CHAPTER 2 THEORIES

In this project, a dynamic model of direct methanol fuel cell (DMFC) is revealed and the effect of variables on dynamic response is explained. Therefore, this chapter presents basic theories of fuel cell and direct methanol fuel cell. Furthermore, fuel cell characteristics which are the key performance measure of a fuel cell are described. The last topic is fuel cell modeling which describes equations used to develop dynamic model. Because of this project is about DMFC which based on proton exchange membrane fuel cell (PEMFC), and then the theories explain based on PEMFC.

2.1 Fuel Cell [7, 8, 9]

Fuel cell is an electrochemical energy converter which regularly uses hydrogen as a fuel and oxygen (or air) as the oxidant in the electrochemical reaction. The fuel cell converts chemical energy of fuel and oxidant directly into electrical energy.

The fuel cell can be distinguished by different characteristics which are reactant type, electrolyte type and operating temperature. The summery of five major types of fuel cells, which differentiated form one another by their electrolyte is showed in Table 2.1.

Table 2.1 Types of fuel cell [10]

Fuel cell type	Mobile ion	Operating temperature	Application and notes
Alkaline (AFC)	OH^-	50-200°C	Used in space vehicles, e.g. Apollo, Shuttle.
Proton exchange membrane (PEMFC)	H^+	30-100°C	Vehicles and mobile applications and for lower power CHP systems
Direct methanol (DMFC)	H^+	20-90°C	Suitable for portable electronic systems of low power, running for long times
Phosphoric acid (PAFC)	CO_3^{2-}	≈220°C	Large numbers of 200-kW CHP systems in use
Molten carbonate (MCFC)	CO_3^{2-}	≈650°C	Suitable for medium- to large-scale CHP systems, up to MW capacity
Solid oxide (SOFC)	O^{2-}	500-1000°C	Suitable for all sizes of CHP systems, 2 kW to multi-MW

Since DMFC is based on proton PEMFC, then PEMFC is described. Proton exchange membrane fuel cells use a thin ($\leq 50\mu m$) proton conductive polymer membrane as the electrolyte. Typically catalyst is platinum supported on carbon and operating temperature is between 60 and 80°C. PEMFCs are a serious candidate for automotive applications, but also far small-scale distributed stationary power generation, and for portable power application as well.

2.2 Components of Fuel Cell [7, 8, 9]

The components of PEMFC consisting of a membrane, electrodes, a gas diffusion layer, and a bipolar plate are showed in Figure 2.1.

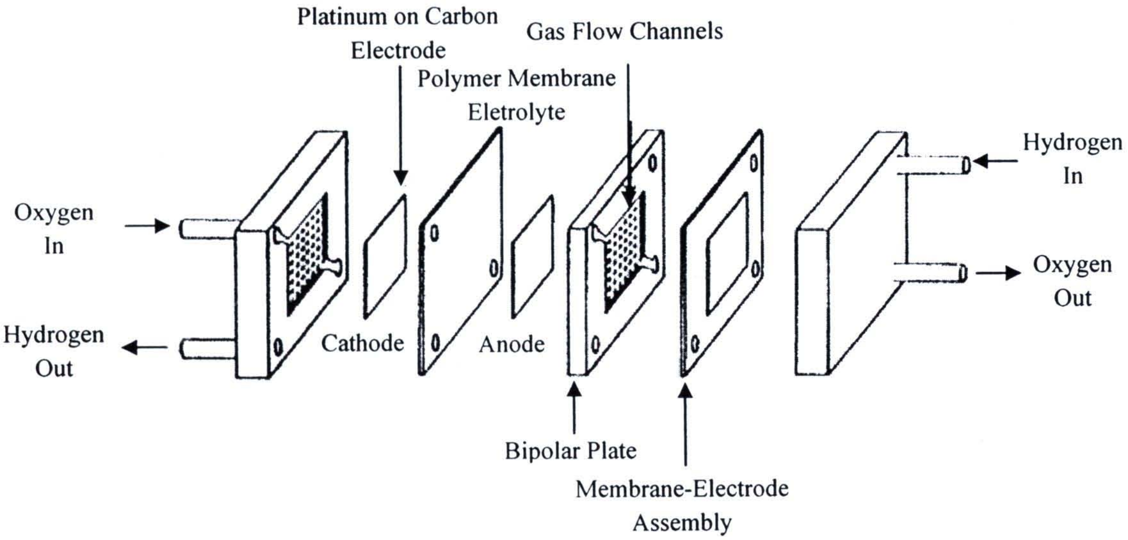
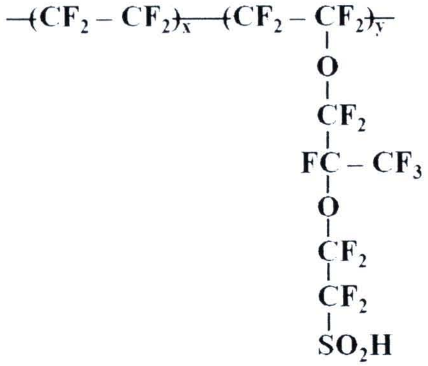


