Modeling and Simulation of Direct Methanol Fuel Cell

by

Sofia Keetasopon

Dissertation submitted in partial fulfillment of
the requirements for the
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Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

(Dr. Nooryusmiza B. Yusoff)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK DARUL RIDZUAN

SEPTEMBER 2011

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

Sofia Keetasopon

SOFIA KEETASOPON

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ABSTRACT

Direct methanol fuel cell (DMFC) is a promising alternative technology due to its advantages provided over traditional power sources especially for portable electronic devices i.e. mobile phones, laptop. However, there are still a large number in research and development stages needed to be done to overcome several factors that may reduce the overall cell performance and efficiency.

In this report, direct methanol fuel cell model is presented. The model is developed by using MATLAB software. The model result is proved that it is in good agreement with the experiment data. The model then used to investigate the effects of other parameters which are methanol concentration and air flow rate. The study revealed that both methanol concentration and air flow rate have effect to the direct methanol fuel cell performance.

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NOMENCLATURE

DMFC	Direct Methanol Fuel Cell
GDL	Gas Diffusion Layer
MEA	Membrane Electrode Assembly
PEMFC	Proton Exchange Membrane Fuel Cell
AFC	Anode Flow Channel
CFC	Cathode Flow Channel
ADL	Anode diffusion layer
CDL	Anode diffusion layer
ACL	Anode catalyst layer
CCL	Cathode catalyst layer
M	Membrane

Superscript

a	anode
c	cathode
O_2	Oxygen
MEOH	Methanol
H_2O	Water
0	Standard Condition

Subscript

a	anode
ac	anode catalyst layer
ad	anode diffusion layer
ah	anode flow channel
ahin	inlet of anode flow channel
c	cathode
cc	cathode catalyst layer
cd	cathode diffusion layer
ah	cathode flow channel
chin	inlet of cathode flow channel
m	proton exchange membrane
ref	reference state

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Today, consumption of energy has been increasingly due to the rapid expansion and development of the technology. The consumption of non-renewable sources causes a lot of damage to the environment and also human activity which has been noticed since the past century. Furthermore, the electricity which generated from fossil fuel also emits high concentration of harmful gases to the atmosphere. Beside those harmful effects, the price of fuel oil also keeps increasing every day due to high demand from various activities.

Many researchers have been searched and developed alternative energy to find alternative sources especially renewable energy to meet the consumer demand and, at the same time, to sustain the environment. This is because most of renewable energy is developed on the purpose of environmental friendly. It can reduce greenhouse gas emissions to the atmosphere which cause the global warming problem.

There are many renewable energy which have been developed and used such as solar, wind, wave, biomass, geothermal, fuel cell and etc. Among the alternative energy, fuel cell can be considered as a leading alternative energy system for transportation and portable application due to its outstanding efficiency and potential in low pollutants emission from combustion process (Lattner & Harold, 2005)

1.2 PROBLEM STATEMENT

Today, many portable electronics devices has been designed and manufactured to support high demand in this edge of technology. Portable electronic devices such as handphone, laptop has became an essential devices for many people all over the world in their daily lives. The power demand increases rapidly faster than battery capacities in the past few years for example in electronic portable device due to more functionality has been added in portable devices such as internet service, social networking, graphic game and etc (Kamarudin, Daud, Ho, & Hasran, 2007). With the additional functions, the portable device is consuming more of the battery power.

Rechargeable battery, as the major power of the device, has limitation on mobility and battery capacity. Since it needs external electrical power source for the recharging, it is not applicable for remote area where the electricity supplied device is inconvenient.

Direct Methanol Fuel Cell (DMFC) has a potential to replace rechargeable battery, as the main power source of electronic portable device e.g. mobile phone, laptop has a limitation on mobility and battery capacity. However, sometimes laboratory experiment can only provides data for certain area. In addition, it takes time for the experimental study to determine the effect to the cell performance of certain parameters.

To overcome this issue, the mathematical model is developed to study the effect of certain parameters of the cell performance. This approach is practicable, economical and less time consuming compared to conducting laboratory experiment.

1.3 OBJECTIVE AND SCOPES OF STUDY

1.3.1 Objectives

1. To develop a model of direct methanol fuel cell.
2. To study effects of direct methanol fuel cell performance via 2 parameters
   i) Methanol concentration
   ii) Air flow rate

1.3.2 Scopes of Study

This project is aims to study effects to the cell performance of the parameters, which includes the methanol concentration and air flow rate for Direct Methanol Fuel Cell, (DMFC) by using MATLAB software to develop the model of the fuel cell. The area of knowledge involves the understanding on fuel cell technology commonly used for portable applications and mainly focuses on Direct Methanol fuel Cell which needed to be comprehended clearly to be able to develop the model.

CHAPTER 2

LITERATURE REVIEW

2.1 FUEL CELL

Due to the environmental impact and energy sustainability concerns have pushed efforts to develop on fuel cell technology, fuel cells are considered as energy conversion device that generated power with low emission and highly efficient source for generating heat and electricity (Rashidi, Dincer, Naterer, & Berg, 2009).

Fuel cell operates like a battery but fuel cell does not require recharging. Fuel cell will generate energy by converting chemical energy into electrical energy via electrochemistry reaction (Kamarudin, Achmad, & Daud, 2009). It will continue producing energy as long as fuel is supplied. Fuel cell operates at low temperature and pressure. It offers high power density and longer life time compared to rechargeable batteries for portable applications (Rashidi, et al., 2009). Various reasons make fuel cell technology become favorable, those including high electric conversion efficiency (35-70 % for different system), independence of size, low environmental impact, reliability and long lasting operation, heat produced is usable for co-generation cycles and flexibility of the fuel used(Yao, et al., 2006).

There are several types of fuel cell which are currently under development. Each one has its own advantages, limitation and potential applications. Proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) are commonly used for portable applications.

2.1.1 Proton Exchange Membrane Fuel Cell (PEMFC)

Proton exchange membrane fuel cell (PEMFC) is also sometime refers to polymer exchange membrane fuel cell. PEMFC use hydrogen as a source of energy unlike direct methanol fuel cell (DMFC) which powered by methanol solution. PEMFC produces electric power from pure hydrogen and air operates operate at relative low temperature about 80°C. New development of PEMFC included membrane electrode assemblies (MEA), better thermal management and more advanced on the cell design (Rashidi, et al., 2009). The reactions occurring in PEMFC are described as:

Anode : $2H_2 \rightarrow 4H^+ + 4e^-$ (1)

Cathode : $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (2)

Net reaction : $2H_2 + O_2 \rightarrow 2H_2O$ (3)

In the PEMFC unit, hydrogen molecules are supplied at the anode side to produce hydrogen proton and electrons. The protons are transported from anode to cathode side through polymeric membrane while electrons are sent around external circuit to generate electricity (Crawley, 2006). Figure 2.1 show the schematic of PEMFC.

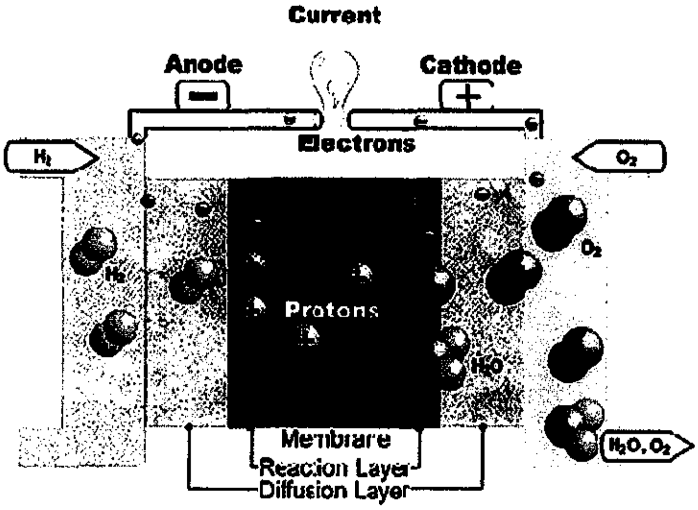

Figure 2.1: Diagram of Proton Exchange Membrane Fuel Cell

(Figure Source : http://www.esru.strath.ac.uk/EandE/Web_sites/00-01/fuel_cells/)

PEMFC are used mainly for transportation applications and also in some stationary applications. The main advantages of this fuel cell are fast startup time since it operates at low temperature and high power density. However, there are also some disadvantages for PEMFC such as high cost due to required an expensive catalyst in order to achieve the better electrochemical reaction and it's difficult in refilling the hydrogen compared to methanol refilling.

