Journal of Applied Sciences

ISSN 1812-5654

science alert

ANSInet
an open access publisher
http://ansinet.com

Journal of Applied Sciences 11 (13): 2426-2430, 2011
ISSN 1812-5654 / DOI: 10.3923/jas.2011.2426.2430

Unsteady State Modeling and Analysis of a Passive Liquid-feed DMFC

Sahriah Basri, Siti Kartom Kamarudin, Wan Ramli Nan Daud and Norhafiz Hashim
Institut of Sel Fuel, Fakulti Kejuruteraan Kimia dan Alam Bina,
Universiti Kebangsaan Malaysia, 43650 Bangi, Selangor, Malaysia

Abstract: A one-dimensional, unsteady state, two phase model has been developed for a liquid-feed DMFC delivery system including the fuel cell itself. The model considers the mass and heat transport in the feed delivery system attached to the anode and cathode of the fuel cell. The effects of feed methanol concentration in the reservoir and current density on mass transport of catalyst layer revealed. It is further revealed that the optimum performance with 4 M methanol concentrations in term of methanol crossover with consideration of time

Key words: Unsteady state, passive liquid-feed DMFC

INTRODUCTION

Passive direct methanol fuel cells are promising high current density compare to battery and have the advantages of high efficiency, reliability, flexibility, durability and easy in maintenance. However, two predominant issues that hinder the application of Direct Methanol Fuel Cell (DMFC) technology are low kinetics of methanol electro-oxidation on the anode catalyst and crossover of un-reacted methanol from the anode to the cathode. Water and thermal management is one of the key factors which ensure its highly efficient steady operation and extend its life-span (Shi *et al*., 2007). There have already been quite a few investigations on water (Shi *et al*., 2007; Scharfer *et al*., 2008; Liu and Wang, 2008) and thermal management (Dohle *et al*., 2002) for a DMFC. Based on experiment, an increase in temperature primarily has a positive impact on the DMFC performance at the same time increase the methanol crossover (Oedegaard and Hentschel, 2006). Some afford must be done to improve and solve the challenging on fabrication of DMFC.

Majority of the modeling on DMFC are focusing on active system and steady state condition. Thus, we have an unsteady state analytical model for a passive DMFC by taking these two factors into account. Moreover, this model could separate the anodic and the cathodic performances individually with a clear crossover effect. Major voltage losses of the DMFC can then be identified from its power delivery curve. In this work, we selected an in-house passive DMFC constructed with known and estimated parameters as a base cell to validate to our model. Modeling work then started with various parameters such as catalyst loadings, thickness and methanol concentrations. The impacts of these parameters individually or in combination on the efficiency of the passive DMFC were analyzed and discussed.

MODEL DEVELOPMENT

The model considers a passive-feed DMFC for 1 dimension system which consists of anode flow channel AFC, anode backing layer ABL, anode catalyst layer ACL, membrane, cathode catalyst layer CCL, cathode diffusion layer CDL and cathode flow channel CFC. Figure 1 represents the layer consideration in the single cell of DMFC. On the anode, methanol from solution tank diffused in anode backing layer to anode catalyst layer.

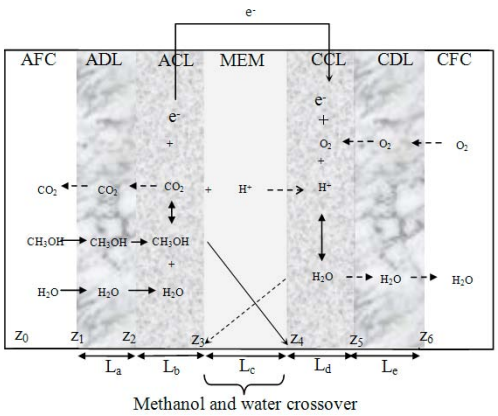

Fig. 1: A schematic diagram of a passive liquid-feed DMFC

Corresponding Author: Sahriah Basri, Institut of Sel Fuel, Fakulti Kejuruteraan Kimia dan Alam Bina,
Universiti Kebangsaan Malaysia, 43650 Bangi, Selangor, Malaysia