Figure 2.1 Assembly of typical PEM fuel cell stack [11]

2.2.1 Membrane

A fuel cell membrane must exhibit relatively high proton conductivity, must present an adequate barrier to mixing of fuel and reactant gases, and must be chemically and mechanically stable in the fuel cell environment. (A fuel cell membrane is relatively high proton conductivity material)

The membranes for PEMFC are produced form perfluorocarbon-sulfonic acid ionomer (PSA) which is a copolymer of tetrafluorethylene (TFE) and various perfluorosulfo-nate monomers. Nafion^{TM} made by Dupont which uses perfluoro-sulfonylfluoride ethyl-propyl-vinyl ether (PSEPVE) is the best-known membrane material. Figure 2.2 shows the chemical structure of perfluofosulfonat ionomer such as Nafion^{TM}.



$$-(CF_2-CF_2)_x-(CF_2-CF(-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_2H))_y-$$

Figure 2.2 Structure of PFSA polymer (Nafion^{TM})

Nafion^{TM} membranes are produced in different sizes and thicknesses. A letter N, followed by a 3- or 4-digit number is marked with a letter is a mark of Nafion^{TM}. The first 2 digits represent equivalent weight divided by 100, and the last digit or two is the membrane thickness in mills (1 mill = 1/1000 inch = 0.0254 mm).

2.2.2 Electrode

A fuel cell electrode is a thin catalyst pressed between membrane and porous. It is an electrically conductive substrate and it is a layer where the electrochemical reactions take place. Since fluids, electrons and protons are species that take part in the reactions, and then the reactions take place on the catalyst surface where all three species have access.

2.2.3 Gas Diffusion Layer

A gas diffusion layer is a layer between the catalyst and bipolar plates. It has several important functions, even though it does not directly participate in the reactions. The gas diffusion layer provides a pathway for reactant, product, and electrons. Moreover, it also serves to conduct heat generated in the electrochemical reactions.

2.2.4 Bipolar Plate

Bipolar plates are electronically conducting and function as cell walls and intercell connectors. The bipolar plates alternate with electrolyte compartments and both must be carefully sealed along the periphery to prevent electrolyte overflow and provide reliable separation of the electrolyte in neighboring compartments.

2.3 Direct Methanol Fuel Cell (DMFC) [8, 10]

DMFC uses methanol which is a highly promising type of fuel. The methanol is fed in a form of liquid then the fuel cell is called ‘Direct methanol’. Methanol is relatively cheap, easily stored and handled. The most problem of DMFC is that the reactions of methanol proceed so much slower than that of hydrogen. The second major problem is the crossover of methanol which affects the performance of the fuel cell.

The electrochemical reactions taking place at the electrodes of DMFC, the overall current-producing reactions and the corresponding thermodynamic values of equilibrium electrode potentials, E^0 and the reversible cell voltage, E_{eq}^0 of the fuel cell are as follows:

$$\text{Anode:} \qquad CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \qquad E_A^0 = 0.02\ \text{V} \tag{2.1}$$

$$\text{Cathode:} \qquad \frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \qquad E_C^0 = 1.23\ \text{V} \tag{2.2}$$

$$\text{Overall:} \qquad CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O \qquad E_{eq}^0 = 1.21\ \text{V} \tag{2.3}$$

Equation 2.3 represents the reversible cell voltage which equals to 1.21 V while the open circuit voltage (OCV) of DMFC is mostly equal to 0.7 V. Therefore, the practical voltages obtained are considerably less than the reversible cell voltage, and the losses are greater than for other types of fuel cell.