2.1.2 Direct Methanol Fuel Cell (DMFC)

Direct Methanol Fuel Cell (DMFC) is the further development of Proton exchange membrane fuel cell (PEMFC). Most of fuel cells are use hydrogen as source of energy, which can be fed hydrogen directly to the fuel cell system or produce hydrogen within fuel cell system by reforming reaction of hydrogen-rich fuels such as methane, methanol, ethanol, gasoline.

Direct methanol fuel cells (DMFCs) are powered by pure methanol fed into fuel cell system. This technology uses methanol as source of energy. It converts liquid methanol fuel into energy directly. Since methanol has very high density energy so they are attractive from energy sector (Wilhelm, Janßen, Mergel, & Stolten, 2011).

DMFC consists of anode and cathode where methanol which is directly oxidized to CO_2 and generate electricity at the surface of Pt/Ru (platinum/ruthenium) catalytic electrodes took place at anode without the need of any intermediate fuel processing and fuel reform step and water which is produced by the reaction between O_2 in the air and protons that migrate from anode to cathode through proton exchange membrane (PEM) (usually Nafion), occurred at cathode side. (Yao, et al., 2006)The reactions occurring in DMFC are described as:

Anode : $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ (4)
Cathode : $1.5O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$ (5)
Net reaction : $CH_3OH + O_2 \rightarrow 2\,H_2O + CO_2$ (6)

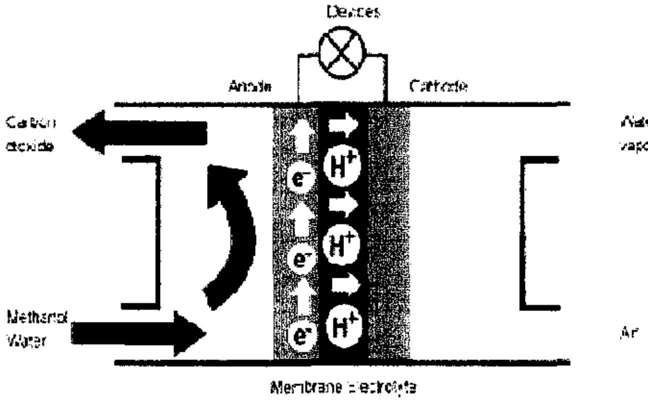

Figure 2.2 : Diagram of Direct Methanol Fuel Cell

(Figure Source: http://fuelcells.caravanmoversonline.co.uk/efoy/howfuelcellswork.html.)

DMFCs can be considered as a potential power sources for portable electronic devices, such as handphone, notebook (Joh, et al., 2010). DMFC offer good advantages such as long life operation, great energy density, convenience for recharging and can be operated at ambient conditions((Shimizu, Momma, Mohamedi, Osaka, & Sarangapani, 2004), (Park, et al., 2008)).

DMFC gives greater energy densities five to ten times of rechargeable batteries, can operates last longer and eventually less costly than alternative battery technologies. These characteristics are referring to longer operation times for laptops and portable mobile phones. Besides, it can be designed for a fast and easy fuel cartridge replacement while rechargeable batteries require hours for recharging a depleted power pack. DMFC has encouraged many studies as promising portable electronic power supply due to its high theoretical energy density of methanol (6100 kWh kg^{-1} at 25°C) which is a much higher that the fuels ((Li, Faghri, & Xu, 2010), (Liu, Zhao, Chen, & Wong, 2005)).

There are two common types of DMFC; passive and actives DMFCs. A passive DMFC which external pumps or other auxiliary fuel device and oxidant supply are removed have been considered as more compromising power sources of electronic devices than a active DMFC due to the much simpler design structures of passive DMFC and parasitic power loss from auxiliary devices is eliminated (Liu, et al., 2005).

DMFC has a potential to replace the battery due to higher energy density compare to the best rechargeable batteries, lithium-polymer and lithium-ion polymer systems. Figure 2.3 shows the theoretical energy density (Wh L^{-1}) of DMFCs and battery systems (Kamarudin, et al., 2009). However, the components cost of micro fuel cell is still an issue (Kamarudin, et al., 2009).

However, as for portable applications, it's desired to have high system power density and simplicity over efficiency and cost. There are many direct methanol fuel cell products which have been releases e.g. Mobion® direct methanol fuel cell chips, which are used as the power sources for consumer electronics application by Mechanical Technology, Inc. (MTI). This fuel cell ships can be achieved over 50 mW/cm^2 of power density(Mench, 2008).

The advantages of direct methanol fuel cell (DMFC) over proton exchange membrane fuel cell (PEMFC) are listed below(Mench, 2008):

- A separate cooling and humidification system are not required due to the anode flow is mostly liquid (gaseous carbon dioxide (CO_2) is a product of methanol oxidation reaction)
- Since methanol solution is used as liquid fuel in the anode, hence this results in lower requirement of parasitic pumping as compared to gas flow.
- DMFC can eliminate fuel storage volume problems since highly dense liquid fuel can be stored at ambient pressure. With highly concentration of methanol (> 10 M), passive DMFC system power densities can be comparable to advanced Lithium-ion batteries.
- Reformer system is not required.

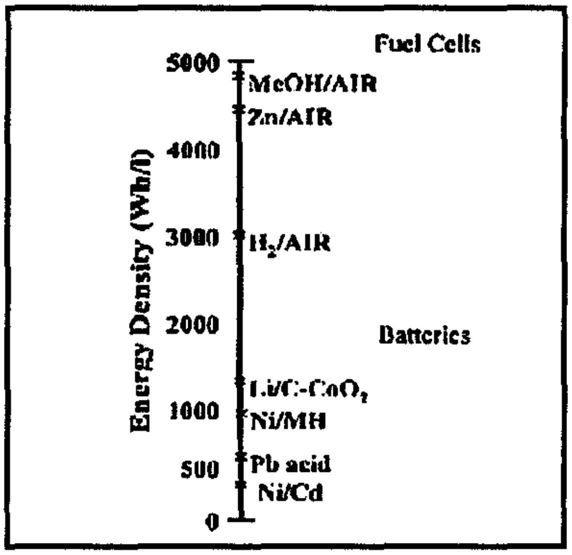

Figure 2.3: Theoretical Energy Densities (Kamarudin, et al., 2009)

2.1.2.1 DMFC Components

DMFC is generally consists of a membrane electrode assembly (MEA), bipolar plate, gasket, current collector and end plate as a basic component. Figure 2.4 shows the basic components of DMFC

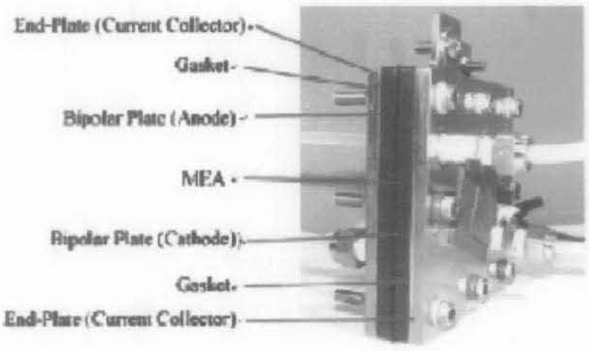

Figure 2.4: Basic components of DMFC (Kamarudin, et al., 2009)

a) Membrane Electrode Assembly (MEA)

One of the components that have a great impact on the overall performance of a DMFC is membrane electrode assembly. The structure of MEA is comprised of an electrolyte membrane which coated by catalyst on both anode and cathode sides and then sandwiched by a gas diffusion layer.