Table 1: Mass balance

Layer	Heat	
Anode diffusion layer	$N_M = D_a^{eff}\frac{\partial C_M}{\partial z} = \sqrt{D_a^{eff}/\pi t}\, e^{-L_a^2/4D_a^{eff}t}\left(C_b - C_{IM}\right)$	(1)
Anode catalyst layer	$\frac{\partial C_M}{\partial t} = D_b^{eff}\frac{\partial^2 C_M}{\partial z} - kC_M$	(2)
Mem-brane	$N_M = \sqrt{D_c^{eff}/\pi t}\, e^{-L^2/4D_c^{eff}t}C_M + \xi_M C_M\frac{I_{cell}}{F} + k_p C_M\frac{\Delta P}{L_c}$	(3)
Cathode catalyst layer	$\frac{\partial C_0}{\partial t} = D_d^{eff}\frac{\partial^2 C_0}{\partial z} - kC_0$	(4)
Cathode diffusion layer	$N_0 = D_e^{eff}\frac{\partial C_0}{\partial z} = \sqrt{D_e^{eff}/\pi t}\, e^{-L_e^2/4Dt}\left(C_{0g} - C_{10}\right)$	(5)

Heat transport:

Table 2: Heat balance

Layer	Heat	
Anode diffusion layer	$\frac{\partial T}{\partial x} = \alpha\frac{\left(T_{ACL} - T_{ADL}\right)}{z_2 - z_1}$	(6)
Anode catalyst layer	$\frac{\partial T}{\partial t} = \alpha\frac{\partial^2 T}{\partial z} + q$	(7)
Membrane	$\frac{T - T_m}{T_0 - T_m} = e^{-\left(\frac{hAt}{c_p\rho V}\right)}$	(8)
Cathode catalyst layer	$\rho c_p\frac{\partial T}{\partial t} = \lambda\frac{\partial^2 T}{\partial z^2} + q$	(9)

Mass transport: A passive liquid feed Direct Methanol Fuel Cell (DMFC) injected the fuel to the tank called Anode Flow Channel (AFC). The system neither external liquid pump nor gas blower. Methanol tank is considered as batch reactor at varying in volume which the principle same as Plug Flow Reactor (PFR). We assume the reaction occur completely and carbon dixide produced with. There are three major components coexisting in AFC side, porous media and fluid channel, such as H_2O, CH_3OH and CO_2. If carbon dioxide is considered in the system, means 2-phase system are consider. Other intermediate are neglected, OH, HO, CO, etc. in the system. The equation related to mass balance and heat transport are shown in Table 1 and 2.

Voltage balance:

$$\frac{r_M}{M_M} = \frac{\left(a_a i_{0M,ref}\frac{kC_M}{C_M + \lambda e^{\alpha_A \eta_A F/RT}}e^{\alpha_A \eta_A F/RT}\right)}{6F} \quad (10)$$

where, M_M is the molecular weight of methanol, n_M is the number of electrons transferred during methanol oxidation (where consumption of 1 mol of methanol can produce n_M = 6 mol electrons), a_a is the specific surface area of the anode, $I_{OM,ref}$ is the reference methanol oxidation exchange current density, $\lambda$is constant in the rate expression and $\alpha_A$is the anodic transfer coefficient.

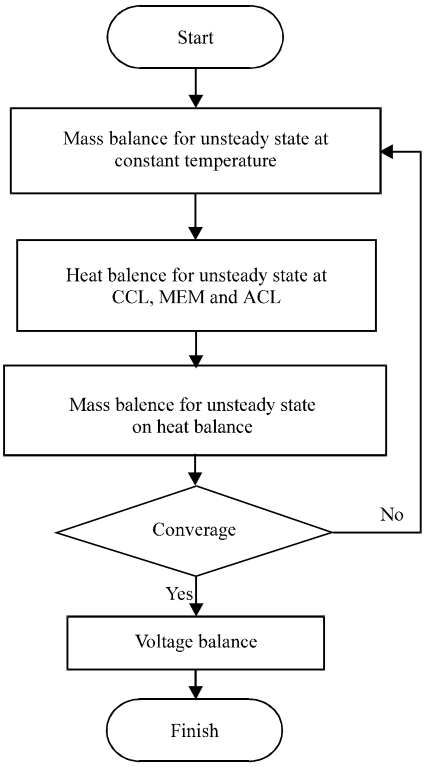

Fig. 2: Schematic diagram analytical solution for unsteady state

Analytical solution: Solution for the mathematical problem made based on Fig. 2.

