The Effect of Different Temperature and Methanol Concentration on Current Density Distribution of Direct Methanol Fuel Cell

by

Nurul Syazwani bte Abd. Jabar

Dissertation submitted in partial fulfillment of
the requirement for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

SEPT 2012

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CERTIFICATION OF APPROVAL

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Approved by,

_____

(Dr. Rajashekhar Pendyala)

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TRONOH, PERAK
September 2012

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 undertaken or done by unspecified sources or person.

……
(NURUL SYAZWANI BTE ABD. JABAR)

ABSTRACT

The effect of different temperature and methanol concentration on current density distribution of DMFC is presented in this paper. DMFC are a subcategory of proton exchange membrane fuel cells (PEMFC) in which methanol is used as the fuel. The performance of direct methanol fuel cell must be evaluated with different possible operating condition for being commercialize especially in the area of small scale portable power production. 2D model is more computational efficient compared to 3D and more accurate than 1D. Hence, two-dimensional model, x-y plane geometry is utilized in the simulation to take into account the transport phenomena in all layers in the cell. The simulation was done based on agglomerate model of PMFC in COMSOL Multiphysics 3.5a. Theory and governing equations involve are Maxwell-Stefan, Darcy's Law, agglomerate model of anode and cathode and porous fluid flow. Different operating parameter which are temperature ranging from 323K to 353K and methanol concentration ranging from 2M to 5M based on literature survey were employed. Finally, the model were analyze with postprocessing tools in COMSOL to get required plot. The result can be concluded that current density distribution increases with increasing temperature and concentration. Future study can be done by assuming membrane to be permeable to the reactant.

ACKNOWLEDGEMENT

My utmost gratitude and appreciation goes to my supervisor, Dr. Rajashekhar whow encourage and guide me from initial to the final level enabled me to develop and understanding of this Final Year Project II. I would also like to thank to Dr Yusmiza for helping me throughout this FYP II who has spent hours in guiding and teaching me along the completion of my project.

Last but not least, I would like to thank my fellow friends at Universiti Teknologi PETRONAS (UTP) for the opportunity to work together with guidance and trust andalso valuable technical knowledge. The persistence in sharing invaluable experiences and profound knowledge would be useful in my future. It was a great moment for me to complete my Final Year Project that gave me a valuable experience for future use.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND STUDY

The interest in renewable and sustainable energy production is increasing as well as the concerns of the health of environment. Alternative energy has recently been focused heavily with funding for research and development in the field (Woolard, 2010). New and effective ways of producing renewable and sustainable energy is in demand. Fuel cells may replace batteries for use in electronic devices and popular for small scale portable applications. Fuel cells are devices which convert electrical energy from an electrochemical reaction.

One of the most popular fuel cells today is the proton exchange membrane fuel cell (PEMFC) which produce power from a hydrogen-oxygen reaction with water as a byproduct. The hydrogen source can be either from compressed hydrogen or secondary source such as methanol or fossil fuels. The sub-category of this fuel cell which is direct methanol fuel cell (DMFC) becoming increasingly popular with methanol-oxygen reaction. Research is currently being conducted to find new ways to apply these both fuel cells and even already being used in market today.

Most of the major automobile companies such as Audi, BMW, Ford Motor Company, GM, Honda, Nissan, and Toyota are currently in the process of producing fuel cell cars for daily as well as commercial use. Besides, fuel cells are also a very viable alternative to replace batteries in forklifts because fuel cells do not self heat as much as batteries. This could reduce the tendency of explode during operation and be refilled instead of exchanged during operation. In smaller scale stationary and portable electronics, a lot of research has also been done to utilizes fuel cells in order to adress the issue. For example, fuel cell power generators is currently being manufactured by Smart Fuel Cell company (Smart Fuel Cell Company) to be used with mobile homes, boats, military applications, and more.

1.1.1 Types of Fuel Cell

Fuel cells are expected to become a power source of the future due to the fact that power generation by fossil fuels has resulted in negative consequences. Besides, the supply of fossil fuels for energy use is expected to last for another 30 years. Changing fuel infrastructure would be costly but new power source that has low pollutant emissions, energy efficient and unlimited supply of fuel is needed (Rajalakshmi & Dhatathreyan, 2008). Therefore, fuel cells that able to fulfill global power needs are now close to commercialization than ever.

A fuel cell is electrochemical cell that consists of negatively charged electrode, positively charged electrode and electrolyte membrane. These fuel cells will convert chemical fuel into electrical energy. Historically, the first fuel cell was invented by Sir William Grove in 1839. However, extensive fuel cell research only began during 1960s at NASA. NASA had developed the first Proton Exchange Membrane (PEM) cells but resulting in difficulties of internal cell contamination and leakage of oxygen trough the membrane (Kulikovsky, 2000).

In general, fuel cells can be classified into five types according to their electrolyte materials, which are alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), solid oxide fuel cell (SOFC) and proton exchange membrane fuel cell (PEMFC). These fuel cells are classified by operating temperature and nature of electrolyte used . Oxidation and reduction reactions that take places are given in Figure 1 according to their type of fuel cells.

Alkaline fuel cells (AFC) typically utilize potassium hydroxide (KOH) with the concentration of 35-50 wt% as the electrolyte. AFC exhibit the highest electrical efficiency among all fuel cells but suffer economically because of the necessity of ultra pure gases for its fuel. The operating temperature for AFCs is between 50 to 200^{o}C. Power output of an AFC is expected is in the range of 500 to 10k W. The major challenge of AFC is potassium hydroxide could not tolerate 300 ppm of carbon dioxide in atmospheric air while air is very necessary for commercial applications as oxidants.

Phosphoric acid fuel cells (PAFC) immobilized liquid phosphoric acid as electrolyte. Simple construction and thermal and chemical stability of the phosphoric acid electrolyte at an operating temperature almost 220^{o}C make PAFC the most advanced system among all fuel cells. Electro-catalysts at both anode and cathode are made from platinum black. It is mainly used in domestic CHP because of its efficiency almost 40% and reliability. The use of volatile and unstable phosphoric acid electrolyte, long time startup and high cost limit the performance of PAFC.

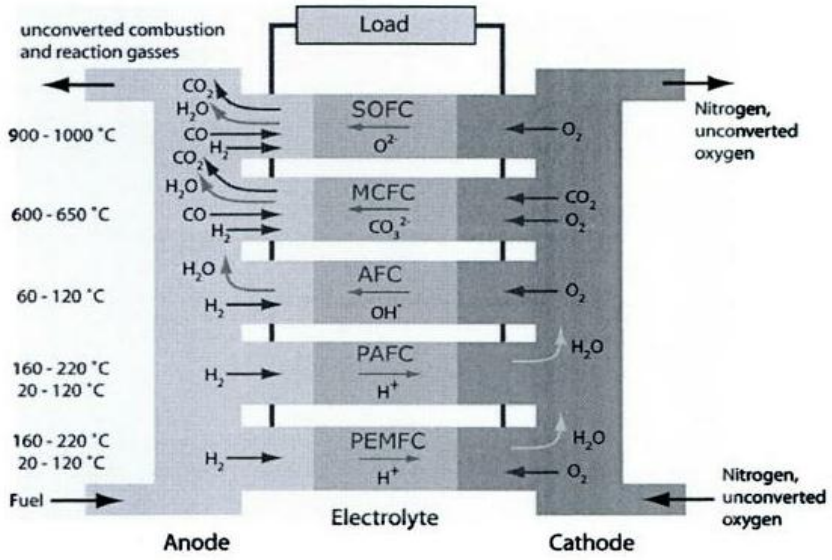

Figure 1: Types of Fuel Cells and Their Reactions (Kulikovsky, 2000)

Molten carbonate (MCFC) uses liquid lithium potassium or lithium sodium carbonate as electrolyte. Molten carbonate fuel cell usually operates at temperature almost 650^{o}C where carbonate ions provides the ionic conduction. Ni and nickel oxide are utilized as the electro-catalyst at anode and cathode. MCFC main application is in distribution power generation because of its advantages in efficiency, emissions, less noise and can be operated in high temperature. The power output of an MCFC is up 10MW and could possibly be more.

Solid ceramic electrolyte (SOFC) employed Yttria stabilized Zirconia (YSZ) as electrolyte. The operating temperature of SOFC range at 500-1000^{o}C with oxygen ions provide the ionic conduction. Because of high temperature of operation, this fuel

cell does not require precious metal and wide range of fuels can be used. SOFC has attracted a lot of attentions with the application in stationary power plants because of its high efficiency and fuels flexibility. Moreover, SOFC is capable to reform CH_4 internally.

