

## CHAPTER 2

### THEORY

This chapter will describe the theory of the proton exchange membrane fuel cell (PEMFC), internal combustion engine and the basic of generator. First, the basic of chemistry and thermodynamics of the fuel cell are discussed in order to understand the theory and physical of the system. Then the basic of electric generator, internal combustion engine and hybrid system are presented.

#### 2.1 Fuel Cell Basic Chemistry and Thermodynamics

Fuel cell is one of an electrochemical energy converter that converts chemical energy of fuel directly into direct current (DC) electricity. In typical of fuel cell, gaseous fuels (hydrogen) are fed continuously to the anode side as shown in Figure 2.1. Oxidant (oxygen) is fed to the cathode side. The electrochemical reactions in fuel cells (during reaction) occur simultaneously on both sides of membrane at anode and cathode side. The basic theory fuel cell reactions are shown in Equation (2.1) through (2.3):

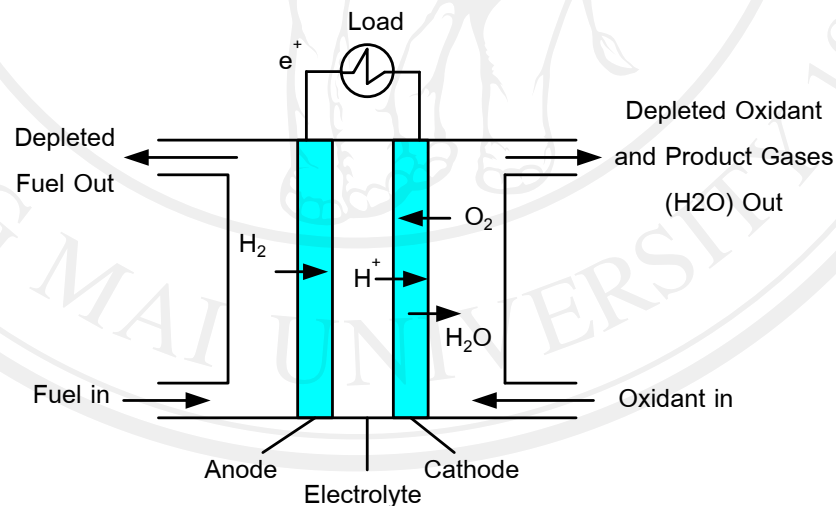
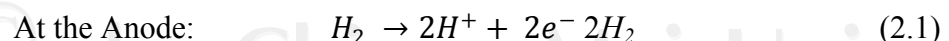
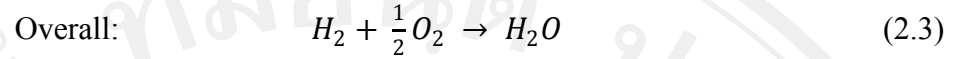
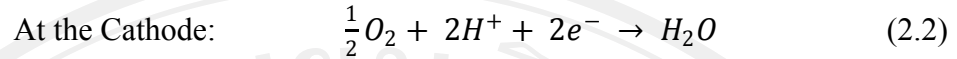


Figure 2.1 Schematic diagram of a PEMFC



The electrical currents are generated when the electrons passed through the external circuit from the anode to the cathode side as shown in Figure 2.1, whereas the protons migrate through the electrolyte to the cathode. The water is formed at the cathode as the by-product which shown in Equation (2.2) by the combination of electrons and protons with oxygen molecule; this is fed continuously to the cathode.



These reactions have several intermediate steps, and there may be some unwanted reactions, but for now these reactions accurately describe the key processes in a fuel cell.

Figure 2.2 shows schematic of a single fuel cell assembly, which consists of a proton conductive polymer electrolyte membrane coupled with two electrodes loaded with platinum catalysts to promote the electron generating hydrogen oxidation and the electron consuming oxygen reduction reaction. The membrane electrode assembly (MEA) is the sandwiched configuration of membrane between the porous electrodes. The gas flow field plates or current collector plates have function on both electrical current collection and reactant gas distribution. The gaskets protect of both reactant gases from the reaction area of PEM fuel cell.

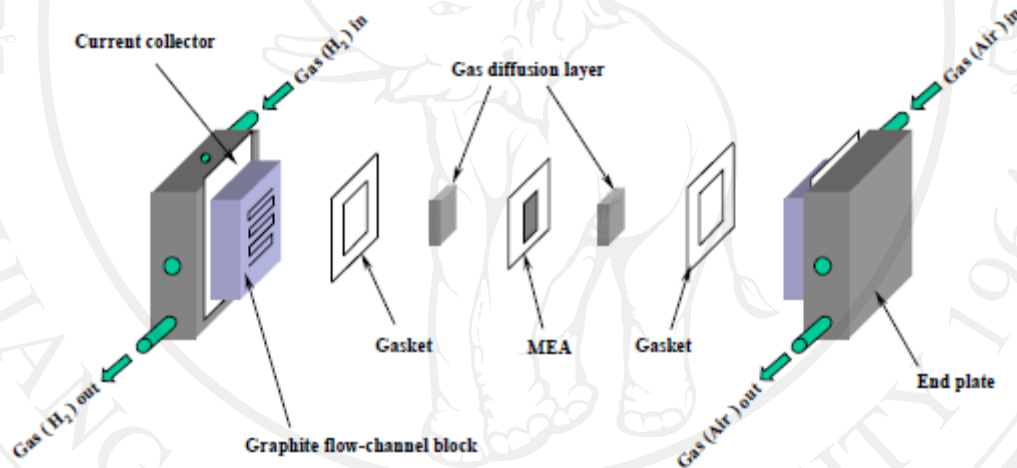


Figure 2.2 Schematic of a single fuel cell assembly

### 2.1.1 Heat of Reaction

The overall reactions are the same as the reaction of hydrogen combustion. Combustion in this process is an exothermic process, which means that there is energy released in the process.



The heat or enthalpy of the chemical reaction in the process is the difference between the heats of formation of products and reaction. For Equation (2.4) this means (Barbir, 2005):

$$\Delta H = (h_f)_{H_2O} - (h_f)_{H_2} - \frac{1}{2}(h_f)_{O_2} \quad (2.5)$$

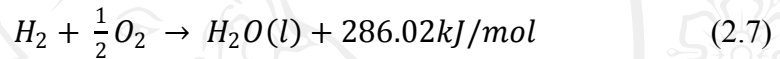
Where  $(h_f)_{H_2O}$  is heat of formation of liquid water at 25°C (-286.02 kJ/mol),

$(h_f)_{H_2}$  is heat of formation of hydrogen molecule at 25°C (0 kJ/mol),  
 $(h_f)_{O_2}$  is heat of formation of oxygen molecule at 25°C (0 kJ/mol),  
 $\Delta H$  is the enthalpy (kJ/mol)

Therefore

$$\begin{aligned}\Delta H &= (h_f)_{H_2O} - (h_f)_{H_2} - \frac{1}{2}(h_f)_{O_2} = -\frac{286.02 \text{ kJ}}{\text{mol}} - 0 - 0 \\ &= -286.02 \text{ kJ/mol}\end{aligned}\quad (2.6)$$

The negative sign for enthalpy in Equation (2.6) of a chemical reaction, by convention, means that heat is being released in the reaction. The reaction of heat being released is an exothermic reaction. For the Equation (2.4) may be rewritten as followed:



The positive sign for enthalpy is used because the enthalpy is placed on the right side of the reaction process, clearly meaning a product of the reaction. This equation is valid at temperature 25°C only, meaning that both the reactant gases and the product water are at 25°C. At temperature 25°C, and atmospheric pressure, water is in liquid form.

