - ABL (domain B)

In this domain, the differential mass balance for methanol at steady state is

$$\frac{dN^B_{MeOH,z}}{dz} = 0$$

(2)

The methanol flux is the Fickian diffusion with an effective diffusivity D_B

$$N^B_{MeOH,z} = -D_B \frac{dc^B_{MeOH,z}}{dz}$$

(3)

Combining Eq. (2) and Eq. (3), the distribution equation for methanol in ABL is

$$\frac{d^2 c^B_{MeOH,z}}{dz^2} = 0$$

(4)

Anode Catalyst Layer - ACL (domain A)

In this domain, there is a methanol oxidation reaction. Therefore, the differential mass balance for methanol at steady state is

$$\frac{dN^A_{MeOH,z}}{dz} = \frac{r_{MeOH}}{M_{MeOH}}$$

(5)

In which the molar rate of methanol consumption $\frac{r_{MeOH}}{M_{MeOH}}$ is calculated from the volumetric current density j as:

$$\frac{r_{MeOH}}{M_{MeOH}} = \frac{-j}{6F}$$

(6)

The current density is related to the concentration of methanol as ([6])

$$j = aI^{MeOH}_{0,ref} \frac{kc^A_{MeOH}}{c^A_{MeOH} + \lambda e^{\alpha_A \eta_A F/RT}} e^{\alpha_A \eta_A F/RT}$$

(7)

In which a is the specific surface area of the anode, $I^{MeOH}_{0,ref}$ is the exchange current density, and k and λ are constants

The methanol flux is the Fickian diffusion with an effective diffusivity D_A

$$N^A_{MeOH,z} = -D_A \frac{dc^A_{MeOH,z}}{dz}$$

(8)

Combining Eq. (5), Eq. (6) and Eq. (8), the distribution equation for methanol in ACL is

$$D_A \frac{d^2 c^A_{MeOH,z}}{dz^2} = \frac{j}{6F}$$

(9)

Membrane (domain M)

The differential mass balance for methanol at steady state in the membrane is

$$\frac{dN^M_{MeOH,z}}{dz} = 0$$

(10)

The methanol flux in the membrane includes the diffusion and electro-osmotic drag as follows:

$$N^{M}_{MeOH,z} = -D_M \frac{dc^{M}_{MeOH,z}}{dz} + \xi_{MeOH} \frac{I_{Cell}}{F}$$

(11)

In which D_M and ξ_{MeOH} are the effective diffusion in membrane and the electro-osmotic drag coefficients of methanol, respectively.

Combining Eq. (10) and Eq. (11), the distribution equation for methanol in membrane is

$$D_M \frac{d^2 c^{M}_{MeOH,z}}{dz^2} = 0$$

(12)

Boundary condition:

At z=0 (the interface between the flow-channel and anode backing layer), there is no mass resistance. Therefore, the concentration is given by the bulk concentration of the flow as:

$$c^{B}_{MeOH,z=0} = c_{bulk}$$

(13)

At $z = \delta_B$ (the interface between ABL and ACL), there are two conditions. First, the local equilirium of the concentrations between two domains is given by a partition coefficient K_I as

$$c^{A}_{MeOH,z=\delta_B} = K_I c^{B}_{MeOH,z=\delta_B}$$

(14)

Second condition is the equality of fluxes between two domains (ABL and ACL)

$$N^{B}_{MeOH,z=\delta_B} = N^{A}_{MeOH,z=\delta_B}$$

(15)

At $z = \delta_B + \delta_A$ (the interface between ACL and membrane), there are two conditions. First, the local equilirium of the concentrations between two domains is given by a partition coefficient K_{II} as

$$c^{M}_{MeOH,z=\delta_B+\delta_A} = K_{II} c^{A}_{MeOH,z=\delta_B+\delta_A}$$

(16)

Second condition is the equality of fluxes between two domains (ACL and membrane) as

$$N^{A}_{MeOH,z=\delta_B+\delta_A} = N^{M}_{MeOH,z=\delta_B+\delta_A}$$

(17)

At $z = \delta_B + \delta_A + \delta_M$: All the methanol crossing the membrane is assumed to consume immediately at the cathode, result in a zero concentration at the membrane/ cathode-layer interface. Thus,

$$c^{M}_{MeOH,z=\delta_B+\delta_A+\delta_M} = 0$$

(18)

Finite difference scheme and overpotential calculation

The spatial independent variable z in the three segments (0, δ_B), (δ_B, $\delta_B + \delta_A$), ($\delta_B + \delta_A$, $\delta_B + \delta_A + \delta_M$) can be discretized into n_B, n_A, n_M subdivisions, respectively, as

$$0 = z^B_1 < z^B_2 < .. < z^B_{n_B} = \delta_B$$

(19)

$$\delta_B = z^A_1 < z^A_2 < .. < z^A_{n_A} = \delta_B + \delta_A$$

(20)

$$\delta_B + \delta_A = z^M_1 < z^M_2 < .. < z^M_{n_A} = \delta_B + \delta_A + \delta_M$$

(21)

In each segment, note that the length of subsegment is equal to Δz_B, Δz_A, Δz_M, respectively.