Polymer electrolyte membrane fuel cell (PEMFC) employed proton-conducting polymer membrane as electrolyte with operating temperature in the range of 30-100^{o}C. The power output of PEMFC is 1-100kW. Hydrogen and methanol are the common reactants used in the system. PEMFC is low temperature. Nafion, a perfluorinated polymer, developed by DuPont is commonly use as electrolyte in this application. Typically, polymer electrolyte membrane is sandwiched between carbon-supported platinum catalysts at anode and cathode.

1.1.2 Direct Methanol Fuel Cell (DMFC)

Direct methanol fuel cells or DMFCs are a subcategory of proton exchange membrane fuel cells (PEMFC) in which methanol is used as the fuel. One of the DMFC's main advantages is having a liquid fuel, water and methanol solution, which carries a high energy density per unit volume and makes fuel handling easier. Direct methanol fuel cells (DMFCs) are the next big thing that many in the industry expected to see an integrated fuel cell in every laptop and mobile phone.

Although classical hydrogen-oxygen fuel cells exhibit superior performance, methanol has a much higher energy density and is much easier to store and transport. The byproducts are also ecologically harmless which is CO_2 and water. This is another reason why DMFC has received so much attention during the past decade.A liquid fuel also reduces the risk of drying out the electrolyte, which is beneficial since the electrolyte conductivity is dependent. A schematic of a DMFC employing an acidic solid polymer electrolyte membrane is shown in Fig. 2. At the anode of a DMFC methanol ionization occurs on the catalyst surface by following reaction:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6\,e^- \qquad (1)$$

Protons then move to the cathode, where they react with oxygen:

$$3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \quad (2)$$

The overall reaction in the cell is:

$$CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O \quad (3)$$

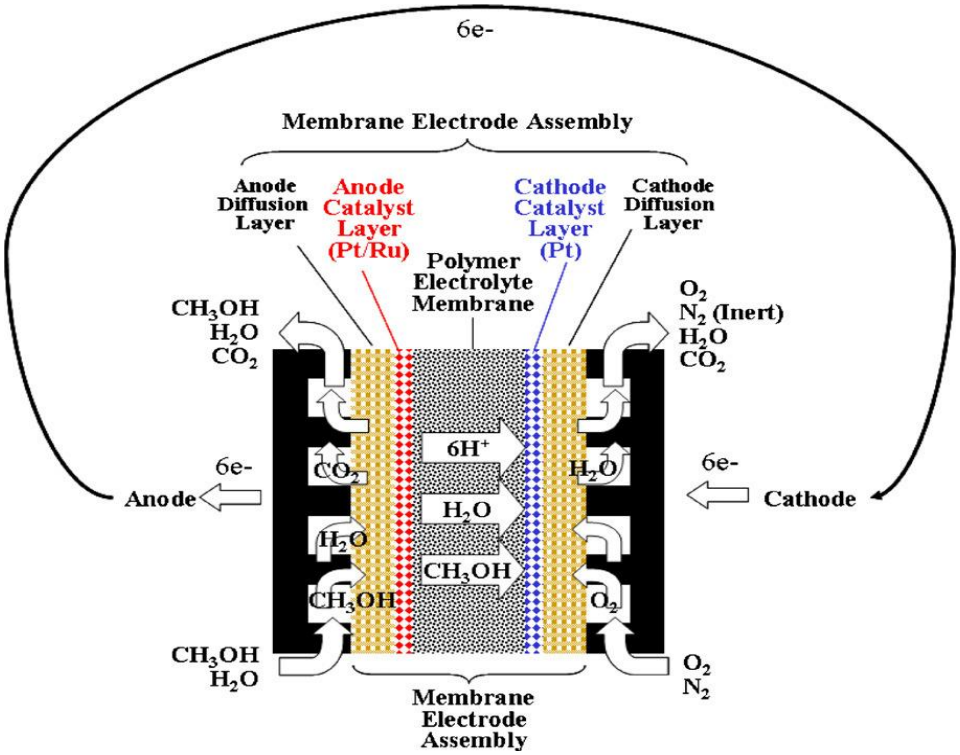

Figure 2: Schematic Diagram of Direct Methanol Fuel Cell (Woolard, 2010)

In a liquid direct methanol fuel cell system, methanol aqueous solutions are fed to the flow field at anode and then transport across the diffusion layer to the catalyst layer, where they will react with water to produce carbon dioxide, protons and electrons as shown in Eq. (1). An acidic electrolyte is advantageous to aid CO_2 rejection since insoluble carbonates form in alkaline electrolytes. The protons produced at the anode migrate through the polymer electrolyte to the cathode where they react with oxygen which usually supplied from air to produce water as shown in Eq. (2). The electrons produced at the anode carry the free energy change of the chemical reaction and travel through the external circuit where they can be made to do useful work, such as powering an electric motor.

1.2 PROBLEM STATEMENT

The performance of direct methanol fuel cell must be evaluated with different possible operating condition for being commercialize especially in the area of small scale portable power production. The engineering and materials challenges that must be overcome to produce fuel cells are require innovative solutions. In direct methanol fuel cells several technical hurdles need to improve such as methanol crossover, cost reduction, design flexibility,overall efficiency, size and weight, independencies and so on. Hence, in order to improve the overall performance and fuel utilization of a DMFC, mass transport of methanol and water within the fuel cell must be fully understood. However, experiment has several limitation such as costly and time consuming, difficult to measure the parameters indide the cell and the result is not replicable. Thus, modelling is one of the strategic tools that helps to understand these hurdles. In 1D model, the accuracy is low due to many assumptions while 3D is computationally intensive. 2D model is more computational efficient compared to 3D and more accurate than 1D. Thus, this project will help to get the insight of direct methanol fuel cell performance efficiently and accurate in 2D model.

1.3 OBJECTIVE AND SCOPE OF PROJECT

The Multiphysics computer program COMSOL was also utilized to create a mass transport model for methanol and water within the DMFC. The research objectives of this work is to study the performance of a DMFC over different operating range which are concentration of methanol at the inlet and temperature by developing two-dimensional model. This project involved several components in direct methanol fuel cells which are membrane, diffusion layer and fuel channel in x-z direction. The temperature and concentration of methanol of fuels are varies to study the performance.

CHAPTER 2

LITERATURE REVIEW

2.1 MODELING OF DIRECT METHANOL FUEL CELL

Several studies about direct methanol fuel cell have been done for the past few years. Most of the studies investigate cell performance by incorporating mass transport of single cell with different layers and electrochemical. However, the coverage and solutions taken for each modeling are varies. In general modeling can be classified into mechanistic, analytical and semi-empirical. Besides, normally, single phase and two phase model is develop for DMFC. However, single-phase models cannot reflect mass transport process in real liquid–gas two-phase flows that occur in DMFC.

The development of a two-phase model of DMFC is more challenging because of the complexity in two-phase mass flows even though it is more realistic. Kulikovsky (2000) has developed few model with 1 dimensional and quasi 2 Dimensional analytical and semi-analytical at 2007. In these models, few factors that could affect cell performance were studied. For example, the effects of diffusive transport of methanol and oxygen through a cell, gaseous bubbles formation in the anode channel, and the non-Tafel kinetics of methanol oxidation on the anode catalyst layer . The effects of water transport in methanol crossover were studied by Liu et al. and Wang et al. Based on their reports, water transport should be considered as one of important aspects in DMFC modeling.

Besides, a two-dimensional, two-phase, multi-component DMFC was modeled by using CFD technique which developed by Wang and Wang (2003) . Another model that utilized computational fluid dynamics (CFD) as the solution technique is done by Ge and Liu (2006) with three dimensional, single phase, multi component mathematical model. Kinetics of the multi-step methanol oxidation reaction that occurs in anode is also taken into account in Garcia et al. one-dimensional, isothermal, and semi-analytical model. Lastly, Oliveira et al. has discussed the

influence of heat transfer in a one-dimensional CFD model. Base on this model, temperature distribution through the cell can be obtained as well as other output such as cell voltage.

2.2 MODEL GEOMETRY

Based on Shi et al (2006), two-dimensional modeling of PEM fuel cell can be conducted in two different modes. First is parallel or perpendicular to the gas flow direction in the gas channel while the second one is modeling geometry is across the membrane in both cases. The objective of the study was to develop and compare 2-D isothermal PEM fuel cell models in two different modes. The work study the performance of fuel cells such as the reactants mass concentration and velocity distribution and output power density.