### 2.1.2 Theoretical Electrical Work

There is no combustion in a fuel cell; hydrogen heating values will be used as a measure of energy input in a fuel cell. These are the maximum amount of the energy that may be extracted from hydrogen and electricity is produced in a fuel cell. In every chemical reaction some entropy is produced, and a portion of the hydrogen's higher heating value cannot be converted into electricity. The portion of the reaction enthalpy that could be converted to electricity in a fuel cell corresponds to Gibbs free energy and is determined by the following Equation;

$$\Delta G = \Delta H - T\Delta S\quad (2.8)$$

In other hands, there are some irreversible losses in energy conversion due to creation of entropy,  $\Delta S$ . Similarly, as  $\Delta H$  for the reactions are the difference between the heats of formation of products and reactants,  $\Delta S$  is the difference between entropies of products and reactants:

$$\Delta S = (s_f)_{H_2O} - (s_f)_{H_2} - \frac{1}{2}(s_f)_{O_2}\quad (2.9)$$

where

$(s_f)_{H_2O}$  is entropy of formation of liquid water at 25°C (0.06996 kJ/mol.K),  
 $(s_f)_{H_2}$  is entropy of formation of hydrogen molecule at 25°C (0.13066 kJ/mol.K),

$(S_f)_{O_2}$  is entropy of formation of oxygen molecule at 25°C (0.20517 kJ/mol.K)

Therefore:

$$\Delta S = 0.06996 \frac{\text{kJ}}{\text{mol.K}} - 0.13066 \frac{\text{kJ}}{\text{mol.K}} - \frac{1}{2}(0.20517) \frac{\text{kJ}}{\text{mol.K}} = 0.163285 \frac{\text{kJ}}{\text{mol.K}} \quad (2.10)$$

Therefore, at temperature of 25°C, out of 286.02 kJ/mol of available energy, 237.34 kJ/mol can be converted into electrical energy and remaining of enthalpy 48.68 kJ/mol is converted into heat.

### 2.1.3 Theoretical Fuel Cell Potential

The potential of a fuel cell system to perform electrical work is measured by output voltage. In general, electrical work is a product of charge ( $Q$ ) and potential ( $E$ ) which can be determined from Equation (2.8):

$$W_{el} = QE \quad (2.11)$$

where

$$\begin{aligned} W_{el} &= \text{electrical work (J/ mol)} \\ Q &= \text{charge (Coulombs/ mol)} \\ E &= \text{potential (Volts)} \end{aligned}$$

The total charge transferred in a fuel cell reaction per mol of  $H_2$  consumed in the process is equal to:

$$Q = nN_{AVG}q_{el} \quad (2.12)$$

where

$$\begin{aligned} n &= \text{number of electron per molecule of } H_2 = 2 \text{ electron per molecule} \\ N_{AVG} &= \text{number of molecule per mole (Avogadro's number)} = 6.022 \times 10^{23} \\ &\text{molecules/mol} \\ q_{el} &= \text{charge of 1 electron} = 1.602 \times 10^{-19} \text{ Coulombs/electron} \end{aligned}$$

The product of Avogadro's number and charge of 1 electron is known as Faraday's constant:  $F = 96,485$  Coulombs/electron-mol. Electrical works can be determined from:

$$W_{el} = nFE \quad (2.13)$$

As mentioned previously equation, the maximum amount of electrical energy generated in a fuel cell corresponds to Gibbs free energy,  $\Delta G$ . The electrical works can be calculated by:

$$W_{el} = -\Delta G \quad (2.14)$$

The theoretical potential of fuel cell is then:

$$E^0 = \frac{-\Delta G^0}{nF} \quad (2.15)$$

Thus, the Gibbs free energy is set the magnitude of reversible voltage for an electrochemical reaction. In a fuel cell, the reactions have a Gibbs free energy change of  $-237.34 \text{ kJ/mol}$  under the standard-state conditions for liquid water product. Because  $n$ , and  $F$  are all known, the theoretical fuel cell potential of hydrogen/oxygen can be calculated by:

$$E^0 = \frac{-\Delta G^0}{nF} = \frac{237,340}{2 \times 96,485} = 1.23 \text{ Volts} \quad (2.16)$$

where  $E^0$  is the standard-state reversible voltage and  $\Delta G^0$  is the standard-state free energy change for the reaction. At STP, thermodynamics dictates that the highest voltage attainable from a fuel cell is 1.23 voltages. If we need more electric potential from fuel cell, we usually have to stack several cells together in series. However, the maximum expected open-circuit voltage of a fuel cell is lower than the theoretical fuel cell voltage. The actual fuel cell voltage is a function of temperature and pressure of reactants and products, which may be derived by Nernst equation. From thermodynamics of system in equilibrium, Nernst equation can be expressed as function of temperature and pressure (Barbir, 2005).

$$\Delta G = \Delta G^0 + RT \ln \left( \frac{P_{H_2O}}{P_{H_2} P_{O_2}^{0.5}} \right) \quad (2.17)$$

where  $R$  is universal gas constant ( $8.314 \text{ J/mol.K}$ ),  
 $T$  is fuel cell operating temperature ( $K$ ),  
 $P_{H_2O}$  is partial pressure of water product ( $Pa$ ),  
 $P_{H_2}$  is partial pressure of hydrogen gas ( $Pa$ ),  
 $P_{O_2}$  is partial pressure of oxygen gas ( $Pa$ )

Equation (2.17) can be converted to voltage by dividing with  $-nF$

$$E(T, P) = E^0 + \frac{RT}{nF} \ln \left( \frac{P_{H_2O}}{P_{H_2} P_{O_2}^{0.5}} \right) \quad (2.18)$$

Remember that this equation is only valid for gaseous product and reactants, when liquid water is produced in a fuel cell,  $P_{H_2O} = 1$ . From Equation (2.18), it follows that at higher reactant pressure the cell potential is higher. Also, if reactants are dilute, their partial pressure is proportional to their concentration and consequently the cell potential is lower.

#### 2.1.4 Effect of Temperature to Cell Potential

The theoretical cell potential changes with temperature can be determined by substituting Equation (2.8) into (2.15) to yields (Barbir, 2005):

$$E^0 = -\left(\frac{\Delta H}{nF} - \frac{T\Delta S}{nF}\right) \quad (2.19)$$

Obviously, an increase in the cell temperature results in a lower theoretical cell potential. Note that both  $\Delta H$  and  $\Delta S$  are negative as shown below for the hydrogen oxidation processes:

$$\text{For liquid: } H_2 + \frac{1}{2}O_2 \rightarrow H_2O(l): \quad \Delta H = -286.02 \frac{\text{kJ}}{\text{mol}}, \Delta S = -0.1633 \text{ kJ/mol}$$

$$\text{For gas: } H_2 + \frac{1}{2}O_2 \rightarrow H_2O(g): \quad \Delta H = -241.98 \frac{\text{kJ}}{\text{mol}}, \Delta S = -0.0444 \text{ kJ/mol}$$

In addition, both  $\Delta H$  and  $\Delta S$  are functions of temperature:

$$h_T = h_{298.15} + \int_{298.15}^T c_p dT \quad (2.20)$$

$$s_T = s_{298.15} + \int_{298.15}^T \frac{1}{T} c_p dT \quad (2.21)$$

Specific heat of any gas is also a function of temperature. An empirical relationship may be used:

$$c_p = a + bT + cT^2 \quad (2.22)$$

where  $a$  is the empirical coefficients ( $H_2 = 28.91404 \text{ J/mol} \cdot \text{K}$ ,  $O_2 = 25.84512 \text{ J/mol} \cdot \text{K}$  and  $H_2O_{(g)} = 30.62644 \text{ J/mol} \cdot \text{K}$ )