- Gas Diffusion Layer (GDL)

At this layer, the methanol solution is diffuse from the methanol reservoir to the catalyst layer and releases water to the cathode at the same time. The condition of a GDL material is must be a porous media and conductive, carbon is the most common material used.

- Electrolyte Membrane

The electrolyte membrane in DMFC works as a separator between the anode and cathode to prevent the mixing of methanol which flow from anode to cathode side. This is the place where anode and cathode catalyst are applied (Kamarudin, et al., 2009). Since the electrolyte membrane will only allow protons to transport from anode to cathode, hence, the criteria of electrolyte membrane must be a highly proton conduction, impermeable to fuels and oxidants, chemically stable and electrically resistive (Mennola, 2000). The most common electrolyte membrane of DMFC is Nafion. Nafion which made for DMFC, is categorized into three types based on thicnkness; Nafion 112, 115 and 117. Coutaneus et al. found that the most suitable of Nafion electrolyte membrane for DMFC application is Nafion 117 as it has the smallest amount of methanol crossover among of the three types (Coutanceau, et al., 2006).

- Anode

The anode electrode is placed at where electro-oxidation of methanol is occurred. The reactions at anode side are very complex and involve with many intermediate steps that create many chemical intermediates as illustrated in figure 2.5.

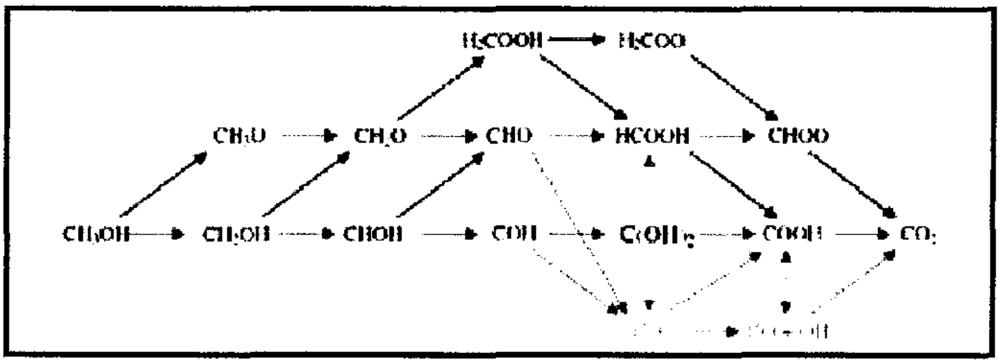

Figure 2.5: Schematic represent of reaction paths and possible intermediate (Kamarudin, et al., 2009)

The indirect mechanisms for carbondioxide (CO_2) formation are indicated by green arrow. The reaction with no generation of a proton/electron is indicated by dotted arrow. The arrow to the right side also involve the generation of a proton/electron pair (not shown) from either surrounding H_2O or carbonaceous species. Methanol oxidation is a vital step which is also a limiting factor of overall performance of the cell. Carbon monoxide is an intermediate which can limit the anodic reaction rate and it's the most stable intermediate formed and the main reason for CO poisoning problem of catalysts Platinum (Pt) which is the most active catalyst for DMFC anodes. Hence, the second catalyst will be added to overcome the problem which is

Ruthenuim (Ru). Pt and Ru will create a combination between CO poisoning resistance and active catalyst ((Dinh, Ren, Garzon, Piotr, & Gottesfeld, 2000), (Kamarudin, et al., 2009)).

- **Cathode**

The cathode electrode is placed at where oxygen reduction reaction is taking place as well as where the methanol crossover problem happens as well. Methanol in the cathode side can create a mixing potential which reduces the overall cell performance. The common cathode catalyst is Platinum (Pt). The cathode is operates at high temperature (50-90 °C), high water content, high potentials (0.6-1.2 V) and low pH value (less than 1) (Kamarudin, et al., 2009).

b) Bipolar Plate

This component is functions for distribute the reactants and also collect and distribute current in some case (Kamarudin, et al., 2009). Good bipolar plate should have a good conductivity and the common material used is metal, graphite or other composite (Lu & Wang, 2004).

c) Gasket

The gasket in DMFC is used to avoid leaking of reactant as well as to separate current between the current collector and end plate. The common material is silicon rubber. Gasket thickness has an impact to the cell performance by increasing the internal resistance which the thicker one can increase the length of DMFC system and also internal resistance (Kamarudin, et al., 2009).

d) Current Collector and End Plate

The current collector is structure for collect the current produce in MEA. Current collector function is to conduct electrons from anode to the external circuit or to the adjacent cathode in a stack. The criteria of current collector must have a high conductivity, good mechanical strength and a uniform transport area. However, for certain current collectors with low thermal conductivity can reduce heat loss and help to maintain the temperature (Chen & Zhao, 2007).

The function of end plate support and maintain the compactness of the system along with bolts. The suitable material must be mechanically strong and should not be electrically conductive material.

2.1.2.2 DMFC Challenges

DMFCs do not face a fuel storage problem as many fuel cells since methanol has higher energy density than hydrogen. It operates via direct electrochemistry reaction of an aqueous methanol solution without reforming of fuel reaction (Rashidi, et al., 2009). However, there are many studies in order to increase fuel cell efficiency and performance such as influence of methanol concentration, influence of air condition as well as temperature and pressure condition which may lead to several technical hurdles such as methanol crossover, heat management and water management.

Methanol concentration has a great influence to DMFC on the current/voltage characteristic. Higher methanol concentration causes high permeation through membrane therefore methanol molecule will be oxidized at cathode. This problem does not only reduce the mass efficiency but also influence on the formation of a mixed potential at cathode and thus reduce voltage efficiency. While lower methanol concentration avoid methanol losses and the formation of a mixed potential (Dohle, Mergel, & Stolten, 2002). Figure 2.6 shows the current/voltage characteristic of a DMFC.

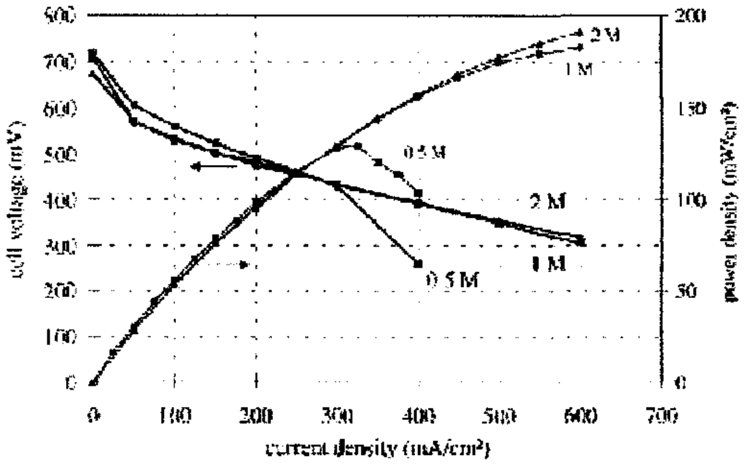

Figure 2.6 : Current/voltage characteristic of a DMFC for different methanol concentration (Dohle, et al., 2002)

Temperature condition also has effect to electrodes' kinetics of DMFC; high temperature tends to increase water vaporization at the cathode which reduces the partial pressure of the oxygen (O_2). Dohle, Mergel et al. studied on heat and power management of a direct methanol fuel cell, they found that, the pressure of the system and the air flow rate have an important influence to both the system power and system efficiency. In addition, they also found that at high operating condition which is above 90°C, require low air flow rates combined with elevated pressure at cathode to maintain the temperature and increasing the pressure causes decreasing in system efficiency due to demand of compression power is increased.

a) Methanol Crossover

DMFC has encouraged many studies as promising portable electronic power supply due to its high theoretical energy density (6100 kWh kg^{-1}). Therefore, high concentration of methanol should be stored in the anode fuel reservoir in order to take its benefit of higher obtainable energy density. However, lead to methanol crossover problem with seriously reduce fuel cell efficiency and performance ((Li, et al., 2010), (Kamarudin, et al., 2007)).