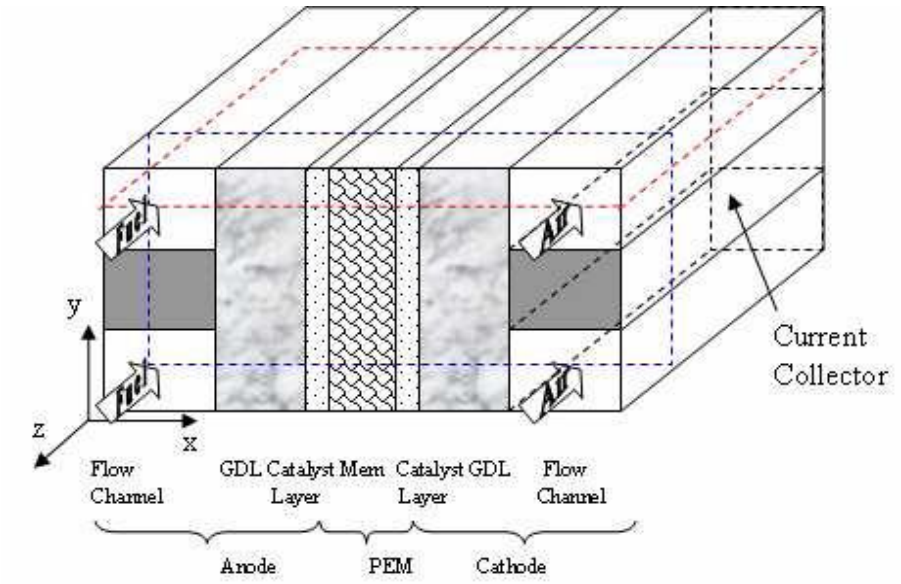

Figure 3: Three Dimensional Diagram of a DMFC and Its Various Components (Shi et al, 2006)

Figure 3 schematically shows a 3D single DMFC and its various components which are membrane, flow channel, gas diffusion layer and catalyst layer on both anode and cathode sides . There are two options to choose the modeling geometry to conduct the 2D simulations. First is in x-y plane as shown in Fig. 3(a), denoted at the blue cut surface, and the other one is in x-z plane as shown in Fig. 3(b).

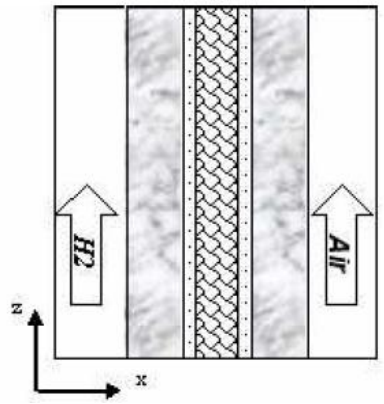

Figure 3(a) : x-z Plane Model Geometry (Shi et al, 2006)

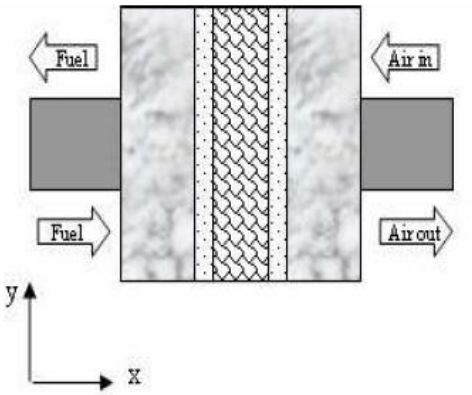

Figure 3(b): x-y Plane Model Geometry (Shi et al, 2006)

However, the available model in comsol tutorial is agglomorate model in x-y plane geometry that demonstrates multiphysics modeling of a proton exchange membrane (PEM) fuel cell with an interdigitated flow field design. The model uses current balances, mass transport equations (Maxwell-Stefan diffusion for reactant, water and nitrogen gas), and momentum transport (gas flow) to simulate a PEM fuel cell's behavior.

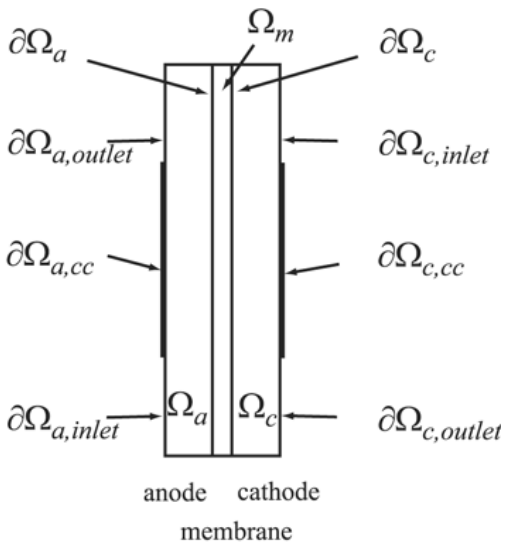

Figure 4: x-y Plane Model Geometry with Based on Agglomerate Model (Tutorial Proton Exchange Memrane Fuel Cell COMSOL Multiphysics 3.5a)

Figure 4 shows the modeled section of the DMFC based on agglomerate model which consists of three domains. Anode domain denote by Ωa, a proton exchange membrane ,Ωm, and a cathode ,Ωc. Each of anode and cathode porous electrodes is in contact with an interdigitated gas distributor. Inlet channel ($\partial\Omega a,inlet$), a current collector ($\partial\Omega a,cc$), and an outlet channel ($\partial\Omega a,outlet$) are available at anode side. The same notation is also being used to define the cathode side.

2.3 THE EFFECT OF METHANOL CONCENTRATION TO DMFC

The overall performance of DMFCs is affected by variety of parameters. The types of parameters are methanol concentration, operating temperature, the inlet flowrate of methanol, and membrane thickness. High performance of DMFC can be obtained by optimizing these parameters without neglecting methanol crossover effects along the crossover flux. Methanol crossover have high significant with higher operating temperatures and methanol concentration.

The effect of methanol concentration to the performance dmfc has been studied by Jung et al (2005) who found that higher methanol concentration would improve voltage and power density at higher currrent density. Figure 5 shows the result of DMFC performance operate at $50^{o}C$ with different methanol concentrations. It show that 3M mehthanol performed the best and voltage and power density increased with the increasing of concentration at high current densities. More methanol will react thus make more power per unit volume to react. However, the voltage was lower with the increasing methanol concentration because lower current densities has less methanol that is needed to react and lower the methanol crossover.

Besides, the optimum concentration of methanol for passive and active DMFC is different. Liu et al. (2006) found that a concentration of 5M will resulted to maximum power density in a passive system. Exothermic reaction between permeate methanol and oxygen on the cathode cause the maximum power density . However, the increasing of concentration will decrease the efficiency because of higher methanol crossover. In active system, the higest performance of DMFC is at low concentrations ranging from 2 to 3M (Abdelkareem & Nakagawa, 2008). Methanol concentration at 1M was found to be the best for active system by Jewet et al (2007) providing with a balance between good supply of reactant and power gain.

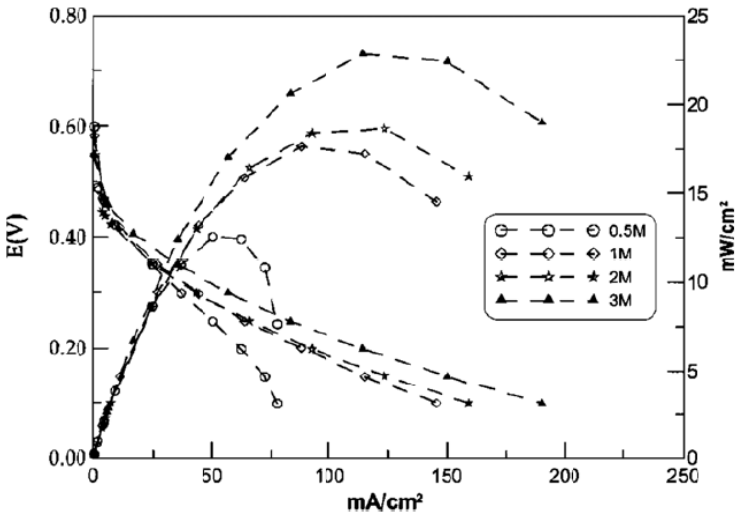

Figure 5 : Result of Various Methanol Concentration at 50^{o}C (Jung et al, 2005)

2.2 THE EFFECT OF TEMPERATURE TO DMFC

Jung et al (2005) also obtained a polarization plot at 80^{o}C and 120^{o}C. However, according figure 4, increased in temperature shifted the optimal methanol concentration to 1M. The increase of operating temperature will increase the reactions of methanol provided with higher concentrations. This is because, catalyst is more prone to cabon monoxide poisoning. Besides, the higher temperature will allows more protonation in catalyst which leads to higher performance but at the same time will allows more methanol crossover.