$b$  is the empirical coefficients ( $H_2 = -0.00084 \text{ J/mol} \cdot \text{K}$ ,  $O_2 = 0.012987 \text{ J/mol} \cdot \text{K}$  and  $H_2O_{(g)} = 0.009621 \text{ J/mol} \cdot \text{K}$ )

$c$  is the empirical coefficients ( $H_2 = 2.01E-06 \text{ J/mol} \cdot \text{K}$ ,  $O_2 = -3.9E-06 \text{ J/mol} \cdot \text{K}$  and  $H_2O_{(g)} = 1.18E-06 \text{ J/mol} \cdot \text{K}$ )

Substituting Equation (2.22) into Equations (2.20) and (2.21) and integrating yields:

$$\Delta H_T = \Delta H_{298.15} + \Delta a(T - 298.15) + \Delta b \frac{(T-298.15)^2}{2} + \Delta c \frac{(T-298.15)^3}{3} \quad (2.23)$$

$$\Delta S_T = \Delta S_{298.15} + \Delta a \ln\left(\frac{T}{298.15}\right) + \Delta b(T - 298.15) + \Delta c \frac{(T-298.15)^2}{2} \quad (2.24)$$

Where  $\Delta a$ ,  $\Delta b$ , and  $\Delta c$  are the differences between the coefficients  $a$ ,  $b$ , and  $c$  respectively, for products and reactants at temperatures below  $100^\circ\text{C}$  that is:

$$\Delta a = a_{H_2O} - a_{H_2} - \frac{1}{2} a_{O_2},$$

$$\Delta b = b_{H_2O} - b_{H_2} - \frac{1}{2} b_{O_2}, \text{ and}$$

$$\Delta c = c_{H_2O} - c_{H_2} - \frac{1}{2} c_{O_2} \quad (2.25)$$

At temperature below 100°C, changes of  $C_p$ ,  $\Delta H$ , and  $\Delta S$  are very small as shown in Table 2.1, but at higher temperatures, such as those experienced in solid oxide fuel cells. The theoretical cell potential decreases with temperature. However, in operating fuel cell, in general, a higher cell temperature results in a higher cell potential. This is because the voltage losses in operating fuel cells decrease with temperature, and this more than compensates for the loss of theoretical cell potential.

Table 2.1 Change of Enthalpy, Gibbs Free Energy, and Entropy of Hydrogen/Oxygen Fuel Cell Reaction ( $kJ/mol.K$ ) with Temperature and Resulting Theoretical Cell Potential

$T$ (K)	$\Delta H$	$\Delta S$	$\Delta G$	$E_{th}$ (V)
298.15	-286.02	-0.16328	-237.34	1.230
333.15	-284.85	-0.15975	-231.63	1.200
353.15	-284.18	-0.15791	-228.42	1.184
373.15	-283.52	-0.15617	-225.24	1.167

### 2.1.5 Theoretical Fuel Cell Efficiency

The efficiency of any energy conversion device is defined as the ratio between useful energy output and energy input. In case of a fuel cell, the useful energy output is the electrical energy produced, and energy input is enthalpy of hydrogen, that is, hydrogen's higher heating value (HHV). Assuming that all of the Gibbs free energy can be converted into electrical energy, the maximum possible (theoretical) efficiency ( $\epsilon$ ) of a fuel cell is:

$$\epsilon = \frac{\Delta G}{\Delta H} \quad (2.26)$$

At STP condition, a fuel cell has  $\Delta G = -237.43 \text{ kJ/mol}$  and  $\Delta H_{HHV} = -286.02 \text{ kJ/mol}$ . Therefore, the yield of reversible HHV efficiency for a fuel cell is:

$$\epsilon = \frac{-237.43 \text{ kJ/mol}}{-286.02 \text{ kJ/mol}} = 0.83 \quad (2.27)$$

If both  $\Delta G$  and  $\Delta H$  in Equation (2.26) are divided by  $nF$ , the fuel cell efficiency may be expressed as a ratio of two potentials:

$$\epsilon = \frac{-\Delta G}{-\Delta H} = \frac{\frac{-\Delta G}{nF}}{\frac{-\Delta H}{nF}} = \frac{1.23}{1.482} = 0.83 \quad (2.28)$$

where  $\frac{-\Delta G}{nF} = 1.23 \text{ V}$  is the theoretical cell potential.

$\frac{-\Delta H}{nF} = 1.482 \text{ V}$  is the potential corresponding to hydrogen's higher heating value, or the thermoneutral potential.

### 2.1.6 Effect of Pressure to Cell Potential

All of the previous equations were valid at atmospheric pressure. However, a fuel cell may operate at any pressure, typically from atmospheric all the way up to 6-7 bars (Barbir, 2005). For an isothermal process, and with a little bit of basic thermodynamics, the change in Gibbs free energy may be shown to be:

$$dG = V_m dP \quad (2.29)$$

Where:  $V_m$  is molar volume, ( $\text{m}^3/\text{mol}$ ), and  $P$  is pressure (Pa). For an ideal gas:

$$PV_m = RT \quad (2.30)$$

Therefore:

$$dG = RT \frac{dP}{P} \quad (2.31)$$

After integration:

$$G = G_0 + RT \ln \left( \frac{P}{P_0} \right) \quad (2.32)$$

Where  $G_0$  is Gibbs free energy at standard temperature and pressure ( $25^\circ\text{C}$  and 1 atm), and  $P_0$  is the reference or standard pressure (1 atm). For any chemical reaction:



The change in Gibbs free energy is the change between products and reactants:

$$\Delta G = mG_C + nG_D - jG_A - kG_B \quad (2.34)$$

After substituting into Equation (2.32)

$$\Delta G = \Delta G_0 + RT \cdot \ln \left[ \frac{\left( \frac{P_C}{P_0} \right)^m \left( \frac{P_D}{P_0} \right)^n}{\left( \frac{P_A}{P_0} \right)^j \left( \frac{P_B}{P_0} \right)^k} \right] \quad (2.35)$$

This is known as the Nernst Equation, where  $P$  is the partial pressure of the reactant or product species and  $P_0$  is reference pressure. For the hydrogen/oxygen fuel cell reaction, the Nernst Equation becomes:

$$\Delta G = \Delta G_0 + RT \cdot \ln \left[ \frac{P_{H_2O}}{P_{H_2} P_{O_2}^{0.5}} \right] \quad (2.36)$$

By introducing Equation (2.19) into Equation (2.36)

$$E = E_0 + \frac{RT}{nF} \ln \left( \frac{P_{H_2O} P_{O_2}^{0.5}}{P_{H_2}} \right) \quad (2.37)$$

Note that the previous equations are only valid for gaseous products and reactants. When liquid water is produced in a fuel cell,  $P_{H_2O} = 1$ . From Equation (2.37) it follows that at higher reactant pressures the cell potential is higher. Also, if the reactants are diluted, for example, if air is used instead of pure oxygen, their partial pressure is proportional to their concentration and consequently the cell potential is lower. In case of air versus oxygen, the theoretical voltage loss/gain is:

$$\Delta E = E_{O_2} - E_{Air} = \frac{RT}{nF} \ln \left( \frac{P_{O_2}}{P_{Air}} \right)^{0.5} = \frac{RT}{nF} \ln \left( \frac{1}{0.21} \right)^{0.5} \quad (2.38)$$

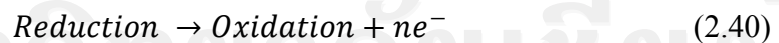
From Equation (2.1) and (2.2), the reactions happen on an interface between the ionically conductive electrolytes and electrically conductive electrode. Because there are gases involved in fuel cell electrochemical reactions, the electrodes must be porous allowing the gases to arrive to, as well as product water to leave the reaction sites. Note that these are the overall reactions and that in both cases there are several intermediary sequential and parallel steps involved.