RESULTS AND DISCUSSION

These results consist of three components which are mass balance, heat balance and voltage balance.

Figure 3a-d show the methanol and oxygen distribution through the layer at difference time. Methanol concentration at the first 15 h abruptly drops because the platinum as catalyst works effectively at ACL. Oxygen can diffuse into the cathode from the ambient due to the air breathing action of the cell. Air from surrounding will pass through CFC then diffused at CDL. Diffusion process is very slow with time and z direction because oxygen concentration at CDL increases slowly as shown in Fig. 3c and d.

Fig. 4a and b show the temperature distribution for each layer ACL and ADL. For ACL layer, temperature increase abruptly then start to decrease after 2 h. This shows the activity of reaction between methanol and water to produce proton and electron. Heat is transfer

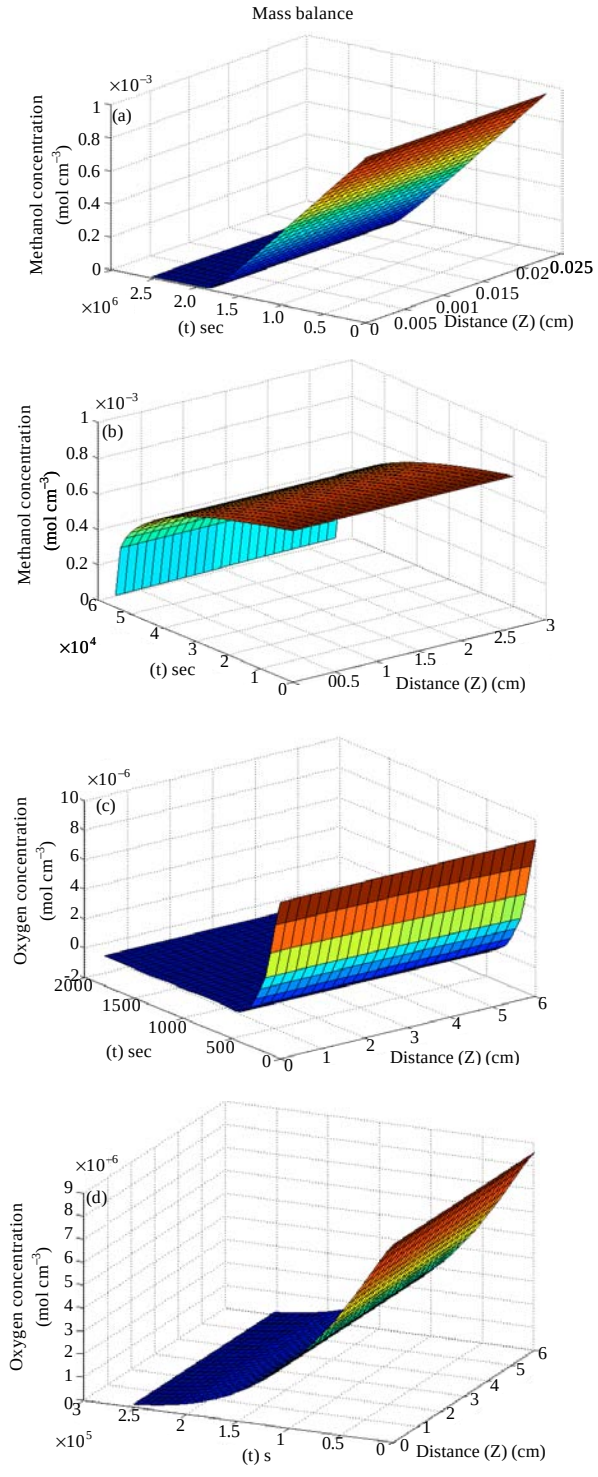

Fig. 3: (a) Methanol Concentration at ABL, (b) Methnaol Concentration at ACL, (c) Oxygen Concentration at CCL and (d) Oxygen Concentration at CDL

