



Development of Conceptual Design Model of Direct Methanol Fuel Cell for a Portable Application

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This paper presents development of conceptual design model of DMFC for a portable application. The target power for the design is 0.4 watt per single cell, with 4 cm² active area. The current density and fuel cell voltage were fixed to 0.175 A/cm² and 0.57 V respectively. In order to develop new design, mass and heat transport will be analysed to get a better performance in the system. The new design will be applied to the portable applications such as cellphone, laptops and etc.

1. Introduction

Since methanol is one of the fuels with a very high specific energy, it is the best selection in choosing fuel in DMFC. Furthermore, methanol is also a great extend easier to store and transport without auxiliary devices for intermediate fuel processing and fuel reforming steps which are required by hydrogen-oxygen fuel cells. In DMFC system, the byproducts are ecologically inoffensive carbon dioxide and water. These are the reasons why DMFC system has been regarded as a potential substitution to conventional batteries for powering various low-power devices.

A number of studies (Bernardi, 1990; Springer et al., 1991; Fuller and Newman, 1993; Argyropoulos et al., 1999a; Scott et al., 1999; He et al., 2000; Berning et al., 2002; Nordlund and Lindbergh, 2002; Wang and Wang, 2003; Murgia et al., 2003; Baschuk et al., 2003) have been reported simulating PEMFC and DMFC, but most of them were isothermal models, except for a few papers that took into account thermal effects for simulating solid oxide fuel cell (Yuan et al., 2003; Li et al., 2004; Li and Suzuki, 2004). For instance, Nordlund and Lindbergh (2002) proposed an isothermal agglomerate model based on the reaction mechanism for the electrochemical oxidation of methanol to study the influence of the porous structure on the direct methanol fuel cells. Wang and Wang (2003) used two-phase multi component model to simulate a DMFC. The anode and cathode electrochemical reactions, diffusion and convection of both gas and liquid phases in the backing layers and flow channels, mixed potential effect due to methanol crossover and the effect of methanol feed concentration were explored.

Even though experimental approaches can give the visualization result, mathematical programming approaches is more favorable to researchers these days since its can give the instant result without time consuming. Since 1999's, Argyropoulos et al. (1999a; 1999b) developed a two-phase flow pattern in the anode channel under various operating conditions. This flow visualization on the anode side can

lead to a valuable understanding of CO₂ bubble dynamics in a DMFC. However, the drawback of their studies is that they were done under low cell performance. To further flow visualization studies, Lu and Wang (2004) have developed a transparent DMFC that allows for visualization of bubble dynamics on the anode side and liquid droplet dynamics on the cathode.

2. Conceptual Model Development

The conceptual design model will be discussed in this section is referring to model with the power is about 0.4 watt for single cell. Methanol solution was fed into the system through anode side whereas oxygen was fed through cathode side. These feeds were fed at condition of 25°C and 1 atm. Mole of species can be calculated using the equation as follows:

$$n_p = \frac{iA}{nF} \quad (1)$$

with n_p is mole of species; i is current density; A is active area, n is number of mole; and F is faraday constant.

To make the development of the model more comprehensible, Figure 1 will be used which is consists of:

- An anode flow channel (AFC), anode diffusion layer (ADL) and anode catalyst layer (ACL) at anode side
- A polymer electrolyte membrane
- A cathode catalyst layer (CCL), cathode diffusion layer (CDL) and cathode flow channel (CFC) at cathode side

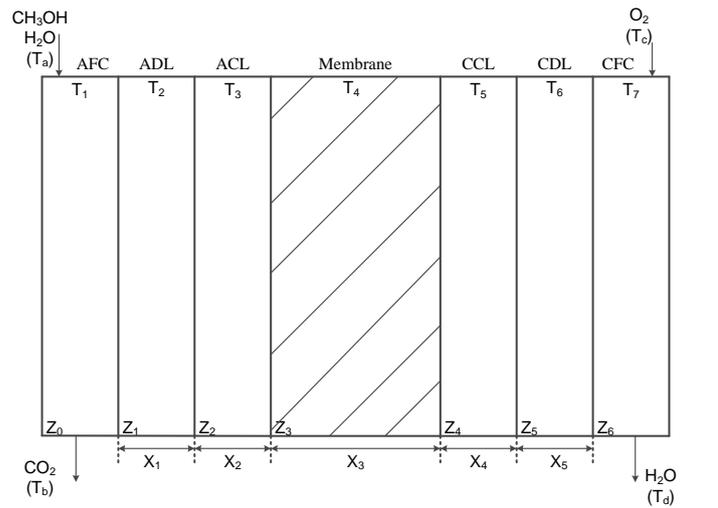


Figure 1: schematic diagram of MEA in DMFC system

2.1 Mass transport

The mass transport process occurred in DMFC system involved methanol, water and oxygen. Based on Figure 1, at anode side, methanol and water transport from storage tank to the AFC is described as follows:

$$N_i = h_i(C_i^0 - C_i^{AFC}) \quad (2)$$

where i represents methanol (MeOH) or water (H₂O), N is the molar flux, C_i^0 and C_i^{AFC} are the molar concentration of methanol or water in the storage tank and at the AFC respectively. In the ADL and ACL, methanol and water flux are explained based on the concentration gradient by Fick's law as follows:

$$N_i = -D_i^{eff, ADL} \frac{dC_i^{ADL}}{dz}, \quad i \text{ represents methanol or water} \quad (3)$$

$$N_i = -D_i^{eff, ACL} \frac{dc_i^{ACL}}{dz}, \quad i \text{ represents methanol or water} \quad (4)$$

where $D_i^{eff, ADL}$ and $D_i^{eff, ACL}$ represent the effective diffusion coefficients of methanol and water in the ADL and ACL, respectively.