### 2.1.7 Reaction Rate

Electrochemical reactions involve both a transfer of electrical charge and a change in Gibbs energy. The rate of an electrochemical reaction is determined by an activation energy barrier that the charge must overcome in moving from electrolyte to a solid electrode or vice versa. The speed at which an electrochemical reaction proceeds on the electrode surface is the rate at which the electrons are released or consumed which is the electrical current. Current density is the current (of electrons or ions) per unit area of the surface. From Faraday's law it follows that current is proportional to the charge transferred and the consumption of reactant per unit area:

$$i = nFj \quad (2.39)$$

where  $nF$  is the charge transferred (Coulombs mol<sup>-1</sup>) and  $j$  is the flux of reactant per unit area (mol s<sup>-1</sup> cm<sup>-2</sup>). Therefore, the reaction rate may be easily measured by a current measuring device placed external to the cell. However, the measured current or current density is actually the net current, that is, the difference between forward and reverse current on the electrode. In general, an electrochemical reaction involves either oxidation or reduction of the species:



In a hydrogen/oxygen fuel cell the anode reaction is oxidation of hydrogen, in which hydrogen is stripped of its electrons, and the products of this reaction are protons and electrons. The cathode reaction is oxygen reduction and water is generated as a product. On an electrode at equilibrium conditions, that is, when no external current is being generated, both processes, oxidation and reduction, occur at equal rates:



The consumption of the reactant species is proportional to their surface concentration. For the forward reaction of Equation (2.42), which is the reaction described by Equation (2.41), the flux is:

$$j_f = k_f C_{OX} \quad (2.43)$$

where  $k_f$  is forward reaction (reduction) rate coefficient, and  $C_{OX}$  is surface concentration of the reacting species. Similarly, for the backward reaction of Equation (2.42), which is the reaction described by Equation (2.40), the flux is:

$$j_b = k_b C_{Rd} \quad (2.44)$$

where  $k_b$  is backward reaction (oxidation) rate coefficient, and  $C_{Rd}$  is surface concentration of reaction species. Each of these two reaction either releases or consumes electrons. The net current generated is the difference between the electrons released and consumed.

$$i = nF(k_f C_{OX} - k_b C_{Rd}) \quad (2.45)$$

At equilibrium, the net current is equal to zero, although the reaction proceeds in both directions simultaneously. The rate at which these reactions proceed at equilibrium is called the exchange current density.

### 2.1.8 Reaction Constants: Transfer Coefficient

From the Transition State Theory (Frano Barbir, 2005), it may be shown that the reaction rate coefficient for an electrochemical reaction is a function of the Gibbs free energy:

$$k = \frac{k_B T}{h} \exp\left(\frac{-\Delta G}{RT}\right) \quad (2.46)$$

where  $k_B$  is Boltzmann's constant, and  $h$  is Planck's constant. The Gibbs free energy for electrochemical reactions may be considered to consist of both chemical and electrical terms. In that case, for a reduction reaction:

$$\Delta G = \Delta G_{ch} + \alpha_{RD} FE \quad (2.47)$$

and for an oxidation reaction:

$$\Delta G = \Delta G_{ch} - \alpha_{RD} FE \quad (2.48)$$

The subscript  $ch$  denote the chemical component of the Gibbs free energy,  $\alpha$  is a transfer coefficient,  $F$  is the Faraday's constant, and  $E$  is the potential. The forward

(reduction) and backward (oxidation) reaction rate coefficients in Equation (2.45) are then respectively:

$$k_f = k_{o,f} \exp \left[ \frac{-\alpha_{Rd} FE}{RT} \right] \quad (2.49)$$

$$k_b = k_{o,b} \exp \left[ \frac{-\alpha_{ox} FE}{RT} \right] \quad (2.50)$$

### 2.1.9 Current Potential Relationship – Butler – Volmer Equation

By introducing Equation (2.49) and (2.50) into Equation (2.45) the net current, density is obtained:

$$i = nF \left\{ k_{o,f} \exp \left[ \frac{-\alpha_{Rd} FE}{RT} \right] - k_{o,b} \exp \left[ \frac{-\alpha_{ox} FE}{RT} \right] \right\} \quad (2.51)$$

At equilibrium, the potential is  $E_r$  and the net current is equal to zero, although the reaction proceeds in both directions simultaneously. The rate at which these reactions proceed at equilibrium is called the exchange current density:

$$i_o = nF k_{o,f} C_{ox} \exp \left[ \frac{-\alpha_{Rd} FE_r}{RT} \right] = nF k_{o,b} C_{Rd} \exp \left[ \frac{-\alpha_{ox} FE_r}{RT} \right] \quad (2.52)$$

By combining the Equations (2.46) through (2.49) into Equation (2.45), a relationship between the current density and potential is obtained:

$$i = i_o \left\{ \exp \left[ \frac{-\alpha_{Rd} F(E-E_r)}{RT} \right] - \exp \left[ \frac{-\alpha_{ox} F(E-E_r)}{RT} \right] \right\} \quad (2.53)$$

This is known as the Butler-Volmer Equation, where  $E_r$  is the reversible or equilibrium potential. Note that the reversible or equilibrium potential at the fuel cell anode is 0V by definition, and the reversible potential at the fuel cell cathode is 1.229V (at 25°C and atmospheric pressure) and it does vary with temperature and pressure as shown in previous section. The difference between the electrode potential and the reversible potential is called over potential. It is the potential difference required to generate current. The Butler-Volmer Equation (2.53) is valid for both anode and cathode reaction in a fuel cell:

$$i_a = i_{o,a} \left\{ \exp \left[ \frac{-\alpha_{Rd,a} F(E_a - E_{r,a})}{RT} \right] - \exp \left[ \frac{-\alpha_{ox,a} F(E_a - E_{r,a})}{RT} \right] \right\} \quad (2.54)$$

and

$$i_c = i_{o,c} \left\{ \exp \left[ \frac{-\alpha_{Rd,c} F(E_c - E_{r,c})}{RT} \right] - \exp \left[ \frac{-\alpha_{ox,c} F(E_c - E_{r,c})}{RT} \right] \right\} \quad (2.55)$$

The over potential on the anode is positive ( $E_a > E_{r,a}$ ), which makes the first term of the Equation (2.54) negligible in comparison with the second term, that is, the oxidation current is predominant and the equation may be reduced to:

$$i_a = -i_{o,a} \exp \left[ \frac{-\alpha_{ox,a} F(E_a - E_{r,a})}{RT} \right] \quad (2.56)$$

Note that the resulting current has a negative sign, which denotes that the electrons are leaving the electrode (net oxidation reaction). Similarly, the over potential on the cathode is negative ( $E_c < E_{r,c}$ ), which makes the first term of the Equation (2.55) much larger than the second term, that is, the reduction current is predominant and equation may be reduced to:

$$i_c = i_{o,c} \exp \left[ \frac{-\alpha_{Rd,c} F (E_c - E_{r,c})}{RT} \right] \quad (2.57)$$

The transfer coefficients in the previous equation for hydrogen/oxygen fuel cells using Pt catalyst seem to have value around 1. Note that in some literature there is an  $n$  parameter in the previous equation denoting the number of electrons involved. Clearly, on the fuel cell anode side,  $n = 2$ , and on the cathode side,  $n = 4$ . In that case it is the product of  $n\alpha$  that has value around 1. Larminie and Dicks (2003) list a value of  $\alpha = 0.5$  for the hydrogen fuel cell anode (with two electrons involved) and  $\alpha = 0.1$  to 0.5 for the cathode. Newman (1991) specifies  $\alpha$  in range between 0.2 and 2.