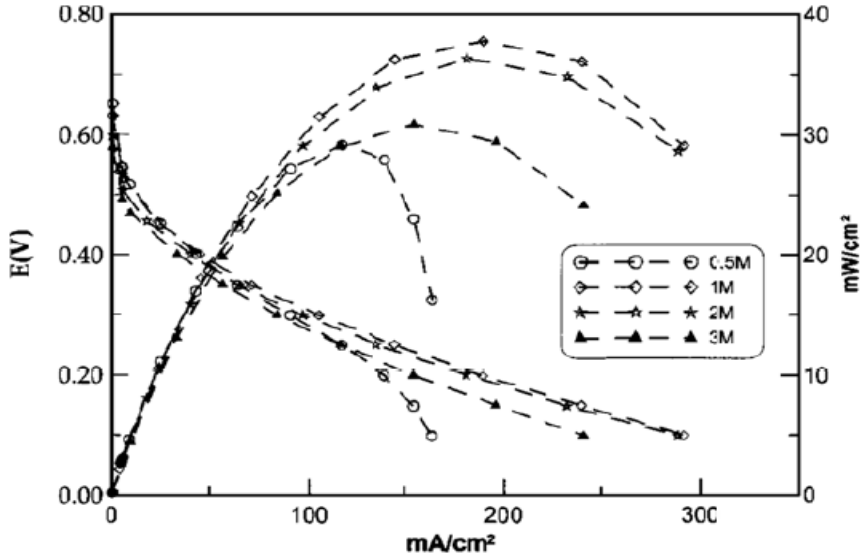

Figure 6 : Result of Various Methanol Concentration at 80^{o}C (Jung et al, 2005)

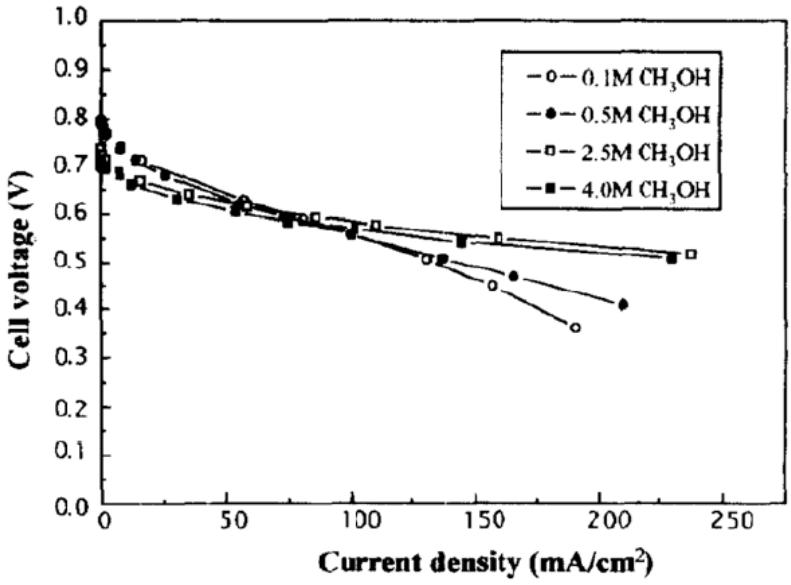

Figure 7 : Result of Various Methanol Concentration at 120^{o}C (Jung et al, 2005)

Based on figure 7, 2.5M performed better than 4M methanol and 0.5M methanol. This results shows that the performance of DMFC is based on the balance between methanol concentrations and operating temperature. Another study by Jung et al (1998) is about the effect of temperature on DMFC by using Nafion 112 at 1M

methanol at figure 8. It shows that temperature has strong influences on the performance of DMFC.

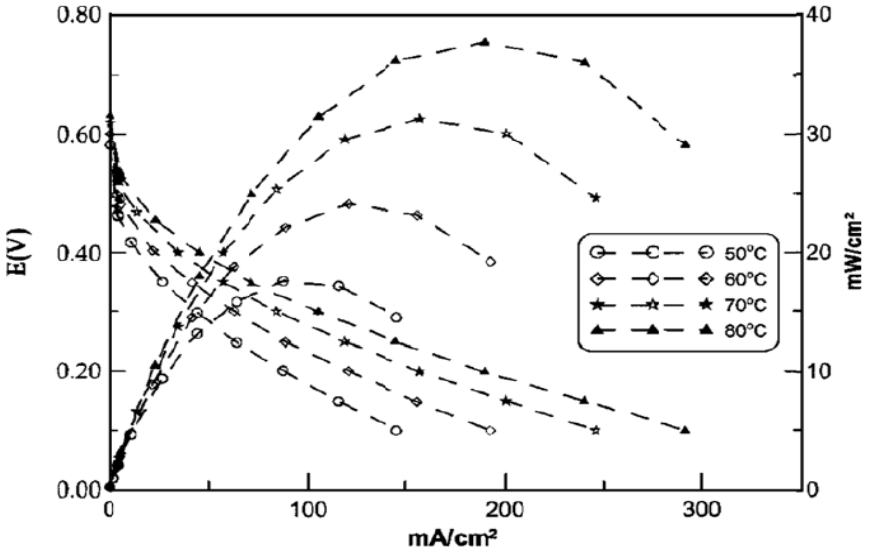

Figure 8: Result of Various Temperature at 1M Methanol Concentrations (Jung et al, 2005)

2.4 NAFION BASED PROTON EXCHANGE MEMBRANE (PEM)

Proton exchange membrane determines operational range of fuel cell such as feasible temperatures, pressures and so on. Important properties of PEM to perform effectively are posses' high proton conductivity, impermeable to gas, achieved balance water transport posses high thermo mechanical and chemical stability to fuel conditions and electrical insulator.

The widely known membrane material is Nafion, invented by Dupont which uses perfluoro-sulfonylfluoride ethyl-propyl-vinyl ether (PSEPVE) (Wilkinson, 2009). Typically, the equivalent weight of Nafion is 1100. Protonic conductivity depends on membrane structure and water content. Water uptake can be expressed as number of water molecules per sulfonic acid groups present in polymer Protonic conductivity at $\lambda = 14$ is about 0.06 Scm^{-1}. Protonic conductivity dramatically increases with temperature and at reaches 0.18 S cm^{-1} at 80 ^{o}C. Liu et al (2006) has developed the ionic conductivity related to water content and temperature which is:

$$\kappa = (0.005139\lambda - 0.00326) \exp\left[1268\left(\frac{1}{303} - \frac{1}{T}\right)\right] \quad (4)$$

In general, diffusivity of methanol in Nafion®, as well as methanol in water exhibits exponential temperature dependence, DMeOH/PEM = 4.9×10^{-10} m^2 s^{-1} at 333K and DMeOH/H_2O = 2.8×10^{-9} m^2 s^{-1} at 363K as reference values. And $\Delta E/R$ = 2436K for Nafion® 117.

CHAPTER 3

METHODOLOGY

3.1 MODEL BUILDING SEQUENCE FOR COMSOL MULTIPHYSICS

Figure 7 is the model-building sequence to develop dmfc model by using comsol. The geometry of model must be determined together with assumption. Unknown parameter and boundary conditions that suitable according to governing equations are later being fit in the model. The model is asses and solve by comsol multiphysics. The result will then analyze. In this project, the parameter describing electrochemical reactions are based on agglomerate model. Materials properties are base on--.