Methanol crossover is the situation at which methanol molecules are directly oxidized by oxygen on the cathode side (positive electrode) and turn into carbon dioxide (CO_2) due to diffusion through the membrane from anode to cathode (Han & Liu, 2007). Methanol crossover causes two harmful consequence : self discharge of methanol producing additional heat instead of electricity and even more drastic reduction of the cathode voltage (Broussely & Archdale, 2004).

Methanol crossover is a serious problem which might cause severe effect to the cell performance such as decrease cell voltage, current density and fuel utilization. The study of methanol crossover of DMFC under different operating conditions can help to discover the optimal operating conditions (Han & Liu, 2007). The development of a new proton conducting membrane is one general approach for dealing with methanol crossover problem (Kamarudin, et al., 2007).

Han and Liu was conducted an experiment to determine the methanol crossover rate for DMFC by measuring concentration of CO_2 which exit at cathode side in real time. They found that cell performance and methanol crossover rate increase with cell temperature, when the temperature is below 60°C methanol crossover rate increase with the cell current density and it remains almost constant from 60-80°C. They also found that cathode humidification factor has no effect to cell performance and the experiment results show that the optimal performance occurs when the methanol concentration are 1M or 0.5M.

A huge number of studies were carried out to overcome the methanol crossover problem, including the developing of new proton conducting membrane with a high proton conductivity and low methanol permeability and also modification of the existing membrane like Nafion by surface modification using physical treatment or coating the surface with a thin film, conversion to a composite membrane with organic or inorganic materials (Abdelkareem & Nakagawa, 2007).

b) Water Management

In DMFC, the products of overall electrochemical reaction are CO_2 and water (H_2O). Water will be consumed at the anode by methanol oxidation and from water crossover which caused by electro-osmotic drag of proton migration in proton exchange membrane (PEM) at the same time as being produced at the cathode. To reduce the loss of methanol and to maintain the reaction, water in the anode stream need to be refilled. Moreover, the excess of water accumulation causes cathode flooding which blocks access of oxygen to the cathode electrode. This happens when the rate of water generation is faster than the rate of water removal. Therefore, the flooding problem is related to methanol and water fluxed through the membrane as well as oxygen reduction reaction rate (Abdelkareem & Nakagawa, 2007).However, without water, the proton will refuse permeating through the membrane which resulting in lower performance and each proton should go along with 2.5 water molecules to permeate through the membrane (Yao, et al., 2006).

The main objectives of water management are to supply water for the anode reaction, remove water produced at the cathode catalyst layer as well as keep high water content in the membrane to reduce the proton conductive resistance(Li, et al., 2010).

b) Heat Management

High temperature condition has a tendency to increase methanol crossover situation and decrease the efficiency because more energy required evaporating the liquid methanol fuel (Y.H, 2006). Methanol crossover is one of factors that rise temperature in the cell due to releasing of heat at cathode from oxidation reaction of crossover methanol (Kamarudin, et al., 2007)

Dohle, Mergel et al. studied on heat and power management of a direct methanol fuel cell, they found that, vaporization at the cathode influences the overall heat balance of the fuel cell and with respect to thermal efficiency, raised cathode pressures and reduced operating temperature are favorable since this limits water vaporization on the cathode side, furthermore, increasing in operating temperature leads to a sharp drop in thermal efficiency.

CHAPTER 3

METHODOLOGY

3.1 PROJECT RESEARCH METHODOLOGY

For this project research, the project work follows a specified sequence as shown in Figure 3.1 below.

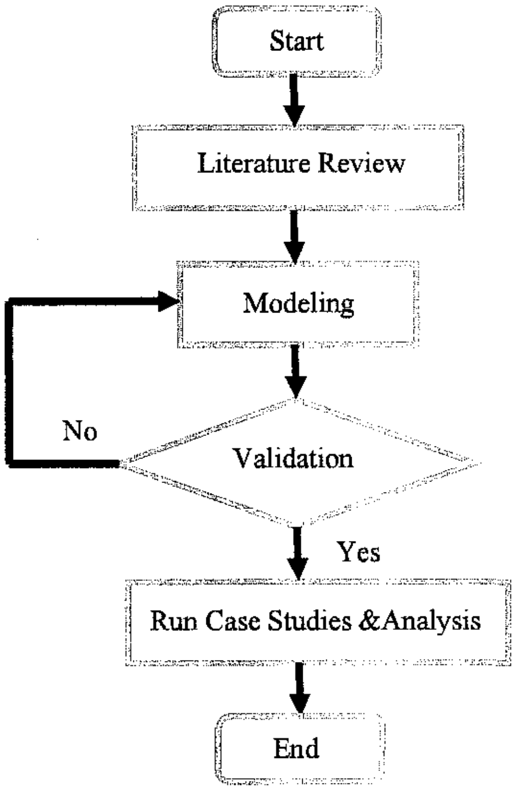

Figure 3.1: Flowchart of Modeling and Simulation of direct Methanol Fuel Cell

This project started with literature review in order to review and study on journals and researches related to the project scope which require an understanding on direct methanol fuel cell (DMFC) and identify the research that relevant to be used along with proposed method for further analysis.

The project then continued on modeling part. This part is to design the model of direct methanol fuel cell based on information from literature review as well as validate the model by compare the model result with the experimental data to see whether the model can be fit and tally with the experimental data or not.

After validated model was obtained, the project work continued with next step which was simulating case studies to observe the effect to cell performance. The result gave useful information to the discussion as expected.

3.2 TOOL/ SOFTWARE

The required software to use in order to develop the model is MATLAB software. In the first stage, MATLAB is used to develop the model by using the equations and parameters involved based on the literature with creative method to gain the expected result.

3.3 MODEL ASSUMPTIONS

Most of research studies on DMFC technology were focused on experimental investigation to develop understanding but somehow experiment studies also have some limitations which give difficulties to measure the parameters inside the cell. It is costly, time consuming, results are not replicable and so on (Zhongying Shi, 2006). The model is developed based on the following assumptions(Guo & Ma, 2004).

1. The fluid flow in the cell is considered as in steady state.
2. The electrochemical reaction is occurred under the constant temperature.
3. The pressure drop in the flow channel will be ignored.
4. The fluid flow velocity in the channel is assumed to constant.
5. Hydrogen proton can only transport through electrolyte while electron is transport through solid carbon phase.
6. Methanol and water are considered on the anode side while oxygen, water and nitrogen are considered at cathode side.
7. Methanol concentration in the cathode catalyst is neglected.

3.3.1 Model Equations

The Analytical models of DMFC are very useful for building the understanding on effect of basic parameter to the cell performance. In this project study, mathematical model is applied to study the effects of methanol concentration and air flow rate to the cell performance. The model is developed based on the equations and parameters from a literature (Shakeri, 2009). The model equations are shown as the following:

$$I_{cell}(\eta_a) = \frac{W_{ad}}{\lambda_3 F D_{ad}^{MEOH}}\left(1/6 - \frac{n_d^{MEOH}}{\lambda_5}\left[\frac{exp(\lambda_4) - 1}{(1+\lambda_3)\lambda_4} - 1\right]\right) I_{cell}$$

$$-C_{ahin}^{MEOH}\frac{exp(\lambda_4)-1}{(1+\lambda_3)\lambda_4\lambda_5} = 0 \tag{7}$$

$$I_{cell}(\eta_c) = \frac{W_{cd}}{\lambda_1 F D_{cd}^{O_2}}\left(1/4 - \frac{3}{2}\frac{n_d^{MEOH}}{\lambda_5}\left[\frac{exp(\lambda_2-1)}{(1+\lambda_1)\lambda_2} - 1\right]\right) I_{cell} - C_{chin}^{O_2}\frac{exp(\lambda_2-1)}{(1+\lambda_1)\lambda_2} -$$

$$\frac{3}{2\lambda_1}\frac{W_{cd}}{D_{cd}^{O_2}}\left(\frac{exp(\lambda_2)-1}{(1+\lambda_1)\lambda_2} - 1\right)\frac{exp(\lambda_4)-1}{(1+\lambda_3)\lambda_4\lambda_5}\frac{D_m^{MEOH}}{W_m}C_{ahin}^{MEOH} = 0 \tag{8}$$