### 2.1.10 Exchange Current Density

Exchange current density,  $i_o$ , in electrochemical reactions is analogous to the rate constant in chemical reactions. Unlike the constants, exchange current density is concentration dependent (as can be seen directly from Equation (2.52)). It is also a function of temperature (from Equation (2.46)). The effective exchange current density (per unit of electrode geometrical area) is also a function of electrode catalyst loading and catalyst specific surface area. If the reference exchange current density (at reference temperature and pressure) is given per actual catalyst surface area, then the effective exchange current density at any temperature and pressure is given by the following equation:

$$i_o = i_o^{ref} a_c L_c \left( \frac{P_r}{P_r^{ref}} \right)^\gamma \exp \left[ -\frac{E_c}{RT} \left( 1 - \frac{T}{T_{ref}} \right) \right] \quad (2.58)$$

where  $i_o^{ref}$  is a reference exchange current density (at reference temperature and pressure, typically 25°C and 101.25 kPa) per unit catalyst surface area,  $A_{cm^2Pt}$ ,  $a_c$  is catalyst specific area (theoretical limit for Pt catalyst is 2400 cm<sup>2</sup>mg<sup>-1</sup>, but state-of-art catalyst has about 600-1000 cm<sup>2</sup>mg<sup>-1</sup>, which is further reduced by incorporation of catalyst in the electrode structures by up to 30%),  $L_c$  is catalyst loading (state-of-art electrodes have 0.3-0.5 mgPtcm<sup>-2</sup>; lower loadings are possible but would result in lower cell voltages),  $P_r$  is reactant partial pressure, kPa,  $P_r^{ref}$  is reference pressure, kPa,  $\gamma$  is pressure coefficient (0.5 to 1.0),  $E_c$  is activation energy, 66 kJmol<sup>-1</sup> for oxygen reduction on Pt,  $T$  is temperature, K, and  $T_{ref}$  is reference temperature, 298.15K. The product  $a_c L_c$  is also called electrode roughness, meaning the catalyst surface area, cm<sup>2</sup>, per electrode geometric area, cm<sup>2</sup>. Instead of the ratio of partial pressure, a ratio of concentrations at the surface may be used as well. Exchange current density is a measure of an electrode's readiness to proceed with the electrochemical reaction. If the exchange current density is high, the surface of the

electrode is more active. In a hydrogen/oxygen fuel cell, the exchange current density at the anode is much larger than at the cathode. The higher the exchange current density, the lower the energy barrier that the charge must overcome moving from electrolyte to the catalyst surface and vice versa. In other words, the higher the exchange current density, the more current is generated at any over potential.

### 2.1.11 Voltage Losses

If a fuel cell is supplied with reactant gases, but the electrical circuit is not closed, it will not generate any current, and one would expect the cell potential to be at, or at least close to, the theoretical cell potential for given conditions (temperature, pressure, and concentration of reactants).

#### 2.1.11.1 Activation Polarization

Some voltage difference from equilibrium is needed to get the electrochemical reaction going, as shown previously. This is called activation polarization, and it is associated with sluggish electrode kinetics. The higher the exchange current density, the lower the activation polarization losses. These losses happen at both anode and cathode; however, oxygen reduction requires much higher over potential, that is, it is a much slower reaction than hydrogen oxidation. As mentioned before, at relatively high negative over potentials, such as those at the fuel cell cathode, the first term in the Butler-Volmer equation becomes predominant, this allowed for expression of potential as a function of current density:

$$\Delta V_{act,c} = E_{r,c} - E_c = \frac{RT}{\alpha_c F} \ln \left( \frac{i}{i_{o,c}} \right) \quad (2.59)$$

Similarly, at the anode at positive over potentials the second term in the Butler-Volmer equation becomes predominant:

$$\Delta V_{act,a} = E_a - E_{r,a} = \frac{RT}{\alpha_a F} \ln \left( \frac{i}{i_{o,a}} \right) \quad (2.60)$$

Note that by definition, in electrochemistry, the reversible potential of the hydrogen oxidation reaction is zero at all temperature (Bard et al, 1980). That is why the standard hydrogen electrode is used as a reference electrode. Therefore, for hydrogen anodes  $E_{r,a} = 0V$ . Activation polarization of the hydrogen oxidation reaction is much smaller than activation polarization of the oxygen reduction reaction. A simplified way to show the activation losses is to use the so-called Tafel equation:

$$\Delta V_{act} = a + b \log(i) \quad (2.61)$$

where

$$a = -2.3 \frac{RT}{\alpha F} \log(i_o), \text{ and } b = 2.3 \frac{RT}{\alpha F}$$

Term  $b$  is called the Tafel slope. Note that at any given temperature the Tafel slope depends solely on transfer coefficient,  $\alpha$ . For  $\alpha = 1$ , the Tafel slope at 60°C is -60mA per decade, what is typically found for oxygen reduction on Pt.

$$E_{cell} = E_c - E_a = E_r - \Delta V_{act,c} - \Delta V_{act,a} \quad (2.62)$$

$$E_{cell} = E_r - \frac{RT}{\alpha_c F} \ln\left(\frac{i}{i_{o,c}}\right) - \frac{RT}{\alpha_a F} \ln\left(\frac{i}{i_{o,a}}\right) \quad (2.63)$$

If anode polarization is neglected, the previous equation becomes:

$$E_{cell} = E_r - \frac{RT}{\alpha F} \ln\left(\frac{i}{i_o}\right) \quad (2.64)$$

### 2.1.11.2 Internal Currents and Crossover Losses

Although the electrolyte, a polymer membrane, is not electrically conductive and is practically impermeable to reactant gases, some small amount of hydrogen will diffuse from anode to cathode, and some electrons may also find a shortcut through the membrane. Because each hydrogen molecule contains two electrons, this fuel crossover and the so-called internal current are essentially equivalent. The total electrical current is the sum of external current and current losses due to fuel crossover and internal currents:

$$I = I_{ext} + I_{loss} \quad (2.65)$$

Current divided by the electrode active area,  $A$ , is current density,  $A/cm^2$ :

$$i = \frac{I}{A} \quad (2.66)$$

Therefore:

$$i = i_{ext} + i_{loss} \quad (2.67)$$

If this total current density is used in the equation that approximates the cell potential, the following equation results:

$$E_{cell} = E_r - \frac{RT}{\alpha F} \ln\left(\frac{i_{ext} + i_{loss}}{i_o}\right) \quad (2.68)$$

Therefore, even if the external current is equal to zero, such as at open circuit, the cell voltage may be significantly lower than the reversible cell potential for given conditions. Indeed, open circuit potential of hydrogen/air fuel cells is typically below 1V, most likely about 0.94 to 0.97V (depending on operating pressure)

$$E_{cell,OCV} = E_r - \frac{RT}{\alpha F} \ln\left(\frac{i_{loss}}{i_o}\right) \quad (2.69)$$

### 2.1.11.3 Ohmic (Resistive) Losses

Ohmic losses occur because of resistance to the flow of ions in the electrolyte and resistance to the flow of electrons through the electrically conductive fuel cell components. These losses can be expressed by Ohm's law:

$$\Delta V_{ohm} = iR_i \quad (2.70)$$

where  $i$  is current density,  $A/cm^2$ , and  $R_i$  is total cell internal resistance (which includes ionic, electronic, and contact resistance,  $\Omega cm^2$ ) Typical values  $R_i$  are between 0.1 and 0.2  $\Omega cm^2$ .