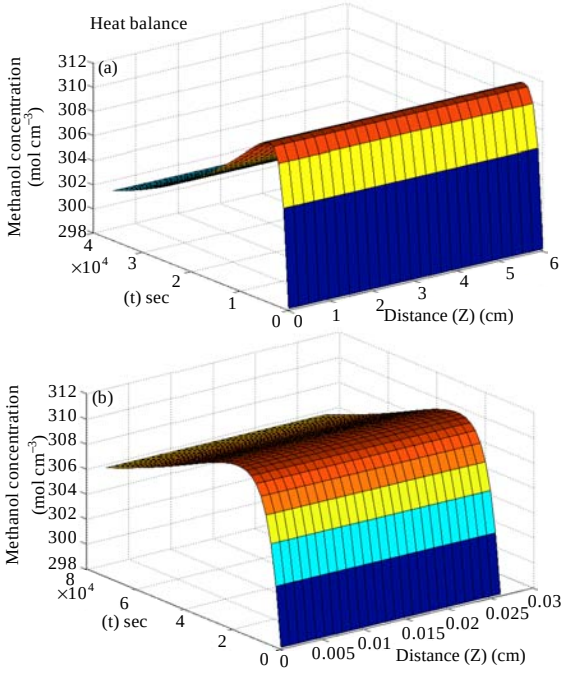

Fig. 4: (a) Temperature distribution at ACL for 10 h after methanol injected to the reservoir and (b) Temperature distribution at ACL for 10 h after methanol injected to the reservoir

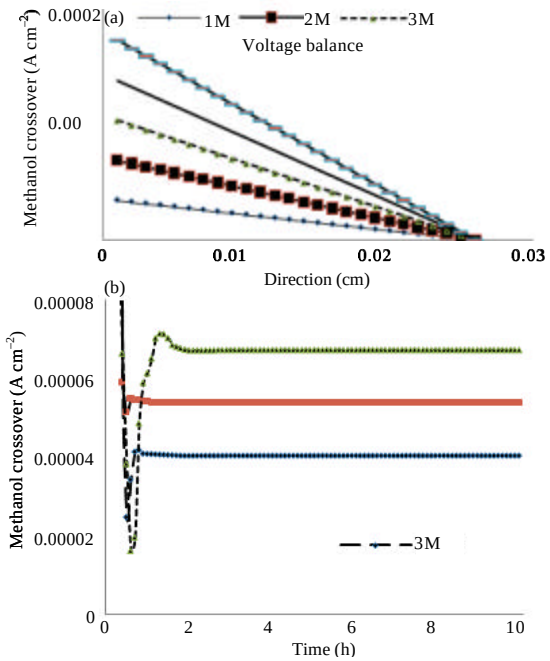

Fig. 5: Methanol crossover through (a) z-direction and (b) time

from the ACL to the ADL. Here, temperature at ADL is depends on the ACL. Form the figure, temperature also increase at ADL then decrease slowly after 6 h.

In this study, current density set as constant of 20 mA cm^{-2} and then run the simulation at various methanol concentrations from 1 M to 5 M which is optimum methanol concentration. The results in Fig. 5a shows the effect of methanol crossover have increase proportionally to the bulk methanol concentration. Figure 5b shows the trend of methanol crossover through the membrane along the experiment for 10 h. 5 Molar concentrations show the highest effect of methanol crossover to current density.

CONCLUSION

A unsteady state of direct methanol fuel cell with mass and heat transport for both anode and cathode are take into consideration. The model takes into account mass transfer from the anode flow and fragment heat due to the electrochemical reaction in the anode and cathode side.

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support given for this work by the Ministry of Science Technology and Innovation (MOSTI) under the Science Fund No: 03-01-02 SF0032.