The λ_i values for above equation are expressed as following:

$$\lambda_1 = \frac{1}{4F}\frac{W_{cd}}{D_{cd}^{O_2}}\frac{I_{ref}^{O_2}}{C_{ref}^{O_2}}exp\left(\frac{\alpha_c}{RT}\eta_c\right) \tag{9}$$

$$\lambda_2 = -\frac{1}{4F(1+\lambda_1)}\frac{L_{ch}}{h_{ch}S_{ch}}\frac{I_{ref}^{O_2}}{C_{ref}^{O_2}}exp\left(\frac{\alpha_c}{RT}\eta_c\right) \tag{10}$$

$$\lambda_3 = \frac{1}{6F}\frac{W_{ad}}{D_{ad}^{MEOH}}\frac{I_{ref}^{MEOH}}{C_{ref}^{MEOH}}exp\left(\frac{\alpha_a}{RT}\eta_a\right) \tag{11}$$

$$\lambda_4 = -\frac{L_{ah}}{h_{ah}S_{ah}}\frac{D_{ad}^{MEOH}}{W_{ad}}\frac{\lambda_3}{1+\lambda_3} \tag{12}$$

$$\lambda_5 = 1 - \frac{1}{\lambda_3}\left[\frac{exp(\lambda_4)-1}{(1+\lambda_3)\lambda_4} - 1\right]\frac{W_{ad}}{D_{ad}^{MEOH}}\frac{D_m^{MEOH}}{W_m} \tag{13}$$

The E_{cell} value is assummed to be equal to E_{cell}^0

$$E_{cell} = E_{cell}^0 \tag{14}$$

For η_a and η_c are modified from Tafel kinetics (Mench, 2008):

$$\eta_a = \frac{R}{\alpha_a F} \ln\left(\frac{I_{cell}}{I_{ref}^{a}}\right) \quad (15)$$

$$\eta_c = \frac{R}{\alpha_c F} \ln\left(\frac{I_{cell}}{I_{ref}^{c}}\right) \quad (16)$$

The η_a and η_c values can be calculated by using equation (7) and (8) at specific I_{cell}. The cell voltage and power density will be calculated using equation (17) and (18) as following.

$$V = E_{cell} - \eta_c - \eta_a - I_{cell}\frac{W_m}{\sigma_m} - I_{cell}R_{contact} \quad (17)$$

$$\text{Power density, } P = V * I_{cell} \quad (18)$$

The value of each parameter used in model shown in Table 3.1 is taken from literaure(Ge & Liu, 2005; Guo & Ma, 2004; Shakeri, 2009).

Table 3.1: Model Parameters.

Parameter	Symbol	Unit	Value
Temperature	T	K	348.15
Length of anode channel	L_{ah}	cm	3
Length of cathode channel	L_{ch}	cm	3
Number of anode channel	m_{ch}	cm	10
Number of cathode channel	m_{ah}	cm	10
Width of anode channel	W_{ah}	cm	0.2
Width of anode channel	W_{ch}	cm	0.2
Depth of anode channel	h_{ah}	cm	0.2
Depth of anode channel	h_{ch}	cm	0.2
Thickness of ADL	W_{ad}	cm	0.03
Thickness of CDL	W_{ad}	cm	0.03
Thickness of ACL	W_{ac}	cm	0.005
Thickness of CCL	W_{cc}	cm	0.003
Thickness of membrane	W_m	cm	0.0206
Electro-osmotic drag coefficient of water	$n_d^{H_2O}$		$2.9exp\left(1029\left[\frac{1}{333} - \frac{1}{T}\right]\right)$
Electro-osmotic drag coefficient of methanol	n_d^{MEOH}		$x^{MEOH} n_d^{H_2O}$
Conductivity of membrane	σ_m	S/cm^1	$0.073exp\left(1268\left[\frac{1}{298} - \frac{1}{T}\right]\right)$
Diffusion coefficient of methanol in membrane	D_m^{MEOH}	cm^2/s	$4.9 * 10^{-6}exp\left(\frac{2436}{333} - \frac{2436}{T}\right)$

Diffusion coefficient of methanol in anode diffusion layer	D_{ad}^{MEOH}	cm^2/s	$\varepsilon D_{H_2O}^{MEOH}$
Diffusion coefficient of methanol in water	$D_{H_2O}^{MEOH}$		$2.8 * 10^{-5} exp\left(\frac{2436}{353} - \frac{2436}{T}\right)$
Diffusion coefficient of oxygen in cathode diffusion layer	$D_{cd}^{O_2}$	cm^2/s	0.001
Ideal electromotive force of the fuel cell under standard condition	E_{cell}^0	V	1.213
Correction factor of diffusion coefficient	ε		0.55
Transfer coefficient	α_a		0.8
Transfer coefficient	α_c		0.8
Contact resistance	$R_{contact}$	Ω/cm^2	0.8
Reference concentration of methanol	C_{ref}^{MEOH}	mol/cm^{-3}	0.001
Reference concentration of oxygen	$C_{ref}^{O_2}$	mol/cm^{-3}	$C_{ref}^{O_2} = (P * 10^{-6})/(RT)$
Reference exchange current density of anode	I_{ref}^{a}	A/cm^2	$I_{ref}^{a} = W_{ac} i_a$
Reference exchange current density of cathode	I_{ref}^{c}	A/cm^2	$I_{ref}^{c} = W_{cc} i_c$
Reference exchange current density per unit volume of anode	i_a	A/cm^3	0.011
Reference exchange current density per unit volume of anode	i_c	A/cm^3	0.011
Methanol Concentration at anode inlet	C_{ahin}^{MEOH}	mol/cm^3	$2.0 x 10^{-3}$
Oxygen Concentration at cathode inlet	$C_{chin}^{O_2}$	mol/cm^3	$C_{chin}^{O_2} = 0.21 x 10^{-6} (P/RT)$
Molar fraction	x^{MEOH}		$C_{ac}^{MEOH}\left(C_{ac}^{MEOH} + \frac{\rho_{H_2O}}{M_{H_2O}}\right)^{-1}$
Inlet flow rate of anode	V_{ah}	cm^3/min	1
Inlet flow rate of cathode	V_{ch}	cm^3/min	1000
Velocity of fluid in anode channel	S_{ah}	cm/s	$V_{ah}(60 m_{ah} W_{ah} h_{ah})^{-1}$
Velocity of fluid in cathode channel	S_{ch}	cm/s	$V_{ch}(60 m_{ch} W_{ch} h_{ch})^{-1}$
Universal gas constant	R	J/mol K	8.314
Faraday's constant	F	$A\ s\ mol^{-1}$	96,487

3.3.2 Model Geometry

The model was designed and operated as similar as possible with the experiment conducted in the laboratory, in order the reduce percentage different between the model results and the experiment. Based on the experiment (C.Xu, 2006; Ge & Liu, 2005; Scott, Taama, Kramer, Argyropoulos, & Sundmacher, 1999), the following model is constructed as Figure 9.

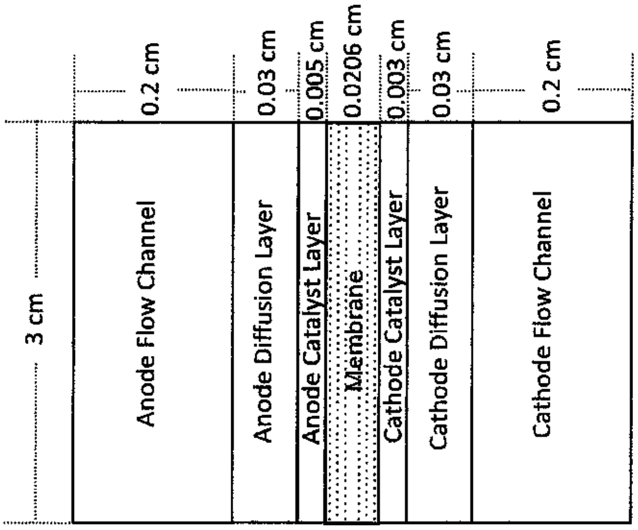

Figure 3.2: Model Geometry based on experiment set-up

CHAPTER 4

RESULTS AND DISCUSSION

4.1 MODEL VALIDATION

At the initial stage of the project, the model was developed to generate the result which is comparable with the experimental data. In this project, MATLAB software was used to develop the model. The polarization curve can be obtained from the model; plot of current density (A/cm^2) and cell voltage (V). The model validation was done before proceed with case study and analysis which used to observe the effect of certain parameters to cell performance.