#### 2.1.11.4 Concentration Polarization

Concentration polarization occurs when a reactant is rapidly consumed at the electrode by the electrochemical reaction so that concentration gradients are established. We learned before that the electrochemical reaction potential changes with partial pressure of the reactants, and relationship is given by the Nernst equation:

$$\Delta V = \frac{RT}{nF} \ln \left( \frac{C_B}{C_s} \right) \quad (2.71)$$

where  $C_B$  is bulk concentration of reactant,  $mol cm^{-3}$ , and  $C_s$  is concentration of reactant at the surface of the catalyst,  $mol cm^{-3}$ . According to Fick's Law, the flux of reactant is proportional to concentration gradient:

$$N = \frac{D.(C_B - C_s)}{\delta} A \quad (2.72)$$

where  $N$  is flux of reactants,  $mols^{-1}$ ,  $D$  is diffusion coefficient of the reacting species,  $cm^2 s^{-1}$ ,  $A$  is electrode active area,  $cm^2$ , and  $\delta$  is diffusion distance,  $cm$ . In steady state, the rate at which the reactant species is consumed in the electrochemical reaction is equal to the diffusion flux:

$$N = \frac{1}{nF} \quad (2.73)$$

By combining Equation (2.61) and (2.62), the following relationship is obtained:

$$i = \frac{nF.D.(C_B - C_s)}{\delta} \quad (2.74)$$

The reactant concentration at the catalyst surface thus depends on current density (the higher the current density, the lower the surface concentration). The surface concentration reaches zero when the rate of concentration exceeds the diffusion rate (the reactant is consumed faster than it can reach the surface. Current density at which this happens is called the limiting current density. A fuel cell cannot produce more than the limiting currents because of there are no reactants at the catalyst surface. Therefore, for  $C_s = 0$ ,  $i = i_L$ , and the limiting current density is then:

$$i_L = \frac{nF.D.C_B}{\delta} \quad (2.75)$$

By combining Equation (2.71), (2.74), and (2.75), a relationship for voltage loss due to concentration polarization is obtained:

$$\Delta V_{conc} = \frac{RT}{nF} \ln \left( \frac{i_L}{i_L - i} \right) \quad (2.76)$$

The output cell voltage of developing fuel cell is less than thermodynamically predicted voltage output due to irreversible losses. Figure 2.3 shows characteristic of  $i$ - $v$  curve of FC performance that depends on output voltage and current density. The output cell voltage depends on parameters which shown in physical equations. There are three major types of fuel cell loss, which occurred in fuel cell as follow: Activation losses, Ohmic losses, and Concentration losses. The activation losses mostly affect in initial part of curve. The ohmic losses are mostly apparent in the middle section of the curve, and the concentration losses are most significant in the tail of  $i$ - $v$  curve.

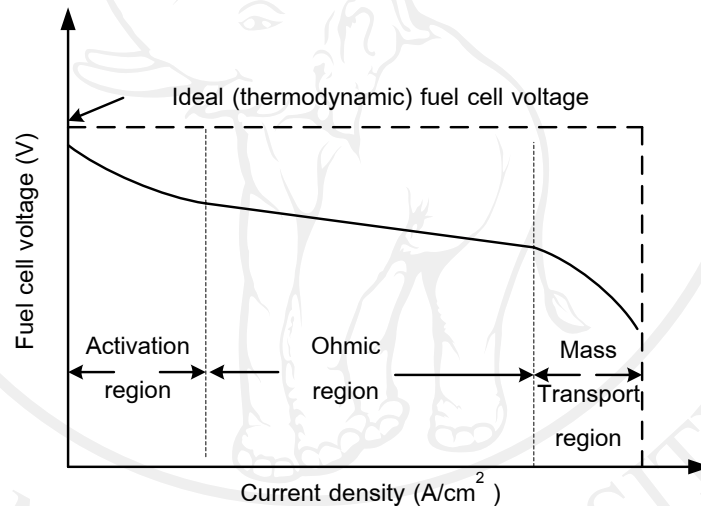


Figure 2.3 The  $i$ - $v$  curve schematic of FC

The output cell voltage of a single cell can be determined from:

$$V_{cell} = E_{cell,OCV} - \Delta V_{act} - \Delta V_{ohm} - \Delta V_{conc} \quad (2.77)$$

An ideal fuel cell would supply any amount of current while maintaining a constant voltage determined by thermodynamics. In practice, the actual voltage output of a real fuel cell is less than the ideal thermodynamically predicted voltage. Furthermore, the more current that is drawn from a real fuel cell, the lower the voltage output of the cell, limiting the total power that can be delivered. The power ( $P$ ) delivered by a fuel cell is given by the product of current and voltage.

$$P = iV_{cell} \quad (2.78)$$

### 2.1.11.5 Reactants Flow Rates

The reactants flow rate at the inlet of a fuel cell must be equal to or higher than the rate at which those reactants are being consumed in the cell. The rates (in mol/s) at which hydrogen and oxygen are consumed and water is generated are determined by Faraday's Law:

$$\dot{N}_{H_2} = \frac{I}{2F} \quad (2.79)$$

$$\dot{N}_{O_2} = \frac{I}{4F} \quad (2.80)$$

$$\dot{N}_{H_2O} = \frac{I}{2F} \quad (2.81)$$

where:

$\dot{N}$  is consumption rate (mol/s)

$I$  is current (A)

$F$  is Faraday's constant (C/mol)

The mass flow rates of reactants consumption (in g/s) are then:

$$\dot{m}_{H_2} = \frac{I}{2F} M_{H_2} \quad (2.82)$$

$$\dot{m}_{O_2} = \frac{I}{4F} M_{O_2} \quad (2.83)$$

The mass flow rate of water generation (in g/s) is:

$$\dot{m}_{H_2O} = \frac{I}{2F} M_{H_2O} \quad (2.84)$$

Most often, the flow rates of gases are expressed in standard liters per minutes (SLPM). Standard liter is a quantity of gas that would occupy 1 liter of volume at standard conditions, namely atmospheric pressure, 101.3kPa, and 15°C. Note that most chemical handbooks and textbooks refer to 25°C as standard or reference temperature, but in technical fluid mechanics standard temperature is 15°C. To avoid confusion with standard temperatures, in Europe it is common to use normal liter or normal m<sup>3</sup>, where the temperature has been normalized to 0°C.