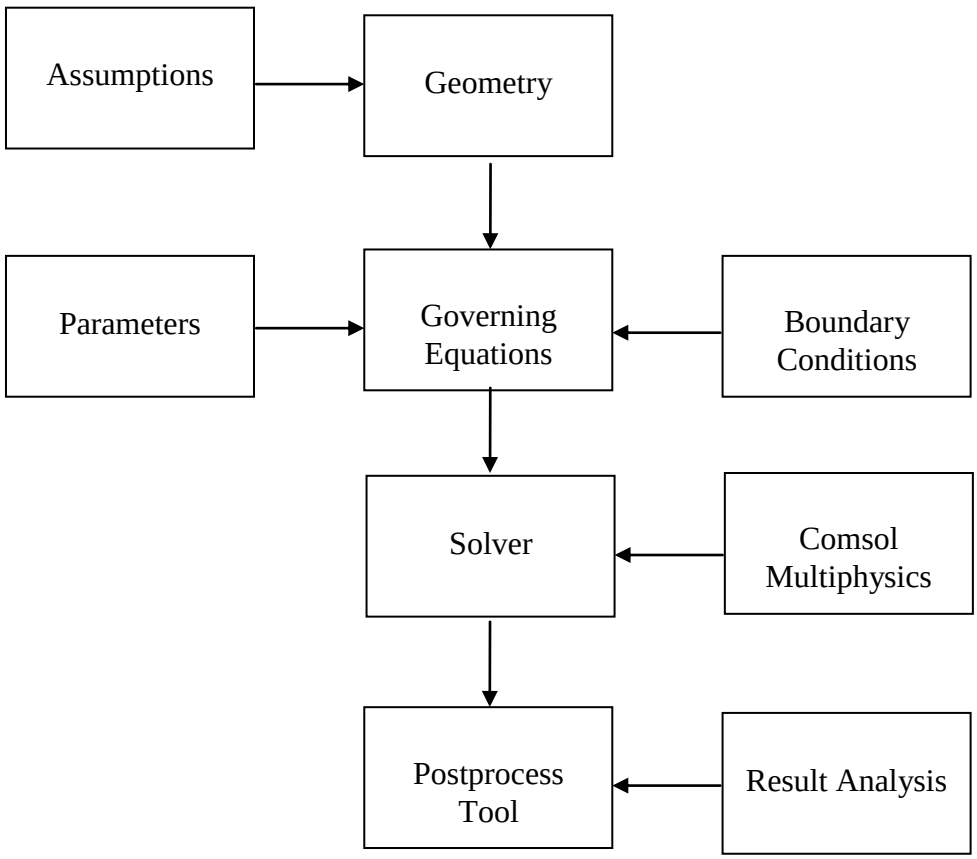

Figure 9: Model-building Sequence.

3.2 THEORY AND GOVERNING EQUATIONS

3.4.1 Charge Balances

The potential distributions in three subdomain utilizes the following equations which describe by Conductive Media DC application mode.

$$\begin{aligned} \nabla.\left(\kappa_{s,eff}\nabla\phi_s\right) &= 0 && \text{in } \Omega a \\ \nabla.\left(\kappa_{m,eff}\nabla\phi_m\right) &= 0 && \text{in } \Omega m \\ \nabla.\left(\kappa_{s,eff}\nabla\phi_s\right) &= 0 && \text{in } \Omega c \end{aligned} \qquad (5)$$

solid-phase effective electronic conductivity (S/m) is denoted by $\kappa_{s,eff}$ and membrane ionic conductivity (S/m) is denoted by $\kappa_{m,eff}$. Besides, ϕ_s is the potential (V) in the electrode phases and ϕ_m is the potential in the membrane. The charge-transfer current density expression can be generally described by using the Butler-Volmer electrochemical kinetic expression as a boundary condition.

Inward normal ionic current densities at anode and cathode boundaries, , are specified according to electolyte potential equation.

$$i_e = L_{act}\,(1-\varepsilon_{mac})\,j_{agg} \qquad (6)$$

Here, *e* stands for "a" (anode) or "c" (cathode), L_{act} is the thickness of active layers (m), ε_{mac} is the porosity (the macroscopic porosity), and $j_{agg,a}$ and $j_{agg,c}$ are the current densities based on the agglomerate model. The potential at the anode current collector is at reference level which is zero. Total cell voltage will serves as the boundary condition at the cathode current collector according to following equations :

$$\begin{aligned} \phi_s &= 0 && \text{at } \partial\Omega a,cc \\ \phi_s &= V_{cell} && \text{at } \partial\Omega c,cc \end{aligned} \qquad (7)$$

The rest of the boundaries is set as electric insulation boundary condition.

3.4.2 Agglomorate Model for Anode and Cathode

In agglomerate model, current density in active layer is describes as consisting agglomerates of ionic conductor material and electrically conducting particles covered partially with catalyst. The combination of diffusion equation and Butler-Volmer electrode kinetic equation cab be used to express current density analytically constant electric and ionic potentials.

$$j_{agg,e} = -6\eta_e F \left(\frac{D_{agg}}{R_{agg}^2}\right)(1 - \lambda_e \coth \lambda_e)\beta_e \tag{8}$$

Here, D_{agg} is the agglomerate gas diffusivity (m^2/s), R_{agg}^2 is the agglomerate radius (m), η_e is a "charge transfer" number (1 for the anode and –2 for the cathode), and F is Faraday's constant (C/mol). The overvoltages at the anode and the cathode are given bybelow equation where E_{eq} (V) denotes the equilibrium voltage :

$$\eta_a = \phi_s - \phi_m - E_{eq,a}$$

$$\eta_c = \phi_s - \phi_m - E_{eq,c} \tag{9}$$

The dissolved hydrogen and oxygen concentrations at the surface of the agglomerates are related to the molar fractions of the respective species in the gas phase through Henry's law where K is Henry's constant ($Pa.m^3/mol$).

$$C_{agg,\ MeOH} = \frac{p_M x_M}{K_{MeOH}} \tag{10}$$

$$C_{agg,\ O_2} = \frac{p_O x_O}{K_O} \tag{11}$$

3.4.2 Porous Media Fluid Flow

Darcy's Law is utilizes to model gas flow in gas backings. Continuity equation define as velocity by following equations:

$$\nabla.(\rho\,\mathbf{u}) = 0 \qquad \text{in } \Omega a \text{ and } \Omega c \qquad (12)$$

where ρ is the mixture density of the gas phase (kg/m^3) and **u** denotes the gas velocity (m/s). Based on Darcy's law, the velocity is depends on gradient of pressure, the viscosity of the fluid, and the structure of the porous media according to following equations:

$$\mathbf{u} = \frac{k_p}{\eta}\nabla p \qquad (13)$$

At the inlets and outlets you specify the pressure:

$$p = p_{a,in} \qquad \text{at } \partial\Omega a,\text{inlet} \qquad (14)$$

$$p = p_{ref} \qquad \text{at } \partial\Omega a,\text{outlet}$$

$$p = p_{c,in} \qquad \text{at } \partial\Omega c,\text{inlet} \qquad (15)$$

$$p = p_{ref} \qquad \text{at } \partial\Omega c,\text{outlet}$$

3.4.3 Maxwell-Stefan Mass Transport

The model takes into account each species in anode which are MeOH, H_2O and CO_2 and at cathode which are O_2, H_2O and N_2. Maxwell-Stefan multicomponent diffusion is governed by the equations :

$$\frac{\delta}{\delta t}\rho w_i + \nabla\left[-\rho w_i \sum_{j=1}^{N} D_{ij}\left\{\frac{M}{M_j}(\nabla w_j + w_j\frac{\nabla M}{M} + (x_j - w_j)\frac{\nabla P}{P}\right\} + w_j\rho u + D_l^T\frac{\nabla T}{T}\right] = Ri \qquad (16)$$

Where D_{ij} is diffusion coefficient (m^2 s^{-1}), D^T, multi component thermal diffusion coefficient (Pa.s), R_1 is reaction rate (kg/m^3.s), x is mole fraction, w is mass fraction,

while M is molecular mass (kg/mol). Reaction rate, R, corresponding to each species on the anode and cathode side given by the equation :

$$R_{MeOH} = -\frac{j_a}{2F} M_{MeOH} \quad (17)$$

$$R_{O_2} = -\frac{|j_c|}{4F} M_{O_2} \quad (18)$$

$$R_{H_2O} = -\frac{|j_c|}{2F} M_{H_2O} \quad (19)$$

3.3 2-DIMENSIONAL MODELING

3.3.1 Assumptions

Assumption has to be set to simplify the mode and increase accuracy. To understand model's limitation as well as interpret the result accurately, the assumptions have to be understood. The main assumptions used in the modeling are as follows

1. Laminar Flow
2. Ideal gas mixture
3. Constant operating temperature (isotermal) and pressure
4. Vapor form of water (Single Phase)
5. O2, H2O and N2on the cathode
6. MeOH and H2O on the anode
7. The formation of CO2 bubbles are neglected

3.3.2 Module and Dependant Variables

Table 1: Mode on Comsol Multiphysics and Dependat Variables

Variables	Value
Conductive Media DC (electrodes)	Solid Phase Potential
Conductive Media DC (membrane)	Electrolyte Potential
Darcy's Law	Pressure
Maxwel-Stefan Difussion and	Mass fraction of MeOH, O2 and CO2

Convection (anode)	
Maxwel-Stefan Difussion and Convection (cathode)	Mass fraction of O2, N2 and H2O

3.3.3 Operating Temperature and Concentration

Table 2: Operating Parameter of DMFC

Variables	Value
Temperature (K)	325, 345, 355,
Methanol Concentration at Inlet (M)	2, 3, 4, 5

3.3.4 Geometry

Table shows the length and thickness of each domain for two-dimensional model geometry in Comsol Multiphysic.