In fuel cells, all fluxes can be represented in single characteristic flux, the current density or charge flux of the fuel cell. At anode side, methanol and water flux are related to the current density and permeation flux of methanol and water through the membrane, N_{MeOH}^{Mb} and $N_{H_2O}^{Mb}$; by:

$$N_{MeOH} = \frac{I_{cell}}{6F} + N_{MeOH}^{Mb} \quad (5)$$

$$N_{H_2O} = \frac{I_{cell}}{6F} + N_{H_2O}^{Mb} \quad (6)$$

The transport of methanol and water through the membrane is assumed to be due to the effect of the concentration gradient and electro-osmotic force as shown:

$$N_{MeOH} = -D_{MeOH}^{eff, Mb} \frac{dc_{MeOH}^{Mb}}{dz} + \xi_{MeOH} \frac{I_{cell}}{F} \quad (7)$$

$$N_{H_2O}^{Mb} = -D_{H_2O}^{eff, Mb} \frac{dc_{H_2O}^{Mb}}{dz} + \eta_d \frac{I_{cell}}{F} \quad (8)$$

with electro-osmotic drag; ξ_{MeOH} and η_d is defined as the number of methanol and water molecules dragged by the hydrogen ions moving through the membrane.

At cathode side, oxygen and water transport is spotted. Oxygen extracted from the air reacts with electron and proton to produce water as a waste in DMFC system. Additionally, there is part of oxygen is disbursed due to the methanol crossover to form an internal current and a mixed potential. Therefore the oxygen flux is related to the current density and the permeation flux of methanol through the membrane by:

$$N_{O_2} = \frac{\gamma_{O_2}}{4F} I_{cell} + \gamma_{cross, O_2} N_{MeOH}^{Mb} \quad (9)$$

γ_{O_2} represents the stoichiometric coefficient of oxygen in the cathode reaction for oxygen reduction; whereas, γ_{cross, O_2} represents stoichiometric coefficient of oxygen in the cathode reaction for methanol oxidation (overall reaction).

On the other hand, water flux is related to the water production from the oxygen reduction and methanol crossover oxidation (overall reaction) and the net water flux transported from the anode to the cathode, as follows:

$$N_{H_2O} = \frac{\gamma_{H_2O}}{4F} I_{cell} + \gamma_{cross, H_2O} N_{MeOH}^{Mb} + N_{H_2O}^{Mb} \quad (10)$$

γ_{H_2O} represents the stoichiometric coefficient of water in the cathode reaction for oxygen reduction; whereas, γ_{cross, H_2O} represents stoichiometric coefficient of water in the cathode reaction for methanol oxidation (overall reaction).

In the CCL and CDL, oxygen and water flux can be based on the concentration gradient as:

$$N_j = -D_j^{eff, CCL} \frac{dc_j^{CCL}}{dz}, \quad j \text{ represents oxygen or water (at cathode side)} \quad (11)$$

$$N_j = -D_j^{eff, CDL} \frac{dc_j^{CDL}}{dz}, \quad j \text{ represents oxygen or water (at cathode side)} \quad (12)$$

where $D_j^{eff, CCL}$ and $D_j^{eff, CDL}$ are the effective diffusion coefficient of oxygen and water in the CCL and CDL.

2.2 Heat Transport

Heat transport is detected in DMFC system because of electrochemical reaction occurred. This reaction is exothermic process which is; it will release heat while the reaction happened. The electrochemical reaction (methanol oxidation and oxygen reduction) occurred at ACL and CCL.

At the anode side, heat generated by the electrochemical reaction in ACL is given by:

$$Q_{ACL} = I_{cell} \eta_A - I_{cell} \left(\frac{\Delta H_A - \Delta G_A}{6F} \right) \quad (13)$$

Equation 14 explained, the first term represents the heat due to the activation and mass transfer overpotentials at the anode and the second term represents the entropy change of the anodic electrochemical reaction, with ΔH_A denoting the anodic reaction enthalpy and ΔG_A the Gibbs free energy.

At cathode side, heat generated at the CCL can be determined using the following equation:

$$Q_{CCL} = (I_{cell} + I_{MeOH})\eta_C - (I_{cell} + I_{MeOH}) \left(\frac{\Delta H_C - \Delta G_C}{4F} \right) - I_{MeOH} \left(\frac{\Delta H_A - \Delta G_A}{6F} \right) \quad (14)$$

In this equation, the first term represents the heat due to the activation and mass transfer overpotentials and mixed potential caused by methanol crossover through cathode. Second term represents the entropy change of cathodic electrochemical reaction, with ΔH_C denoting the cathodic reaction enthalpy and ΔG_C , the Gibbs free energy; while the third term represents the entropy change of methanol oxidation reaction due to methanol crossover.