For any ideal gas, moles and volumes are directly related by the equation of state:

$$PV = NRT \quad (2.85)$$

Molar volume is:

$$v_m = \frac{V}{N} = \frac{RT}{P} \quad (2.86)$$

At standard conditions, that is, atmospheric pressure and 15°C, molar volume is:

$$v_m = \frac{RT}{P} = \frac{8.314 \times 288.15}{101,300} = 0.02365 \text{ m}^3/\text{mol}$$

$$v_m = 23.65 \frac{\text{liter}}{\text{mol}} = 23,650 \text{ cm}^3/\text{mol}$$

The volumetric flow rate of reactants consumption (in standard liters per minute or SLPM) are:

$$\dot{V}_{H_2} = 23.65 \times 60 \times \frac{I}{2F} \quad (2.87)$$

$$\dot{V}_{O_2} = 23.65 \times 60 \times \frac{I}{4F} \quad (2.88)$$

Consumption of the reactants, hydrogen and oxygen, and water generation in the fuel cell is summarized in Table 2.2

Table 2.2 Reactants consumption and water generation (per Amp and per Cell)

	Hydrogen consumption	Oxygen consumption	Water generation (liquid)
mole/s	$5.18 \times 10^{-6}$	$2.59 \times 10^{-6}$	$5.18 \times 10^{-6}$
g/s	$10.4 \times 10^{-6}$	$82.9 \times 10^{-6}$	$93.3 \times 10^{-6}$
cm <sup>3</sup> /s	0.1225	0.06125	$93.3 \times 10^{-6}$
SLPM	0.00735	0.003675	N/A

### 2.1.11.6 Fuel Cell Energy Balance

Fuel cell energy balance requires that the sum of all energy inputs must be equal to the sum of all energy output:

$$\sum(H_i)_{in} = W_{el} + \sum(H_i)_{out} + Q \quad (2.89)$$

The inputs are the enthalpies of all the flows into the fuel cell, namely fuel and oxidant, plus enthalpy of water vapor present in those gases. The outputs are: 1) electric power produced; 2) enthalpies of all the flows out of the fuel cell, namely unused fuel and oxidant, plus enthalpy of water vapor present in those gases, plus enthalpy of any liquid water present in either fuel or oxidant exhaust; and 3) heat flux out of the fuel cell, both controlled through a cooling medium and uncontrolled because of heat dissipation (radiation and convection) from the fuel cell surface to the surroundings.

For each dry gas or a mixture of dry gases, the enthalpy (in J/s) is:

$$H = \dot{m}c_p t \quad (2.90)$$

where:

$\dot{m}$  is mass flow rate of that gas or mixture (g/s)

$c_p$  is specific heat (J/g.K)

$t$  is temperature in °C

Note that the use of degrees Celsius implies that 0°C has been selected as a reference state for all enthalpies.

If a gas is combustible, that is, it has a heating value, its enthalpy is then:

$$H = \dot{m}(c_p t + h_{HHV}^0) \quad (2.91)$$

where  $h_{HHV}^0$  is the higher heating value of that gas (J/g) at 0°C. Typically, heating values are reported and tabulated at 25°C. The difference between the heating value at 25°C and 0°C is the difference between the enthalpies of reactants and products at those two temperatures. For hydrogen it is:

$$h_{HHV}^0 = h_{HHV}^{25} - \left( c_{p,H_2} + \frac{1}{2} \frac{M_{O_2}}{M_{H_2}} c_{p,O_2} - \frac{M_{H_2O}}{M_{H_2}} c_{p,H_2O(l)} \right) \cdot 25 \quad (2.92)$$

And enthalpy of water vapor is:

$$h_v = c_{pv} t + h_{fg} \quad (2.91)$$

Enthalpy of water vapor is:

$$H = \dot{m}_{H_2O(g)} (c_{p,H_2O(g)} t + h_{fg}^0) \quad (2.92)$$

Enthalpy of liquid water is:

$$H = \dot{m}_{H_2O(l)} (c_{p,H_2O(l)} t) \quad (2.93)$$

## 2.2 Theory of Internal Combustion Engine

The purpose of internal combustion engines is the production of mechanical power from the chemical energy contained in the fuel.

### 2.2.1 Brake torque and power

Engine torque is normally measured with a dynamometer. As shown in Figure 2.4.

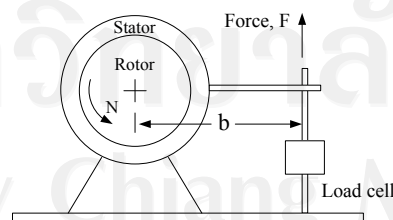


Figure 2.4 Schematic of principle of dynamometer's operation  
(John B. Heywood, 1988)

where  $b$  is distance from center of rotor to load cell

$F$  is the force  
 $T$  is torque

The engine is clamped on a test bed and the shaft is connected to the dynamometer rotor. The rotor is coupled electromagnetically by mechanical friction to a stator, which is supported in low friction bearings. The stator is balanced with the rotor stationary. The torque exerted on the stator with the rotor turning is measured by balancing the stator with weights, spring, or pneumatic meas. The torque exerted by the engine is  $T$ .

$$T = Fb \quad (2.94)$$

The power ( $P_b$ ) delivered by the engine and absorbed by the dynamometer is the product of torque and angular speed is called brake power (John B. Heywood, 1988):

$$P_b = 2\pi NT \quad (2.95)$$

where  $N$  is the crankshaft rotational speed (rev/s)  
 $T$  is torque exerted by the engine (N.m)

### 2.2.2 Indicated work per cycle

Pressure data for the gas in the cylinder over the operating cycle of the engine can be used to calculate the work transfer from the gas to the piston. The cylinder pressure and corresponding cylinder volume throughout the engine cycle can be shown in Figure 2.5. The indicated work per cycle is obtained by integrating around the curve to obtain the area enclosed on the diagram:

$$W_{c,i} = \oint pdv \quad (2.96)$$

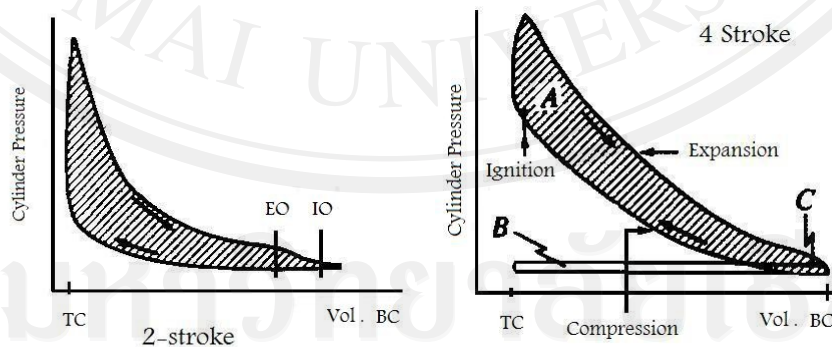


Figure 2.5 p-v diagrams for a two stroke engine and a four stroke engine  
 (John B. Heywood, 1988)

The power per cylinder is related to the indicated work per cycle by:

$$P_i = \frac{W_{c,i}N}{n_R} \quad (2.97)$$

where  $n_R$  is the number of crank revolutions for each power stroke per cylinder. For four stroke cycle,  $n_R$  equals 2; for two stroke cycles,  $n_R$  equals 1. The rate of work transfer from the gas within the cylinder to the piston is called the indicated power.