2.4 Fuel Cell Reaction Kinetics [12]

The electrochemical reactions only occur at the surface of catalyst layer; hence the current is directly proportional to the area of the surface. Therefore, current density is more fundamental than current.

$$j = \frac{i}{A} \tag{2.4}$$

Electrochemical reaction rates can also be expressed on a per unit-area basis.

$$r = \frac{1}{A}\frac{dN}{dt} = \frac{i}{nFA} = \frac{j}{nF} \tag{2.5}$$

Where j is current density
i is current
A is area
n is number of electrons transferred in the electrochemical reaction
dN/dt is rate of the electrochemical reaction
F is Faraday's constant

2.4.1 Net Rate of Reaction

The net rate is given by the difference in rates between the forward and reverse reactions. Equations 2.6 and 2.7 show the chemisorbed hydrogen reaction. The reaction can be split into forward and reverse reactions.

Forward reaction: $$\mathrm{M \cdots H \rightarrow \left(M + e^{-}\right) + H^{+}} \tag{2.6}$$

Reverse reaction: $$\mathrm{\left(M + e^{-}\right) + H^{+} \rightarrow M \cdots H} \tag{2.7}$$

The reaction rates given by r_1 for the forward reaction and r_2 for the reverse reaction. The net reaction rate rr is defined as

$$r = r_1 - r_2 = c_R^* f_1 e^{-\Delta G_{act,1}/RT} - c_P^* f_2 e^{-\Delta G_{act,2}/RT} \tag{2.8}$$

Since $\Delta G_{act,2}$ is related to $\Delta G_{act,1}$ and ΔG_{rxn}: $\Delta G_{rxn} = \Delta G_{act,1} - \Delta G_{act,2}$. Therefore, equation 2.8 can then be expressed in terms of only the forward activation barrier $\Delta G_{act,1}$:

$$r = c_R^* f_1 e^{-\Delta G_{act,1}/RT} - c_P^* f_2 e^{-(\Delta G_{act,1} - \Delta G_{rxn})/RT} \tag{2.9}$$

Where c_R^* is reactant surface concentration
c_P^* is product surface concentration
$\Delta G_{act,1}$ is activation barrier for the forward reaction
$\Delta G_{act,2}$ is activation barrier for the reverse reaction

2.4.2 Butler-Volmer Equation

Butler-Volmer equation is used to describe the rate of the electro-oxidation in the catalyst layer. The net current $(j_1 - j_2)$ is then

$$j = j_0\left(e^{\alpha nF\eta/RT} - e^{-(1-\alpha)nF\eta/RT}\right) \tag{2.10}$$

$$j = j_0^0\left(\frac{c_R^*}{c_R^{0*}}e^{\alpha nF\eta/RT} - \frac{c_P^*}{c_P^{0*}}e^{-(1-\alpha)nF\eta/RT}\right) \tag{2.11}$$

Where η is voltage loss
n is number of electrons transferred in the electrochemical reaction
c_R^*, c_P^* are actual surface concentrations of the rate-limiting species in the reaction
j_0^0 is exchange current density at a standard concentration

Moreover, Butler-Volmer equation (Eqautions 2.10 or 2.11) can explain the relation between current and voltage in electrochemical systems. Since η_{act} represents a voltage loss due to activation, then the Butler-Volmer equation tells that if more electricity (current) from the fuel cell is required, fuel cell will lose the voltage.

2.5 Conservation Equations [7, 12]

2.5.1 Mass Transport

The general equation for mass conservation, which is valid for all the processes inside a fuel cell such as fluid flow, diffusion, phase change, and electrochemical reactions, is:

$$\frac{\partial\rho}{\partial t} + \nabla \cdot (\rho \mathrm{v}) = 0 \tag{2.12}$$

Where ρ is density
v is velocity vector
∇ is operator, $\frac{d}{dx} + \frac{d}{dy} + \frac{d}{dz}$

Mass transport is divided into two major parts: on the first is mass transport in fuel cell flow structures and a second one is the mass transport in fuel cell electrodes. The difference between the two domains is one of length scale which leads to a difference in transport mechanism. For fuel cell flow structures, the transport mechanism is convection transport because dimensions are the large scale (or millimeter of centimeter). While for fuel cell electrodes exhibit porosity, thus mass transport in the electrodes is diffusive transport.