NOMENCLATURES

a_o = Active area per unit volume in anode catalyst layer (cm^{-1})
a_o = Integrated constant (cm^{-1})
A_a = Active area per unit mass of PtRu catalyst ($cm^2\ g^{-1}$)
A_c = Active area per unit mass of Pt catalyst ($cm^2\ g^{-1}$)
Ar = Active area (cm^2)
C_b = Anode channel concentration of methanol (mol cm^{-3})
C_C = Carbon dioxide concentration (mol cm^{-3})
C_M = Methanol Concentration (mol cm^{-3})
C_{1M} = Methanol concentration at z_2 (mol cm^{-3})
C_{2M} = Methanol concentration at z_3 (mol cm^{-3})
$C_{M,ref}$ = Reference methanol concentration (mol cm^{-3})
C_O = Oxygen concentration (mol cm^{-3})
C_{Og} = Oxygen concentration at cathode catalystlayer/ gas diffusion (mol cm^{-3})
$C_{O,ref}$ = Reference oxygen concentration (mol cm^{-3})
C_W = Water concentration (mol cm^{-3})
D_a = Methanol diffusivity in anode catalyst layer ($cm^2\ sec^{-1}$)
D_a^{eff} = Effective diffusivity of methanol in anode catalyst layer ($cm^2\ sec^{-1}$)
D_b = Methanol diffusivity in anode backing layer ($cm^2\ sec^{-1}$)
D_b^{eff} = Effective diffusivity of methanol in anode backing layer ($cm^2\ sec^{-1}$)
D_c = Oxygen diffusivity in cathode catalyst layer ($cm^2\ sec^{-1}$)
D_c^{eff} = Effective oxygen diffusivity in cathode catalyst layer ($cm^2\ sec^{-1}$)
D_d = Oxygen gas diffusivity in cathode gas diffusion ($cm^2\ sec^{-1}$)
D_d^{eff} = effective oxygen gas diffusivity in cathode gas diffusion ($cm^2\ sec^{-1}$)
D_m = Methanol diffusivity in membrane ($cm^2\ sec^{-1}$)
F = Faraday constant (C mol^{-1})
$i_{oM,ref}$ = Reference methanol oxidation exchange current density (A cm^{-2})
$i_{oO,ref}$ = Reference oxygen reduction exchange current density (A cm^{-2})
I_{cell} = Cell discharge current density (A cm^{-2})
I_{leak} = Cross-over current density (A cm^{-2})
j = local transfer current density within catalyst layer (A cm^{-3})
k = Potential dependent rate constant of methanol oxidation (sec^{-1})
k_c = Potential dependent rate constant of oxygen reduction (sec^{-1})
k_p = Permeation constant of pressure induced convection (cm^2/sec/atm)
L_a = Anode catalyst layer thickness (cm)
L_b = Anode backing layer thickness (cm)
L_c = Cathode catalyst layer thickness (cm)
L_d = Cathode gas diffusion thickness (cm)
L_m = Membrane thickness (cm)
n_M = Electrons transferred of methanol oxidation
n_O = NO electrons transferred of oxygen reduction
N_m = Methanol flux at membrane (mol/cm^2/sec)
N_m = Oxygen flux at membrane (mol/cm^2/sec)
R = Universal gas constant (J/mol/K)
R_g = Rg universal gas constant (atm/cm^3/mol/K)

REFERENCES

Dohle, H., J. Mergel and D. Stolten, 2002. Heat and power management of a Direct-Methanol-Fuel-Cell (DMFC) system. J. Power Sour., 111: 268-282.

Liu, F. and C.Y. Wang, 2008. Water and methanol crossover in direct methanol fuel cells-effect of anode diffusion media. Electrochim. Acta, 53: 5517-5522.

Oedegaard, A. and C. Hentschel, 2006. Characterisation of a portable DMFC stack and a methanol-feeding concept. J. Power Sour., 158: 177-187.

Scharfer, P., W. Schabel and M. Kind, 2008. Modelling of alcohol and water diffusion in fuel cell membranes-experimental validation by means of *in situ* Raman spectroscopy. Chem. Eng. Sci., 63: 4676-4684.

Shi, M.H., J. Wang and Y.P. Chen, 2007. Study on water transport in PEM of a direct methanol fuel cell. J. Power Sour., 166: 303-309.