The result of validation ware shown in Figure 4.1 below:

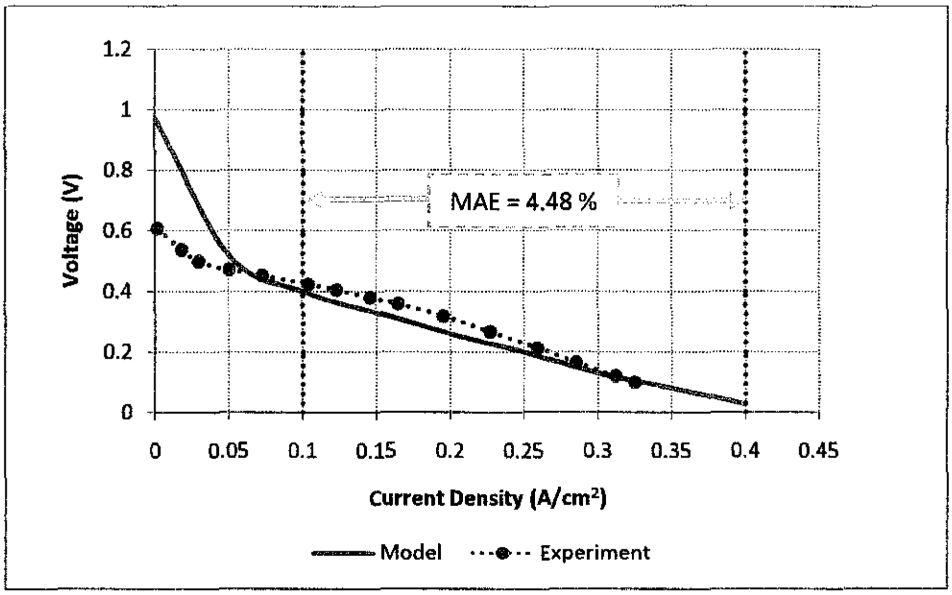

Figure 4.1: Polarization curve of DMFC fed with 2.0 M methanol concentration.

Figure 4.1 illustrated values comparison between the model result and experimental result which conducted by Ge & Liu (2005). The cell operating temperature was 75 °C. The methanol flow rate and the air flow rate are 5 cm^3 /min and 500 cm^3 /min respectively.

Based on the result above, the curve looks similar to reference as the voltage decrease when the current density is increase. In the range between 0.1 and 0.4 of current density shows a good agreement between the model and experimental result.

The percentage error between the results obtained from experimental and model simulation was calculated by using the correlation as following:

$$Mean\ absolute\ percent\ error, \% = \frac{\sum \frac{|Experimental - Model|}{Experimental} \times 100\%}{n} \qquad (19)$$

where n = number of individual points/data

Table 4.1: Calculation of mean absolute percentage error

Voltage	Current Density (A/cm^2)				
	0.1	0.15	0.2	0.25	0.3
Model	0.40	0.34	0.28	0.20	0.13
Experimental	0.41	0.36	0.31	0.21	0.13
[|Exp-Model|/Exp]*100(%)	2.44	5.55	9.67	4.76	0

Therefore, mean absolute percent error, % = (2.44 + 5.55 + 9.67 + 4.76 + 0) / 5

= 4.48 %

From the error calculation, the mean absolute error is 4.48%. The error is considered as small value, hence this model is considered to be reliable.

Once the validated model was obtained, the model was used to run the case study in order to observe the effects of certain parameter to the direct methanol fuel cell performance

4.2 CASE STUDIES

4.2.1 Effect of methanol concentration

As for the study on the effect of methanol concentration, the direct methanol fuel cell model was operated with the difference of methanol concentration. From previous experiment study, it revealed that the optimum concentrations are between 1 and 2 M. The higher concentration, than 2 M, tends to cause methanol crossover problem (Ge & Liu, 2005; Scott, et al., 1999). To avoid this methanol crossover, the optimum methanol concentration values which were selected to use for the study are 1 M, 1.5 M and 2 M. The operating condition used are as following : 75 °C operating temperature, 1 bar cathode pressure, 1000 cm^3/min flow rate of air, 1 cm^3/min of flow rate of methanol solution. The model was operated at extremely high flow rate in order to avoid the occurrence of liquid water along the channel and also the effects of the oxygen depletion.

The model results are illustrated in Figure 4.2 and 4.3 below.

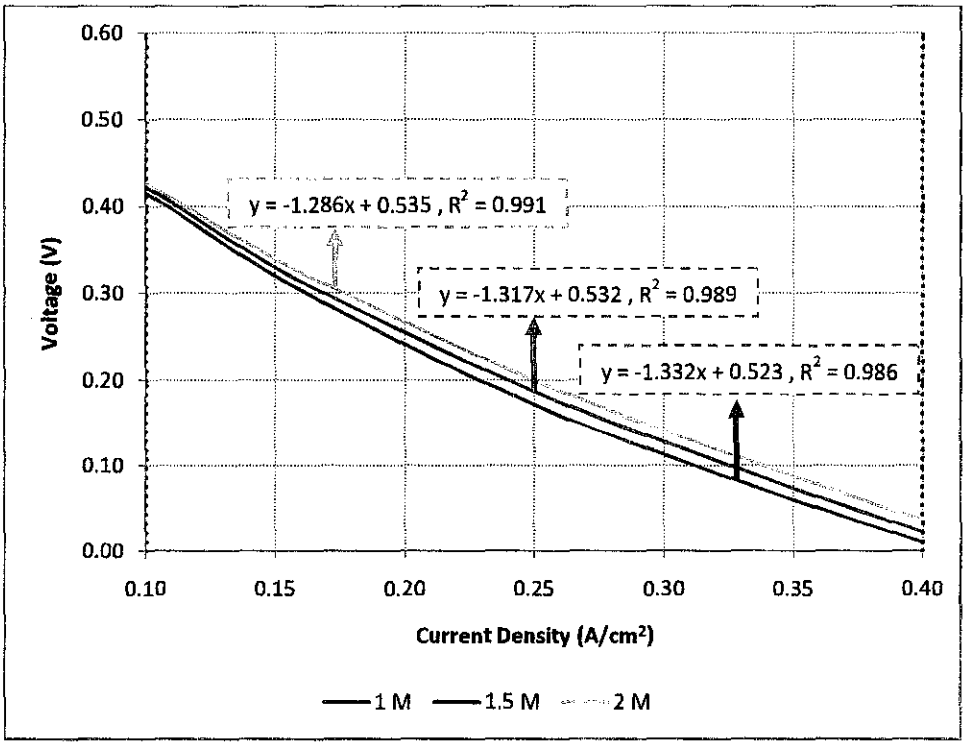

Figure 4.2: Curves of current density and voltage at different methanol concentration

It is observed that methanol concentration on the anode side has an influence on the current density/voltage behavior of a direct methanol fuel cell. As can be seen from Figure 4.2, the cell voltage is slightly increases when methanol concentration increases.

The cell voltage decreases almost linearly toward zero with the increasing of current density, as show in Figure 4.2. The current density gradually increases when the methanol concentration increases. This is because at higher concentration, there is methanol available to be oxidizes. Ge & Liu (2005), has studied the effect of methanol concentration, the concentration of 1.0, 2.0, 3.0, 4.0, 5.0 and 6.0 were used, but results showed that the best concentration is between 1.0 and 2.0 M. At the higher methanol concentrations, approximately, than 2.0 M, the cell voltage dropped significantly. This is the resulting from methanol crossover which are permeation of methanol through membrane(Scott, et al., 1999).