1. Transport in electrode: Diffusive transport

The diffusion flux, J_{diff}, can be calculated using the diffusion equation.

$$J_{diff} = -D\frac{dc}{dx} \tag{2.13}$$

According to the Bruggmann correction, the effective diffusivity in a porous structure can be expressed as

$$D^{eff} = \varepsilon^{1.5}D \tag{2.14}$$

Where	J_{diff}	is	diffusion flux of reactants to the catalyst layer
	D	is	binary gas diffusion coefficient
	D^{eff}	is	effective diffusivity in a porous structure
	ε	is	porosity of the porous structure

When the reactant concentration in the catalyst layer drops all the way to zero, limiting case for mass transport appears. The limiting current density (j_L) can be calculated:

$$j_L = nFD^{eff}\frac{c_R^0}{\delta} \tag{2.15}$$

Concentration differences in the catalyst layer affect fuel cell performance in two ways: first, by decreasing the Nernst voltage and, second, by increasing the activation loss. These effects are examined in detail and found that lead to fuel cell's concentration overvoltage(η_{conc}).

2. Transport in flow structures: Convective transport

This convective mass transport occurs when the density of a species i is different at the electrode surface and the flow channel bulk. Mathematically, the mass flux due to this form of convective mass transfer may be estimated by

$$J_{C,i} = h_m(\rho_{i,s} - \bar{\rho}_i) \tag{2.16}$$

$$h_m = Sh\frac{D}{D_h} \tag{2.17}$$

Where	$J_{C,i}$	is	convective mass flux
	$\rho_{i,s}$	is	density of species i at electrode surface
	$\bar{\rho}_i$	is	mean density of species i in the bulk fluid
	h_m	is	mass transfer convection coefficient
	Sh	is	Sherwood number
	D_h	is	hydraulic diameter

2.5.2 Conservation of Momentum

Momentum conservation is described by the following equation:

$$\frac{\partial(\rho \mathrm{v})}{\partial t} + \nabla \cdot (\rho \mathrm{v}\mathrm{v}) = -\nabla p + \nabla \cdot (\mu^{eff} \nabla \mathrm{v}) + S_m \tag{2.18}$$

Where p is fluid pressure
μ^{eff} is mixture average viscosity
S_m is momentum source term

The first two terms on the right side of the momentum conservation equation represent momentum imparted due to pressure and viscosity, respectively. The source term is different for different regions of the fuel cell, as follow,

For gas channels: $$S_m = 0 \tag{2.19}$$

For backing layers and voids of the catalyst layers:

$$S_m = -\frac{\mu}{K} \varepsilon \mathrm{v} \tag{2.20}$$

Where K is permeability of the gas diffusion layer (or the catalyst layer)
ε is porosity of the gas diffusion layer

This source term for the momentum conservation equation represents a pressure drop arising from Darcy's drag force imposed by the pore walls on the fluid.

2.5.3 Conservation of Species

Species conservation equations representing mass conservation for the individual gas phase species are:

$$\frac{\partial(\varepsilon \rho x_i)}{\partial t} + \nabla \cdot (\mathrm{v} \varepsilon \rho x_i) = \nabla \cdot \left(\rho D_i^{eff} \nabla x_i\right) + S_{s,i} \tag{2.21}$$

Where x_i is mass fraction of gas species
$S_{s,\mathrm{I}}$ is source or sink terms for the species

The first two terms in the species conservation equation represent species accumulation and advection terms, and the first term on the right-hand side represents Fickian diffusion of species in porous medium.

The source term in the species conservation equation, $S_{s,i}$, is equal to zero everywhere except in the catalyst layers where the species are consumed or regenerated in the electrochemical reactions. For the water source term, it is assumed that water is generated as liquid and then it evaporates if the neighboring air or oxygen is not saturated.

2.6 Capillary Pressure [13]

The capillary pressure is the pressures difference of two-phase at the interface. In an operating DMFC at the cathode side, the higher saturation generally occurs in the catalyst layer, and it decreases in the vicinity of the channel implying that capillary transport takes place from high- to low-saturation regions in diffusion layer, as depicted in Figure 2.3.