Governing equations

Inside the domains (ABL, ACL and membrane), the second derivatives in the governing equations are discretized using central difference formulae. The details are as follows

In ABL region, equation (4) is discretized as:

$$D_B \frac{c^B_{MeOH,z+\Delta z} - 2c^B_{MeOH,z} + c^B_{MeOH,z-\Delta z}}{\left(\Delta z_B\right)^2} = 0$$

(22)

Or

$$c^B_{MeOH,i+1} - 2c^B_{MeOH,i} + c^B_{MeOH,i-1} = 0$$

(23)

In ACL region, equation (4) is discretized as:

$$D_A \frac{c^A_{MeOH,z+\Delta z} - c^A_{MeOH,z} + c^A_{MeOH,z+\Delta z}}{\left(\Delta z_A\right)^2} = \\ = \frac{a I^{MeOH}_{0,ref} \dfrac{k c^A_{MeOH,z}}{c^A_{MeOH,z} + \lambda e^{\alpha_A \eta_A F/RT}} e^{\alpha_A \eta_A F/RT}}{6F}$$

(24)

Or

$$D_A \frac{c^A_{MeOH,i+1} - c^A_{MeOH,i} + c^A_{MeOH,i+1}}{\left(\Delta z_A\right)^2} = \\ = \frac{a I^{MeOH}_{0,ref} \dfrac{k c^A_{MeOH,i}}{c^A_{MeOH,i} + \lambda e^{\alpha_A \eta_A F/RT}} e^{\alpha_A \eta_A F/RT}}{6F}$$

(25)

In membrane region, equation (12) is discretized as :

$$D_M \frac{c^M_{MeOH,z+\Delta z} - 2c^M_{MeOH,z} + c^M_{MeOH,z-\Delta z}}{\left(\Delta z_M\right)^2} = 0$$

(26)

Or

$$c^M_{MeOH,i+1} - 2c^M_{MeOH,i} + c^M_{MeOH,i-1} = 0$$

(27)

Boundary conditions

The first derivatives in boundary conditions are approximated using forward difference formulae as follows:

At the left interface, using the forward scheme:

$$\frac{dc_{MeOH,z}}{dz} = \frac{c_{MeOH,z+\Delta z} - c_{MeOH,z}}{\Delta z}$$

(28)

At the right interface, using the backward scheme:

$$\frac{dc_{MeOH,z}}{dz} = \frac{c_{MeOH,z} - c_{MeOH,z-\Delta z}}{\Delta z}$$

(29)

Concentration profile

After discretization, a system of equations for the concentration of methanol is obtained. The system is solved using simple iteration method to find the concentration profile of methanol.

Anode overpotential

From the concentration profile, the cell current can be estimated as:

$$I_{cell} = \int_{\delta_B}^{\delta_B+\delta_A} a I^{MeOH}_{0,ref} \frac{k c^A_{MeOH}}{c^A_{MeOH} + \lambda e^{\alpha_A \eta_A F/RT}} e^{\alpha_A \eta_A F/RT}$$

(30)

In which η_A is assumed to be constant. The integration is numerically calculated using trapezoidal rule. Because η_A is also included in calculation of concentration profile, an iteration is required to find appropriate η_A for a given value of I_{Cell}.

Cathode overpotential

Tafel kinetics with first-order oxygen concentration dependence is used to estimate the oxygen reduction at the cathode.

$$I_{cell} + I_{leak} = I^{O_2}_{0,ref} \frac{c_{O_2}}{c_{O_2,ref}} e^{\alpha_C \eta_C F/RT}$$

(31)

In which I_{leak} is the leakage current density due to the oxidation of methanol crossing the membrane. The leakage current density can be estimated as

$$I_{leak} = 6F N^M_{MeOH,z}$$

(32)

In which $N_{MeOH,z}^{M}$ is estimated from Eq. (11). Then, Eq. (32) is used to obtain η_C for a given value of I_{Cell}.

After the anode and cathode overpotentials are known, the V_{Cell} for a given value of I_{Cell} is calculated using Eq. (1). The parameters used in the model are summarized in Table *1*.