In order to overcome methanol crossover, several approaches have been used. Increasing the electrolyte thickness also can be used to solve the methanol crossover problem which can be explained more through Fick's law equation :

$$\dot{n}_{x-over} = DA\frac{c_a - c_c}{\delta_{PEM}} \tag{20}$$

where

δ_{PEM} is electrolyte thickness

D is diffusion coefficient of methanol in electrolyte

According to the equation above, when electrolyte thickness increases, it results in decreasing of the diffusion of water. However, this approach can lower cell performance due to the path of ion travel is increased. To limit the water and methanol crossover problem, the electrolyte thickness used is typically more than 100 μm.

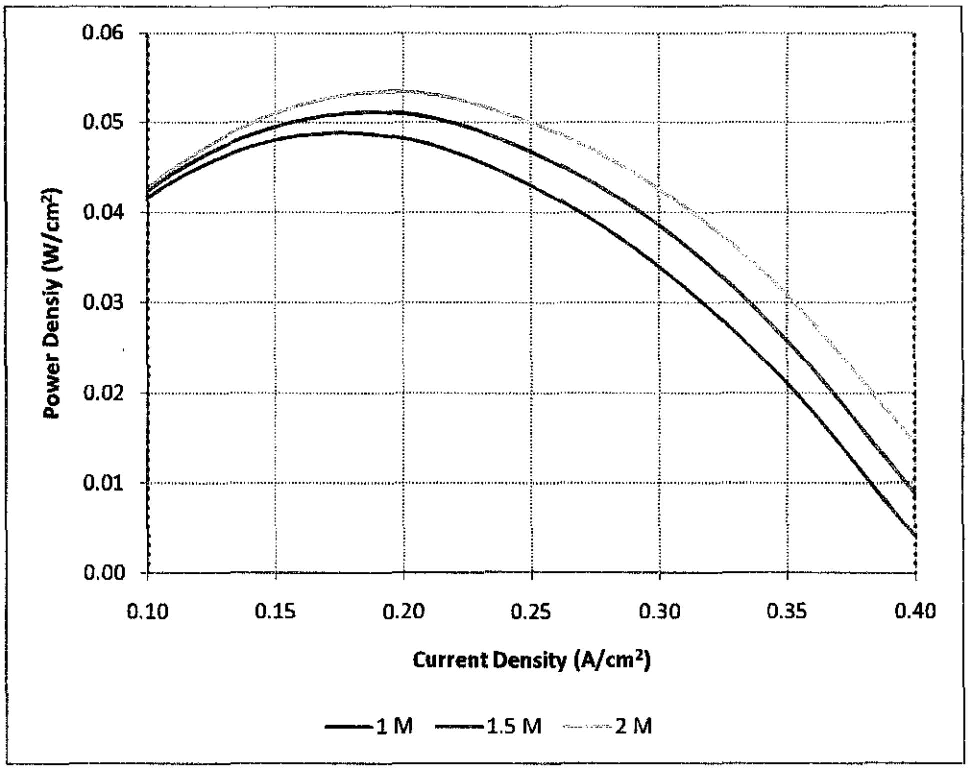

Figure 4.3: Curves of current density and power density at different methanol concentration

The power density (W/cm^2) of different methanol concentration is shown in Figure 4.3. The maximum power density is acquired at 2 M methanol concentration. The results revealed that the power density decreases as the methanol concentration decreases. Though, it slightly decreases from 0.053 W/cm^2 with 2 M, to 0.051 W/cm^2 with 1.5 M and to 0.048 W/cm^2 with 1 M.

4.2.2 Effect of air flow rate

As for the study on the effect of air flow rate, the direct methanol fuel cell model was operated with different of air flow rate. The air flow rates used for study are 500 cm^3/min, 750 cm^3/min and 1000 cm^3/min. The operating condition are as follows : 75 °C operating temperature, 1 bar cathode pressure, 1 cm^3/min flow rate of methanol solution.

The model results are illustrated in Figure 4.4 and Figure 4.5 as below.

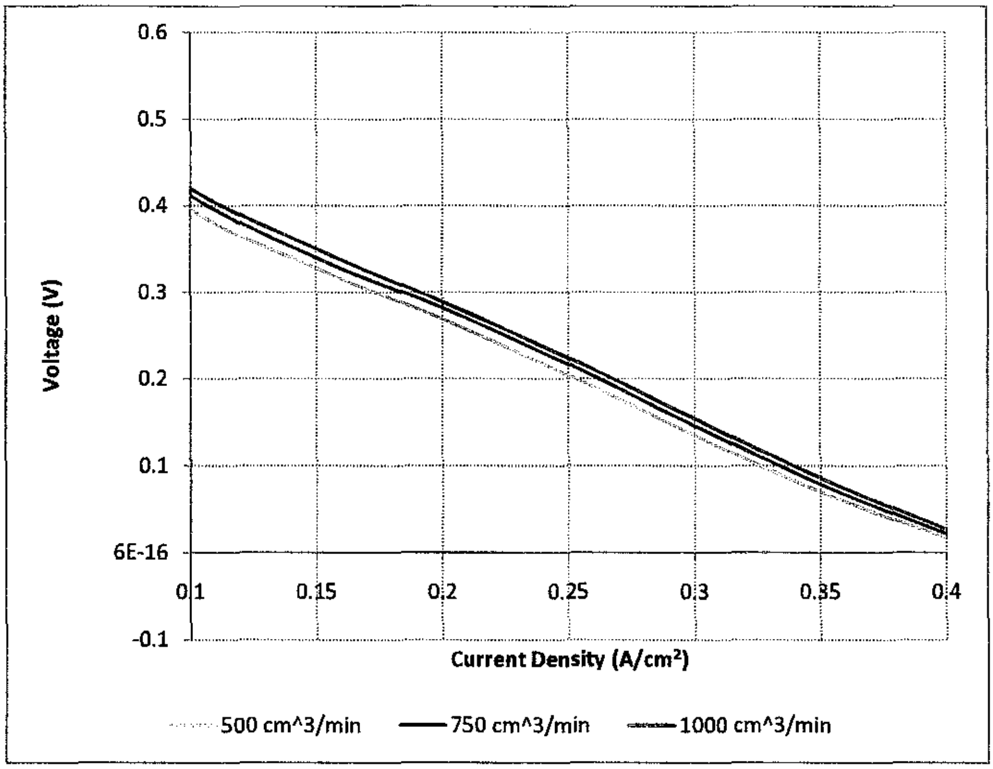

Figure 4.4: Curves of current density and voltage at air flow rate

Based on results obtained, it can be observed that air flow rate at the cathode side has an effects to the density/voltage behavior; the polarization curves of a direct methanol fuel cell. The cell performance slightly increases with the increasing of air flow rate from 500 to 750 cm^3/min as same as from the flow rate from 750 cm^3/min to 1000 cm^3/min.