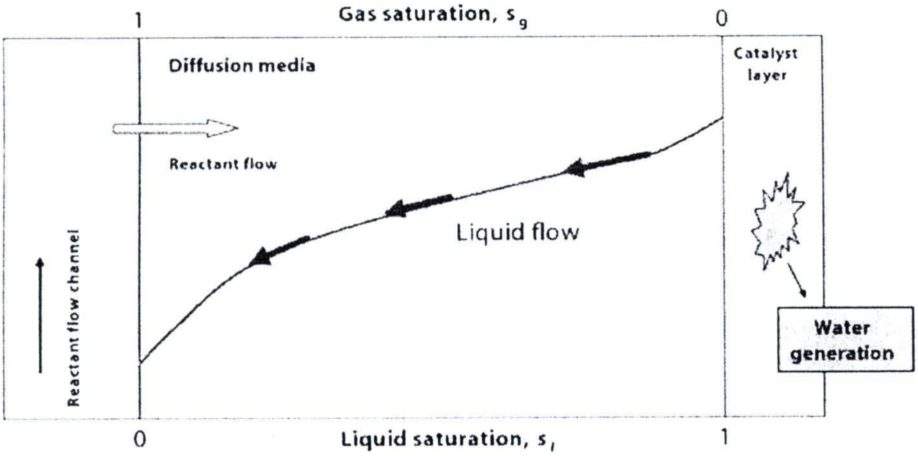


Figure 2.3 Capillary-induced liquid transport in a hydrophobic fuel cell [13]

To predict the liquid-gas transport in diffusion layer, the most important relationship is the relationship between the capillary pressure and the liquid saturation. From soil science, the Leverett function which used to describe the capillary transport behavior of the porous media is investigated.

2.7 Literature Reviews

A two-dimensional, isothermal two-phase mass transport model is developed by W.W. Yang and T.S. Zhao [4]. In this model, a micro-agglomerate model is developed for the cathode catalyst layer. The model also accounts for the effects of both methanol and water crossover through the membrane. The result show that the increase in methanol concentration leads to the significant increase in limiting current density and high mixed overpotential. For the cathode side, the oxygen transportation in agglomerate suffers a high mass transfer resistance because of the rather low diffusivity of oxygen in the liquid water film and Nafion layer.

The work of Ya-Ling He, et al. [5] is concerned about a two-dimensional, two-phase mass transport model. Both gas and liquid velocities in porous medium were calculated to take the phenomenon of liquid-gas counter convection into account. From the phenomenon, gaseous and liquid velocities reduce mass transfer resistance of methanol. Moreover, the physical properties of the anodic porous medium were studied. The results showed that, the increase of porosity and permeability and the decrease of contact angle can improve performance of a DMFC.

Dingding Ye [6] developed two-dimensional two-phase mass transport model to predict methanol and water crossover. In this model, two-phase flow and mass transport distributions including species, pressure and liquid saturation in the membrane electrode assembly are investigated. From the results, diffusion predominates the methanol crossover at low current densities, while electro-osmosis is the dominator at high current densities. In the membrane, water transport depends on electro-osmosis and hydraulic pressure difference across the MEM at low current densities.

A one-dimensional, steady-state, two-phase DMFC model is developed to investigate physiochemical phenomena inside DMFCs. Johan Ko, et al. [3] study the effects of key factors to optimize DMFCs, such as the operating temperature, feed methanol concentration, and anode backing layer properties. From the model, an increase in the operating temperature and methanol concentration result a high mixed-cathode overpotential but increase the limiting current density. Moreover, the methanol crossover through the membrane at high methanol feed concentration can be reduced by increasing thickness and/or decreasing porosity.

Thorsten Schultz, et al. [14] studied the voltage response of a step change in methanol feed concentration. Their one-dimensional multi-component mass transport model of single direct methanol fuel cell (DMFC) was developed based on the Maxwell-Stefan equation and Flory-Huggins activity model. The model was validated with similar experiments. The model based analysis showed that the cell voltage overshoot was resulted from the different time responses of the anode and cathode overpotetials to the change in the methanol concentration.

W.W. Yang and T.S. Zhoa. [15] developed a transient two-dimensional two-phase mass transport model for DMFC and studied the effect of operating conditions such as cell current density, initial current density, methanol concentration and CO surface coverage on cell voltage and anode and cathode overpotential. The results showed that the transient voltage exhibits a significant overshoot in response to a sudden change in current. The methanol permeation through a membrane to a cathode resulted in a strong cathode overpotential overshoot which lead to the voltage overshoot behavior. In contrast, the methanol concentration and CO surface coverage in anode catalyst layer was less effect on anode overpotential. Moreover, the slow mass transport of methanol is one of the key factors that influences the cell dynamic operation.

Purushothama Chippar, et al. [16] presented a transient, one-dimensional, two-phase model for DMFC to investigate the transient thermal behavior of DMFCs and its influences on methanol crossover, cell performance, and efficiency. The simulation results indicate that the insufficient cooling of DMFCs finally lead to thermal runaway, particularly under high methanol-feed concentrations. Therefore, the simulations emphasize the need for an efficient cooling system to stabilize cell operation and enhance cell performance.