2.3 Cell performance

The prediction of cell voltage can be attained with the determination of methanol and oxygen concentration at the catalyst layer, temperature profiles and anodic and cathodic overpotentials as shown below:

$$V_{cell} = E_{cell} - \eta_A - \eta_C - I_{cell} R_{cell} \quad (15)$$

with E_{cell} is the thermodynamic equilibrium potential of the cell and is a function of temperature and pressure, and R_{cell} is the internal resistance of the fuel cell. E_{cell} can be calculated using the equation below:

$$E_{cell} = E_{cell}^0 + \Delta T \left(\frac{\partial E}{\partial T} \right) \quad (16)$$

3. Analytical Solutions

With the specific given of current density and active area (table 1), the volume of methanol, water, oxygen and carbon dioxide can be calculated using equation (1).

Table 1: Typical value design parameters

Parameters	Value	Unit	Parameters	Value	Unit
Active area	4 (2 × 2)	cm ²	Oxygen density	1.141	g cm ⁻³
Current density	0.175	A cm ⁻²	CO ₂ density	0.77	g cm ⁻³
Fuel cell voltage	0.57	V	Methanol density	0.7918	g cm ⁻³
Faraday constant	96,500	C mol ⁻¹	Water Density	1	g cm ⁻³

Methanol:

$$n_{MeOH} = \frac{(0.175)(4)}{(1)(96500)} = 7.25 \times 10^{-6} \text{ mol}_{MeOH}/s$$

$$v_{MeOH} = \frac{(7.25 \times 10^{-6} \text{ mol}_{MeOH}/s)(32.04 \text{ g/mol})(3600 \text{ s/h})}{0.7918 \text{ g/cm}^3} = 1.06 \text{ cm}^3/h$$

Water:

$$n_{H_2O} = \frac{(0.175)(4)}{(1)(96500)} = 7.25 \times 10^{-6} \text{ mol}_{H_2O}/s$$

$$v_{H_2O} = \frac{(7.25 \times 10^{-6} \text{ mol}_{H_2O}/s)(18 \text{ g/mol})(3600 \text{ s/h})}{1 \text{ g/cm}^3} = 0.47 \text{ cm}^3/h$$

Oxygen:

$$n_{O_2} = \frac{(0.175)(4)}{\left(\frac{3}{2}\right)(96500)} = 4.84 \times 10^{-6} \text{ mol}_{O_2}/s$$

$$v_{O_2} = \frac{(4.84 \times 10^{-6} \text{ mol}_{H_2O}/s)(32 \text{ g/mol})(3600 \text{ s/h})}{1.141 \text{ g/cm}^3} = 0.49 \text{ cm}^3/h$$

Carbon dioxide:

$$n_{CO_2} = \frac{(0.175)(4)}{(1)(96500)} = 7.25 \times 10^{-6} \text{ mol}_{CO_2}/s$$

$$v_{CO_2} = \frac{(7.25 \times 10^{-6} \text{ mol}_{H_2O}/s)(48 \text{ g/mol})(3600 \text{ s/h})}{0.77 \text{ g/cm}^3} = 1.63 \text{ cm}^3/h$$

To calculate the concentration of methanol at the ACL, equation (2), (3), (4) and (5) will be combined as shown below:

$$C_{MeOH}^{ACL} = \frac{h_{MeOH} C_{MeOH}^0 - h_{MeOH} C_{MeOH}^{AFC} - D_{MeOH}^{eff, ADL} C_{MeOH}^{ADL} X_1 + \frac{I_{cell}}{6F} + N_{MeOH}^{Mb} - N_{MeOH}}{D_{MeOH}^{eff, ACL} X_2} \quad (17)$$

With the assistant of equation (9), (11) and (12), the concentration of oxygen at the CCL will be calculated by:

$$C_{O_2}^{CCL} = \frac{\frac{1}{4F} I_{cell} + \frac{3}{2} N_{MeOH}^{Mb} - D_{O_2}^{eff, CDL} C_{O_2}^{CDL} X_3 - N_{O_2}}{D_{O_2}^{eff, CCL} X_4} \quad (18)$$

4. Conclusion

The conceptual design presented in this paper will be used to design a new system of DMFC that can target for unsteady state situation with various type of feed condition. With the power of 0.4 watt per fuel cell, stacking will be used to get the target power for the portable applications such as cellphone, laptops and etc. Table 2 shows the comparison between the conceptual designs presented in this paper with the previous conceptual design.

Table 2: Comparison result

Parameters	This study	Basri (2010)	Ko et al. (2010)
Active area	4 cm ²	2 cm ²	4 cm ²
Current density	0.175 A cm ⁻²	0.037 A cm ⁻²	0.167 A cm ⁻²
Fuel cell voltage	0.57 V	0.14 V	0.21 V
Power density	0.1 W cm ⁻²	0.005 W cm ⁻²	0.02 W cm ⁻²

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