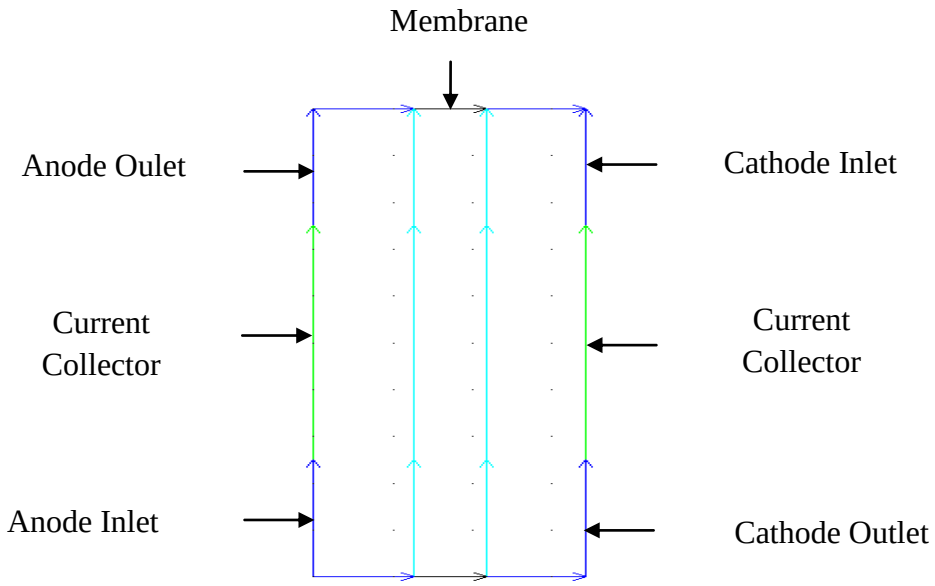

Figure 10: x-y Geometry in Comsol Multiphysics 5.3a

Table 3: Goemetry Parameters

Name	Value (m)
Length of Cell	2e-3

Thickness of Anode and Cathode Layer	2.5e-4
Thickness of PEM (Nafion 117)	1.75e-4
Length of current collector	1e-3

3.3.5 Input Parameter

Table 4: Input Parameter

Input Parameter	Value	Name	Reference
Faraday constant	96485[C/mol]	F	
Gas constant	8.31[J/mol/K]	R	
Temperature of cell	345 [K]	T	
Cell voltage	0.7 [V]	V_cell	
Water drag coefficient	3	drag	
Fluid viscosity	2.1e-5 [Pa*s]	eta	
Reference pressure	1.1013e5 [Pa]	p_ref	
Inlet pressure anode	1.1*p_ref	p_a_in	
Inlet pressure cathode	1.1*p_ref	p_c_in	
Equilibrium potential anode	0 [V]	E_eq_a	
Equilibrium potential cathode	1 [V]	E_eq_c	
Exchange current density anode	1e5 [A/m^2]	i0_a	
Exchange current density cathode	1 [A/m^2]	i0_c	
Conductivity of anode and cathode	1000[S/m]	kapaa_s	
Conductivity of membrane (Nafion 117)	6.7e-2 [S/m] [19]	kappa_m	Deluca, 2008
Permeability of anode and cathode	1e-13 [m^2]	kappa_p	
Permeability of membrane (Nafion 117)	1.15e-10 [m^2] [20]	kappa_pm	Zaidi & Matsuura, 2009
Specific surface area	1e7[1/m]	S	
Aggregate radius	0.1[um]	R_agg	

Active layer length	10 [um]	l_act	
Microscopic porosity inside agglomerate	0.2	eps_mic	
Macroscopic porosity between agglomerates	0.4	eps_mac	
Gas diffusivity in agglomerate	1.2e-10 [m^2/s]*((1-eps_mac) *(eps_mic))^1.5	D_agg	
Effective binary diffusivity, MeOH2_H2O	2.8e-5 [m^2/s]	D_effMeOH_H2O	Deluca, 2008
Effective binary diffusivity, O2_H2O	0.282e-4[m^2/s]/(T/308.1[K])^1.5 *(eps_mac)^1.5	D_effO2_H2O	
Effective binary diffusivity, O2_N2	0.22e-4[m^2/s]*(T/293.2[K])^1.5 *(eps_mac)^1.5	D_effO2_N2	
Effective binary diffusivity, H2O_N2	0.256e-4*(T/307.5[K])^1.5 *(eps_mac)^1.5	D_effH2O_N2	
Inlet weight fraction, MeOH	0.138	wMeOH_in	
Inlet weight fraction, O2	0.21*0.8	wO2_in	
Cathode inlet weight fraction, H2O	0.2	wH2Oc_in	
Molar mass, MeOH	32 [g/mol]	M MeOH	
Molar mass, O2	32 [g/mol]	MO2	
Molar mass, H2O	18 [g/mol]	MH2O	
Molar mass, N2	28 [g/mol]	MN2	
Inlet mole fraction , MeOH	(w MeOH _in/M MeOH)/(w MeOH _in/M MeOH +(1-w	xMeOH_in	

	MeOH _in)/MH2O)		
Inlet mole fraction, O2	(wO2_in/MO2)/(wO2_in/MO2+wH2Oc_in/MH2O+(1-wO2_in-wH2Oc_in)/MN2)	xO2_in	
Henry's law constant, MeOH in agglomerate	4.6e5 [Pa*m^3/mol] [21]	KMeOH	Chemical Summary for Methanol, 1994
Henry's law constant, O2 in agglomerate	3.2e4 [Pa*m^3/mol]	KO2	
Reference concentration, MeOH	xMeOH_in*p_ref/KH2	cMeOH_ref	
Reference concentration, O2	xO2_in*p_ref/KO2	cO2_ref	

3.3.6 Boundary Conditions

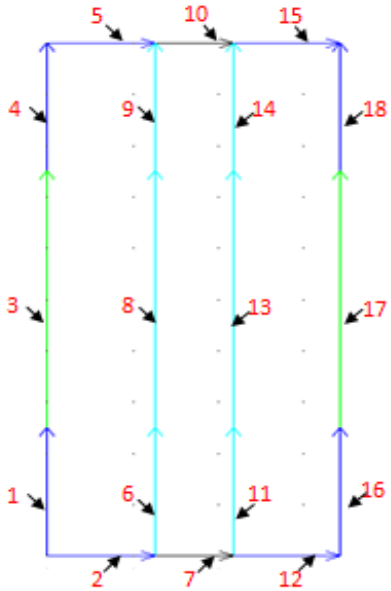

Figure 11: x-y Geometry in Comsol Multiphysics

Table 5: Boundary Conditions of Model

No.	Mode	Boundary No.	Boundary Condition
1	Conductive Media	1,2,4,5,7,10,12,15,16,18,	Electric Insulation
		3,17	Electric Potential
		6,8,9,11,13,14	Inward current flow
2	Darcy's Law	1,4,16,18,	Pressure condition
		2,3,5,7,10,12,15,17,	Insulation/Symmetry
		6,8,9,11,13,14	Inflow/Outflow
3	Maxwel- Stefan	1,18	Mass Fraction
		4,16	Convective flux
		6,8,9,11,13,14	Flux
		2,3,5,12,15,17	Insulation/Symmetry

3.4 PROJECT ACTIVITIES

Table 6: Project Activities

Project Phase	Key Task
Project Propose	Topic Discussion
	Topic Approval
Project Development	Project Introduction
	Comsol Multiphysics 5.3a Familiarization
	Define Model Geometry
	Specify Assumptions, Theory, Equations, Boundary Conditions and Input Parameter.
	Develop DMFC model based on Agglomerate Model
	Finalization of Model
	Solve Model by Comsol Multiphysics 5.3a
Project Evaluation	Solve Model with Different Operating Parameter
	Analyze Model by Postprocessing Tools

Project Closure	Presentation
	Project closure

3.5 KEY MILESTONE

Table 7: Key Milestone

No.	Milestone	Description	Due Date
1	Project Approval and Introduction	Discuss the feasibility and importance of the topic. Acceptance of topic proposed from supervisor.	Week 3
2	Comsol Multiphysics Familiarization	Learn Comsol Multiphysic with tutorials	Week 6
3	Design Geometry	Design model geometry that applicable based on literature review.	Week 6
4	Specify Model	Specify Assumptions, Theory, Equations, Boundary Conditions and Input Parameter.	Week 12
5	Develop DMFC Model in Comsol Multiphysics.	Develop DMFC model based on agglomerate model in Comsol Multiphysics 5.3a	Week 13
6	Model Finalization	Finalize desired model according data validity.	Week 14
7	Analyze model	Analyze model with postprocessing tools with different operating parameter	Week 17
8	Project closed out	Business presentation to company for further action and project closure.	Week 17