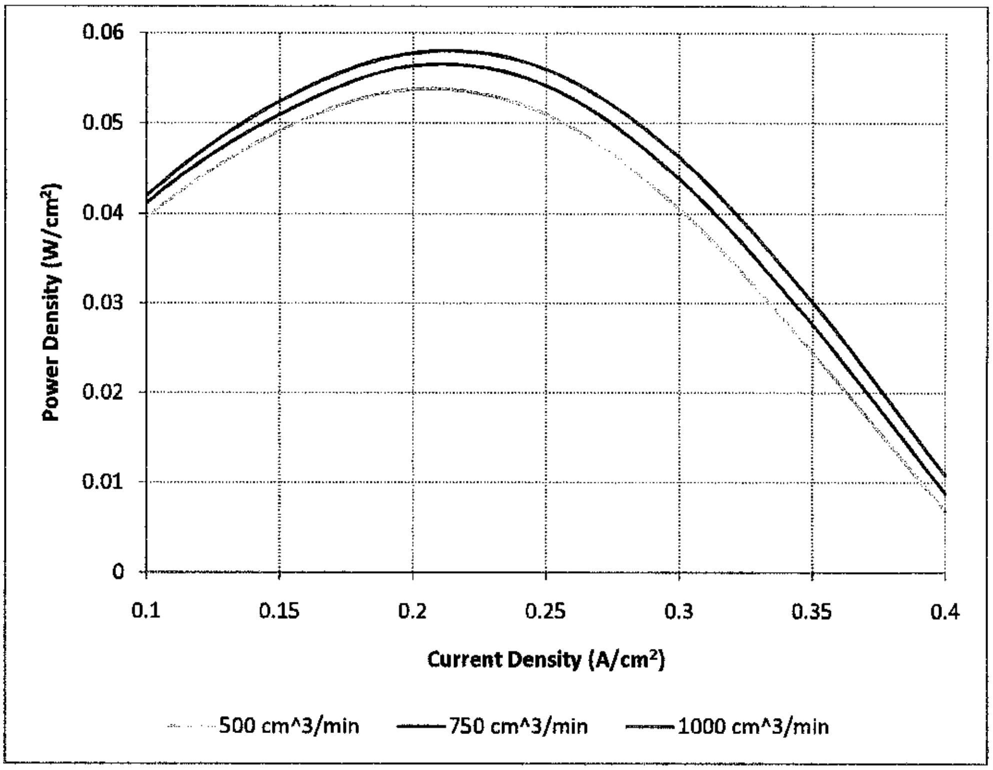

Figure 4.5: Curves of current density and voltage at air flow rate

Results showed that the cell performance increases when air flow rate increases. However, the cell performance will increase with the increasing of air flow rate. From Figure 4.5, it, clearly, showed that the power density is slightly increased when air flow rate increases from 500 cm^3/min with power density value of 0.05380 W/cm^2 to 750 cm^3/min with power density value of 0.05638 W/cm^2, as a result, the power increases approximately 4.8%. While the air flow rate increases from 750 cm^{-3}/min with power density value of 0.05638 W/cm^2 to 1000 cm^3/min with power density value of 0.0578 W/cm^2, the power density value increase approximately 2.4%. This results showed that with the increasing of air flow rate from 750 cm^3/min to 1000 cm^3/min the power density increase twice lesser than, that of, 500 cm^3/min to 750 cm^3/min. Ge & Liu (2005), conducted experiment study to investigate the effect of air flow rate to the cell performance. They found that at lower air flow rate, the concentration of oxygen tends to decrease along the channel, therefore result in decreasing of cell performance.

Additionally, high flow rate of air can remove the cross-overed water and produced water. In order to prevent flooding by air flow rate, the cathode air flow has to be sufficient in order to remove water at its arrival rate and as well, its generated rate at the cathode surface (Mench, 2008).

CHAPTER 5

CONCLUSION AND RECOMMENDATION

Direct methanol fuel cell is one of alternative power source which has currently been given a greater interest and become a major type of fuel cell for research studies and development. In this model study, direct methanol fuel cell model was developed by using MATLAB software. The model was first validated with experimental data and then proceeds with case studies to observe the effects to cell performance.

The model results agreed quite well with experimental data and can be used for study as per objectives; to study the effects of methanol concentration and oxygen flow rate to the cell performance. From the studies, the results showed that both the methanol concentration and air flow rate has an effect to the cell performance.

The cell performance increases as the methanol concentration and air flow rate increases. Though, the air flow rate also has an effect on the cell performance. If the air flow rate increases 1.5 in ratio, the power density will, as well, decrease twice. From this finding if air flow rate is above 1000 cm^3/min, the power density value will increase approximately 1.2%. Then it will be considered no significant effect to cell performance.

It is recommended that further analysis from this model may be conducted by considering other parameters, e.g., anode electrode porosity, cathode electrode porosity, oxygen flow rate, water and methanol crossover rate, as well to achieve better results.

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APPENDICES

APPENDIX 1 : Final Year Project I (May 2011) Proposed Activities Timeline

Activities in FYP I	W 1	W 2	W 3	W 4	W 5	W 6	W 7	W 8	W 9	W 10	W 11	W 12	W 13	W 14	W 15	W 16	W 17
Selection of project topic	▨	▨													Study week	Final Examination Week	Final Examination Week
Preliminary research work - Literature review: fundamental of the project's theories and concepts																	
Submission of extended proposal																	
Oral Proposal Defense																	
Project work continues - Explore more on literature review and model design.							▨	▨	▨	▨							
- Result discussion and conclusion									▨	▨	▨	▨					
Submission of Interim Draft Report													▨				
Submission of Interim Report														▨			

APPENDIX 2 : Final Year Project II (September 2011) Proposed Activities Timeline

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	W 17
Project work continues (preliminary state)																Final Examination Week	Final Examination Week
Submission of progress report								■									
Project work continues - Start the further stage of project																	
Pre EDX Presentation											■						
Submission of draft report												▨					
Submission of Dissertation Submission of Technical paper																	
Oral Presentation																	
Submission of Project Dissertation															■		

APPENDIX 3 : MATLAB Coding (Main Function)

```
function F = myfunction(x,Icell)

wad=0.03;                   % Thickness of anode diffusion layer
iaref=5.5*(10^-5);          % Reference exchange current density of
                              anode
F=96487;                    % Faraday's constant
dmeohad=1.39885*(10^-5);    % Diffusion coefficient of methanol in
                              anode diffusion layer
cmeohref=1*(10^-3);         % Reference concentration of methanol
alpha_a=0.8;                % Transfer coefficient of anode
T=348.15;                   % Temperature
R=8.314;                    % Universal gas constant
sah=0.2083333;              % Velocity of fluid in anode channel
lah=3;                      % Length of anode channel
hah=0.2;                    % Depth of anode channel
nmeohd=0.04709228;          % Electro-osmotic drag coefficient
cmeohahin=2*(10^-3);        % Methanol concentration at anode inlet
dmeohm=6.73667*(10^-6);     % Diffusion coefficient of methanol in
                              membrane
wm=0.0206;                  % Thickness of membrane
wcd=0.03;                   % Thickness of cathode diffusion layer
icref=3.3*(10^-5);          % Reference exchange current density of
                              cathode
alpha_c=0.8;                % Transfer coefficient of anode
docd=1*(10^-3);             % Diffusion coefficient of oxygen in
                              cathode diffusion layer
coref= 3.45481*(10^-5);     % Reference concentration of oxygen
lch=3;                      % Length of cathode channel
hch=0.2;                    % Depth of anode channel
sch=20.833333;              % Velocity of fluid in anode channel
cochin=7.25509*(10^-6);     % Oxygen concentration of cathode inlet
% x(1)                        anode overpotential (na)
% x(2)                        cathode overpotential (nc)


  % solving for lamda 3
lam3=((wad*imeohref)/(6*F*dmeohad*cmeohref))*(exp((alpha_a*F*x(1))/(
R*T)));

  % solving for lamda 4
lam4=(-lah*dmeohad*(lam3))/(hah*sah*wad*(1+(lam3)));

  %solving for lamda 5
temp_1=((exp(lam4)-1)/((1+lam3)*lam4))-1;
lam5=1-(((temp_1)*wad*dmeohm)/((lam3)*dmeohad*wm));

temp_2=(exp(lam4)-1)/((lam4*lam5)*(1+lam3));
temp_3=(1/6)-((nmeohd*(temp_1))/(lam5));

  %Equation 1
A=((wad*(temp_3)*Icell)/(lam3*F*dmeohad))-(cmeohahin*temp_2);

%-------------------------------------------------------------------
```

```
  % solving for lamda 1
lam1=(wcd*ioref*exp((alpha_c*F*x(2))./(R*T)))/(4*F*docd*coref);

  % solving for lamda 2
lam2=(-
lch*ioref*exp((alpha_c*F*x(2))/(R*T)))/(4*F*(1+lam1)*hch*sch*coref);

temp_4=((exp(lam2)-1)/((1+lam1)*lam2))-1;
temp_6=(1/4)-((1.5*nmeohd*(temp_4))/(lam5));

  % Equation 2

  B=((wcd*(temp_6)*Icell)/(lam1*F*docd))-(cochin*(temp_4+1))-
((1.5*wcd*(temp_4)*(temp_2)*dmeohm*cmeohahin)/(lam1*docd*wm));

  % function

 F=[A;B];
```