Table 1 Model parameters

Parameter	**Value**
a	$1000\ cm^{-1}$
D_A	$2.8 \times 10^{-5}\exp(2436(1/353-1/T))\ cm^2/s$
D_B	$8.7 \times 10^{-6}\ cm^2/s$
D_M	$4.9 \times 10^{-6}\exp(2436(1/333-1/T))\ cm^2/s$
$I_{0,ref}^{MeOH}$	$9.425 \times 10^{-3}\exp(33570/R(1/333-1/T))\ A/cm^2$
$I_{0,ref}^{O_2}$	$4.222 \times 10^{-3}\exp(73200/R(1/333-1/T))\ A/cm^2$
K_I	0.8
K_{II}	0.8
k	7.5×10^{-4}
T	343.15 K
U_{MeOH}	0.03 V
U_{O2}	1.24 V
α_a	0.52
α_c	1.55
δ_A	0.0023 cm
δ_B	0.015 cm
δ_M	0.018 cm
κ	0.036 s/cm
λ	$2.8 \times 10^{-9}\ mol/cm^3$
ξ_{MeOH}	$2.5x_{MeOH}$

II. RESULTS AND DISCUSSIONS

The simulation results of the polarization curve for DMFC at different concentrations of the bulk flow are shown in Fig.3. The calculation results well agree with the experimental data report in [5]. However, the difference at the end of the curve is quite high. The disagreement could be due to the assumption that the methanol electro-osmotic drag coefficient is a constant value. It is better to calculate the electro-osmotic drag coefficient at each point, especially at the end of the curve.

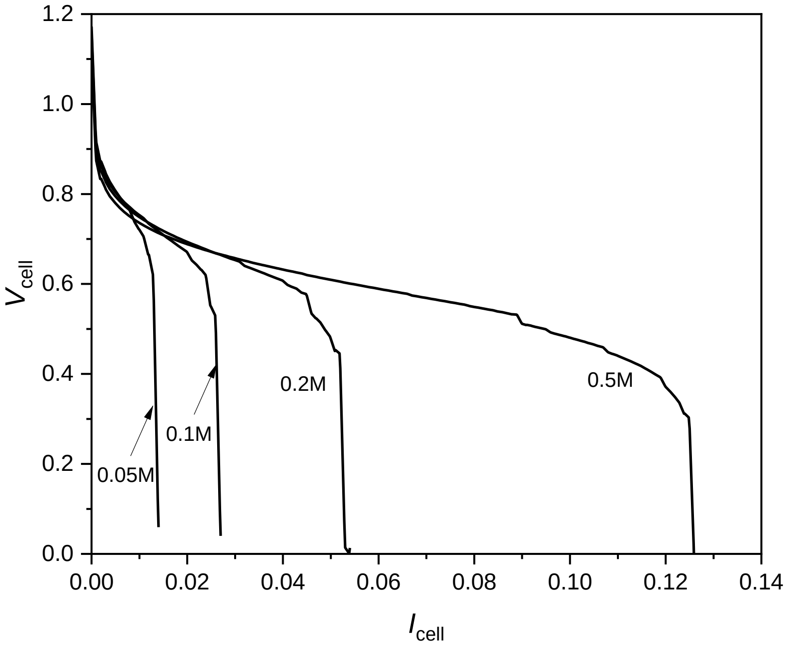

Fig.3 Model predictions for different methanol concentrations

Fig.4 shows concentration profiles across the anode and membrane obtained by the model for the four concentrations at 15 mA/cm^2.

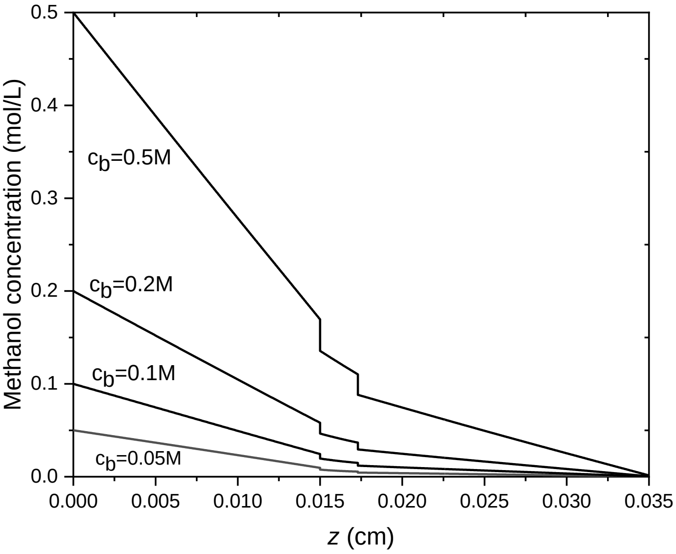

Fig.4 Concentrations profiles for different methanol bulk concentrations

III. CONCLUSIONS

In this study, a finite difference scheme were sucessfully applied to solve the one-dimensional, isothermal model of a DMFC. Using reasonable transport and kinetic parameters from literature, the calculation results well agree with experimental polarization curve. The scheme also is applicable in the estimation of concentration profiles in the anode and membrane as well as predicting the methanol crossover. The computation time is fast enough for real time application.

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