3.6 GANT CHART

Table 8: Gant Chart

Project Activities	Duration/Week													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Project Introduction														
Comsol Familiarization														
Design Geometry														
Specify Model														
Submit Progress Report														
Develop DMFC Model in Comsol Multiphysics.														
Model Finalization														
Analyze Model by Postprocessing Tools														
Poster Presentation														
Submit Dissertation														
Final Presentation														

CHAPTER 4

RESULTS AND DISCUSSION

4.1 SIMULATION

4.1.1 Current Density at Anode Active Layer

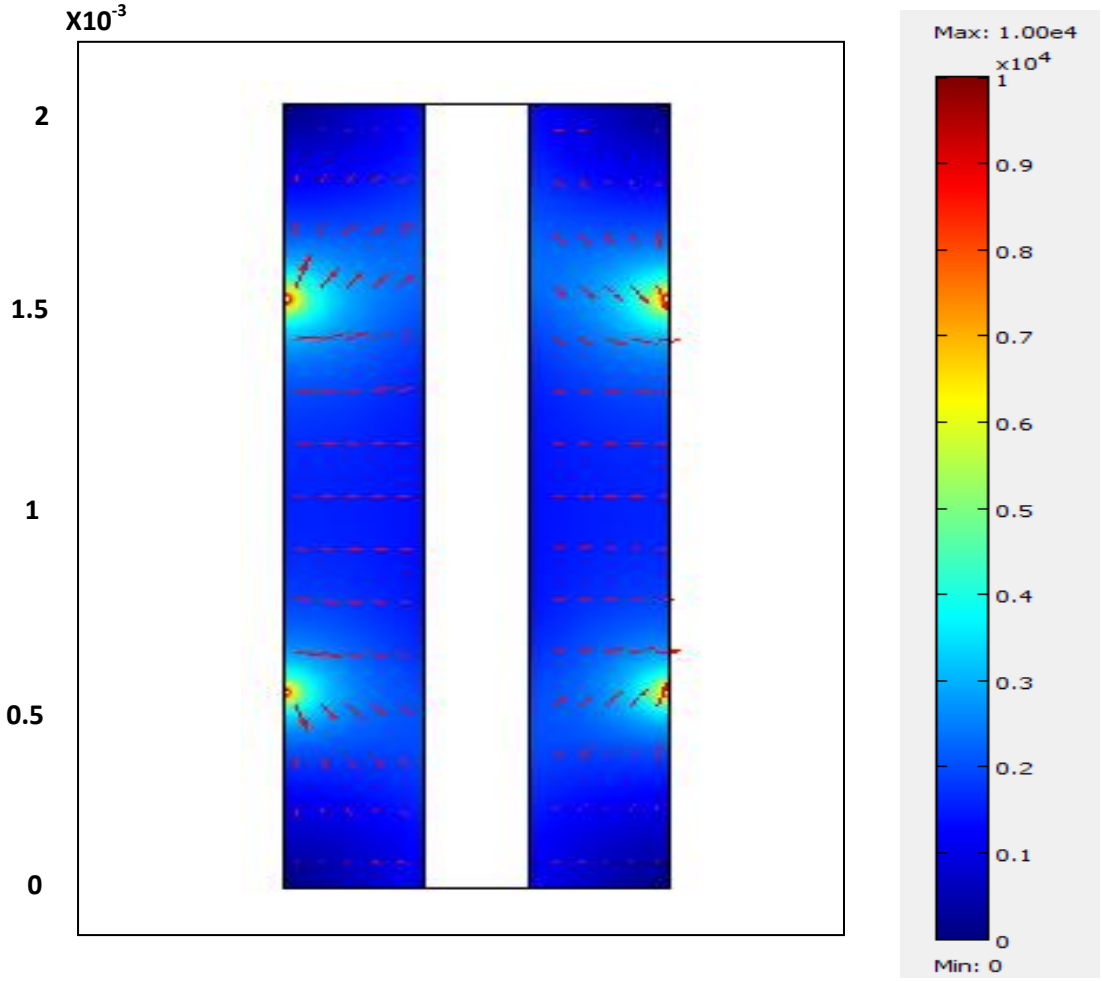

Figure 12: Current density (surface plot) and current vector field (arrow plot) at 0.7 V

Figure 12 shows the current density distribution in the PEM fuel cell. At the corners of current collectors, there are significant current spikes exist. The cell's behavior is further analyzed by plotting current density at active layer as a function of cell's height.

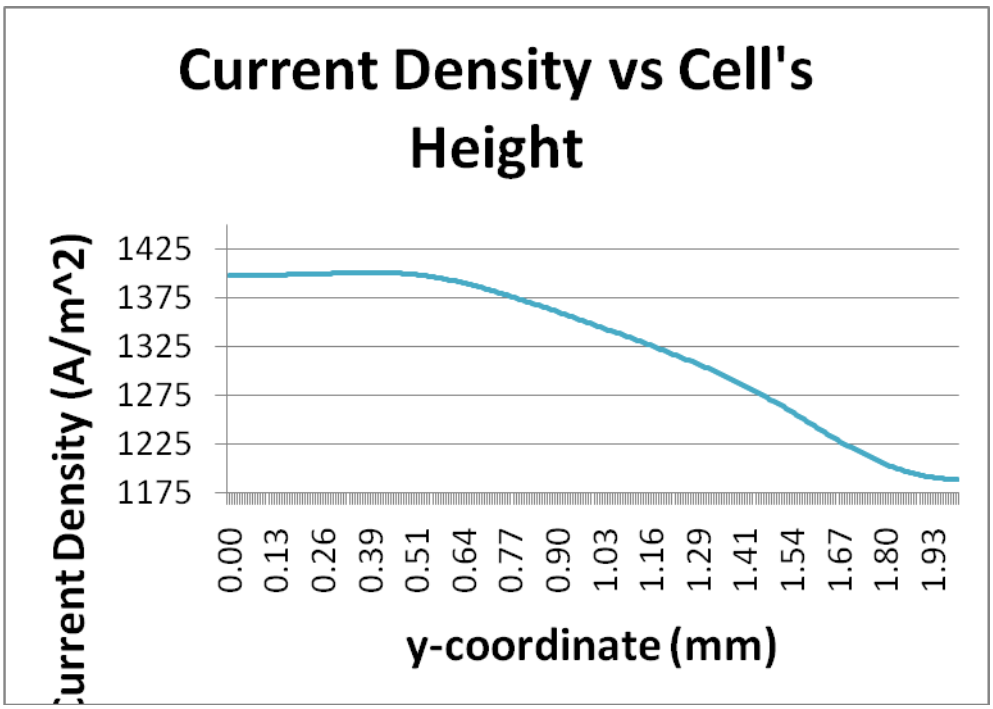

Figure 13: Current-density distribution at the active layer at the anode.

Based on figure 13 most of the current is generated in front of the fuel channel. This phenomenon leads to formation of intensive "torches" of electronic current density near the edges of the current collectors. Physically, the electrons produced starting from front of the fuel channel flow to the nearest point of the current collector. Local overheat may exist by the great current density at the edge. The graph is decreasing because methanol is being consume troughout the cells height.There is no study been done between the anode length with current density. Hence, to make sure the result is acceptable, previous studies on voltage and currents density graph with temperature effect is use. The same case is apply on concetration effect.

4.1.2 Velocity Field

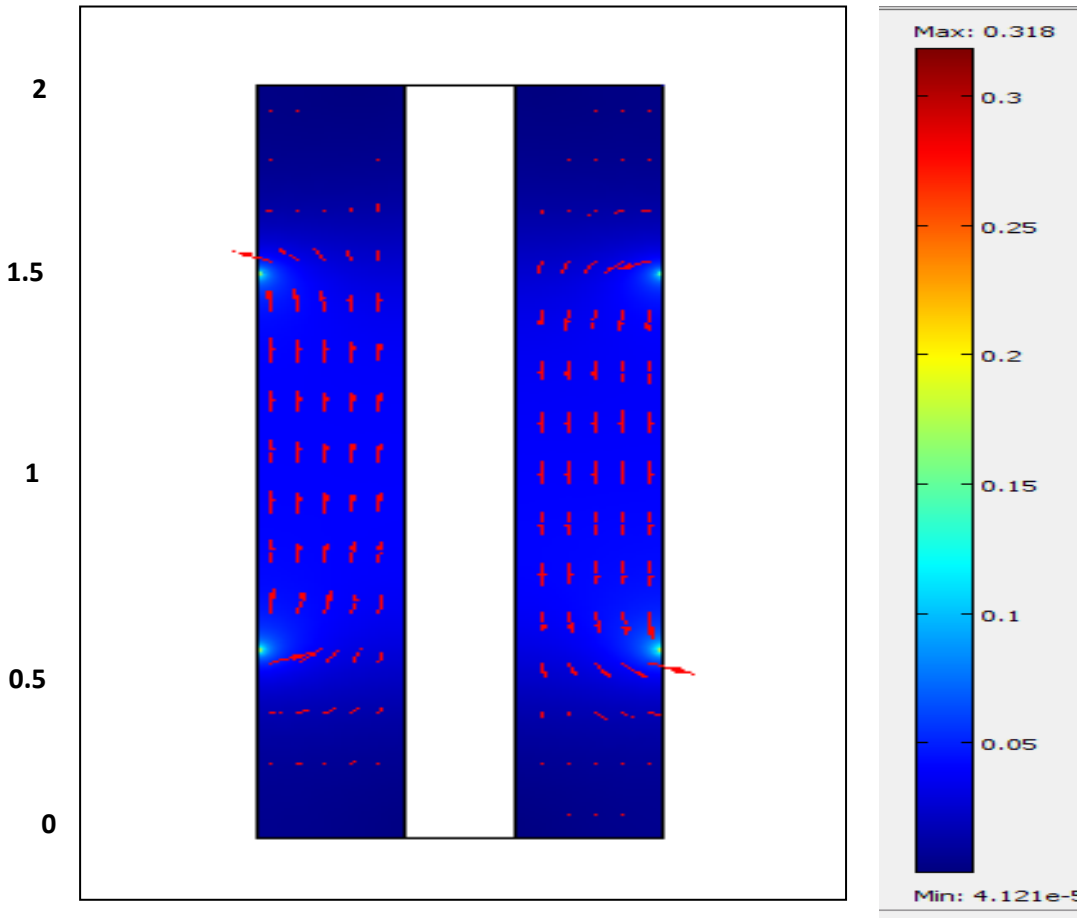

Figure 14: Gas velocity field in the anode and cathode compartments.

Figure 14 shows flow direction of the model. It proved that the reactants move in countercurrent as per set. The highest values of flow-velocity magnitude attained at the current collector corners.

4.2 EFFECT OF DIFFERENT TEMPERATURE

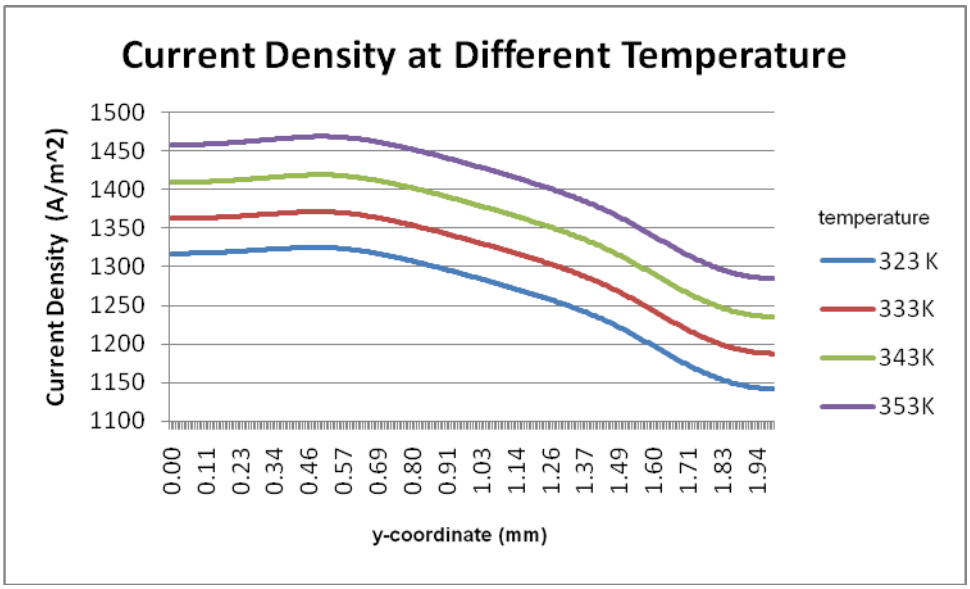

Figure 15: Current-density distribution at different temperature with 3M methanol.

Table 9: Maximum Current Density at Different Temperature

No.	Temperature, K	Max Current Density, A/m^2
1	323	1325.213
2	333	1371.316
3	343	1419.151
4	353	1468.779

Based on the graph in figure 15 above, the current density increases with temperature, as expected from 323K until 353K. The operating temperature of DMFC in this model ranging from 323K to 353K based on literature review. Current density at 353K give the highest current density at anode active layer. The results of maximum current density as well as plot behaviour were compared between previous studies and this project. This result is similar by experimental study of DMFC by Wang et. al. This is because the increase of operating temperature will increase the reactions of methanol.

4.2 EFFECT OF DIFFERENT METHANOL CONCENTRATION

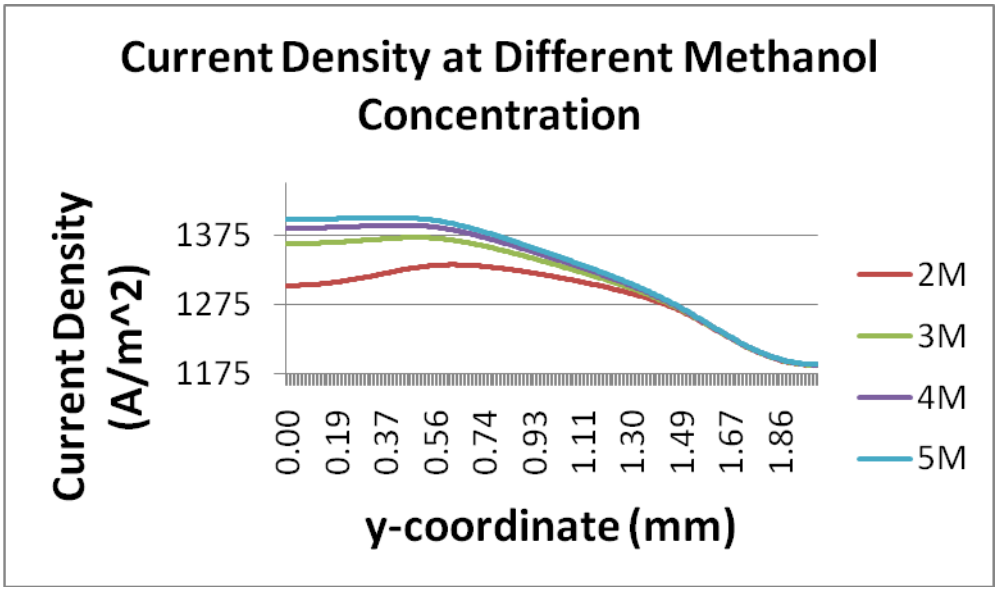

Figure 16: Current-density distribution at different methanol concentration at 343K.

Table 10: Maximum Current Density at Different Methanol Concentration

No.	Concentration, M	Max Current Density, A/m^2
1	2	1332.091
2	3	1371.316
3	4	1389.158
4	5	1400.149

Based on the graph above, the current density increases with concentration, as expected from 2M until 5M. The inlet methanol concentration of DMFC in this model ranging from 2M to 3M based on literature review. Current density at 5M give the highest current density at anode active layer. The effect of methanol concentration to the performance dmfc has been studied by Jung et al who found that higher methanol concentration would improve voltage and power density at higher currrent density. The studies ranging from 0.5 M to 3M and found that at 3M methanol achieved the highest current densities.

CHAPTER 5

CONCLUSION

Two-dimensional, isothermal models of Direct Methanol Fuel Cells were developed in x-y plane geometry and will be solved by commercial software package, Comsol Multiphysics based on agglomerate model. Based on literature review, performance of DMFC is different depending on its operating parameters. The model can help to investigate the performance of DMFC with varies of temperature and methanol concentration.

The models was used to study the current distribution in DMFC components. The x-y model is suitable for fuel cell with interdigitated flow pattern and provide more predictions inside the fuel cell. The current density distribution in DMFC and flow velocity were presented. This model, does not include flow channel but consist of current collector. The result shows that at the corners of current collectors, there are significant current spikes exist. At different temperature and concentration, the current density is increases with increasing operating parameters. This finding is as expected and supported by literature survey that has been done.

To have accurate data permeability of the membrane should be consider as permeable to reactant because there is methanol crossover in DMFC. This phenomenon could effect the performance of DMFC. Others operating conditions also can be consider such membrane thickness and direction of reactant to further study the effect on current density.

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