### 2.2.3 Mechanical efficiency

The indicated power is used to overcome the friction of the bearings, piston, and, other mechanical components of the engine, and to drive the engine accessories which is called friction power.

$$P_i = P_b + P_f \quad (2.98)$$

where  $P_f$  is friction power. Friction power is difficult to determine accurately. One common approach for high speed engines is to drive or motor the engine with a dynamometer and measure the power which has to be supplied by the dynamometer to overcome all these frictional losses. The mechanical efficiency  $\varepsilon_m$ , is the ratio of the brake power delivered by the engine to the indicated power.

$$\varepsilon_m = \frac{P_b}{P_i} = 1 - \frac{P_f}{P_i} \quad (2.99)$$

### 2.2.4 Specific fuel consumption and efficiency

In the engine test, the fuel consumption is measured as a flow rate-mass flow rate per unit time,  $\dot{m}_f$ . The specific fuel consumption (*sfc*) is the fuel flow rate per unit power output. It measures how efficiently an engine is using the fuel supplied to produce work:

$$sfc = \frac{\dot{m}_f}{P_e}, \quad (2.100)$$

Low values of *sfc* are obviously desirable. For SI engine typical best values of brake specific fuel consumption are about  $75 \mu\text{g/J} = 270 \text{ g/kW.h}$ . For CI engines, best values are lower and in large engines can go below  $55 \mu\text{g/J} = 200 \text{ g/kW.h}$ . The fuel energy supplied which can be released by combustion is given by the mass of fuel supplied to the engine per cycle times the heating value of the fuel. The heating value of a fuel,  $Q_{HV}$ , define its energy content. It is determined in a standardized test procedure in which a known mass of fuel is fully burned with air, and the thermal energy released by the combustion process is absorbed by a calorimeter as the combustion products cool down to their original temperature.

This measure of an engine's efficiency, which will be called the fuel consumption efficiency,  $\eta_f$ , is given by:

$$\eta_f = \frac{W_c}{m_f Q_{HV}} = \frac{(P n_R / N)}{(m_f \dot{n}_R / N) Q_{HV}} = \frac{P}{\dot{m}_f Q_{HV}} \quad (2.101)$$

where  $W_c$  is work per cycle.

$m_f$  is the mass of fuel inducted per cycle. Substitution for  $P/\dot{m}_f$  from Equation (2.84) gives

$$\eta_f = \frac{1}{sfc Q_{HV}} \quad (2.102)$$

Typical heating values for the commercial hydrocarbon fuels used in engines are in the range 42 to 44 MJ/kg (18,000 to 19,000 Btu/lbm) (John B. Heywood, 1988).

### 2.2.5 Air/fuel and fuel/are ratio

In engine testing, both the air mass flow rate  $\dot{m}_a$  and the fuel mass flow rate  $\dot{m}_f$  are normally measured. The ratio of these flow rates is useful in defining engine operating conditions:

$$\text{Air/fuel ratio} \quad (A/F) = \frac{\dot{m}_a}{\dot{m}_f} \quad (2.103)$$

$$\text{Fuel/air ratio} \quad (F/A) = \frac{\dot{m}_f}{\dot{m}_a} \quad (2.104)$$

Normally operating range for a conventional SI engine using gasoline fuel is  $12 \leq A/F \leq 18$  ( $0.056 \leq F/A \leq 0.083$ ); for CI engines with diesel fuel, it is  $18 \leq A/F \leq 70$  ( $0.014 \leq F/A \leq 0.056$ )

### 2.2.6 Volumetric efficiency

The intake system of the engine (the air filter, carburetor, and throttle plate, intake manifold, intake port, intake valve) restricts the amount of air which an engine of given displacement can induct to the cylinder. The parameter used to measure the effectiveness of an engine's induction system is the volumetric efficiency;  $\eta_v$ . Volumetric efficiency is only used with four stroke cycle engines. It is defined as the volume flow rate of air into the intake system of the engine divided by the rate at which volume is displaced by the piston:

$$\eta_v = \frac{2\dot{m}_a}{\rho_{a,i} V_d N} \quad (2.105)$$

where  $\rho_{a,i}$  is the inlet air density, and  $V_d$  is the displaced or swept volume. An alternative equivalent definition for volumetric efficiency is

$$\eta_v = \frac{m_a}{\rho_{a,i} V_d} \quad (2.106)$$

where  $m_a$  is mass of air inducted per cycle.

### 2.2.7 Relationships between performance parameters

The importance of parameters defined in previous sections to engine performance becomes evident when power and torque are expressed in terms of these parameters. The power of the engine can be determined by:

$$P = \frac{\eta_f m_a N Q_{HV} (F/A)}{\eta_R} \quad (2.107)$$

For four-stroke cycle engines, volumetric efficiency can be introduced:

$$P = \frac{\eta_f \eta_v V_d N Q_{HV} \rho_{a,i} (F/A)}{2} \quad (2.108)$$

For torque ( $T$ ) can be expressed by:

$$T = \frac{\eta_f \eta_v V_d N Q_{HV} \rho_{a,i} (F/A)}{4\pi} \quad (2.109)$$

### 2.3 Permanent Magnet Synchronous Generator

Electric generator is a machine that converts mechanical power to electrical power. One of the famous generators is permanent magnet synchronous generator (PMSG). The dynamic voltage equation of PMSG are expressed in d-q reference frame is shown as (A. M. O. Haruni, 2010):

$$v_d = -i_d R_s - \omega_r \lambda_q + p \lambda_d \quad (2.110)$$

$$v_q = -i_q R_s - \omega_r \lambda_d + p \lambda_q \quad (2.111)$$

where  $v_d$  and  $v_q$  are the  $d$  and  $q$  axis component of stator voltage;  $\lambda_d$  and  $\lambda_q$  are the  $d$  and  $q$  axis stator flux linkages;  $R_s$  is the stator resistance,  $i_d$  and  $i_q$  are the  $d$  and  $q$  axis component of stator current;  $\omega_r$  is the rotor speed in rad/sec; and  $p$  is the operator  $d/dt$ . Stator flux linkage ( $\lambda_d$  and  $\lambda_q$ ) can be expressed as follows:

$$\lambda_d = -L_d i_d + \lambda_f \quad (2.112)$$

$$\lambda_q = -L_q i_q \quad (2.113)$$

The torque equation of PMSG can be expressed as follows:

$$T_g = -\frac{3}{2} P (\lambda_d i_q - \lambda_q i_d)$$

$$T_g = -\frac{3}{2} P (\lambda_f i_q + [L_d - L_q] i_d i_q) \quad (2.114)$$

## 2.4 DC/DC buck converter

The fuel cell DC output voltage is highly dependent to the load current which imposed a high output voltage variation. In this case, 1200 watts with 47 cells stack a current variation between 45 VDC and 26 VDC. This voltage range is not acceptable for the DC electrical devices (Fei Gao et al, 2009), (G. Kovacevic et al, 2008). One of the key challenges of fuel cell system is the design of an appropriate power converter for power output. Buck converter is an electronic device that is used whenever we want to change DC electrical power from one voltage level to another. Buck converter uses two switches (a transistor and a diode), an inductor and a capacitor. Figure 2.6 shows a DC/DC buck converter diagram. The converter inductance value is calculated from the converter minimum current, in order to ensure that the converter is working appropriately. In order to calculate the values for the output filter (inductance and capacitance) for the buck converter, the PWM (Pulse-Width Modulation) period time  $T_{PWM}$  (s), the converter supply voltage  $V_d$  (V) and the converter minimum current  $I_{min}$  (A) are required (N. Mohan et al., 2002).

$$L > \frac{T_{PWM} \cdot V_d}{8 \cdot I_{min}} \quad (2.115)$$

The converter capacitance value should be chosen to meet the converter dynamic response needs. With the fixed inductance value  $L$  (H) and the converter minimum cutoff frequency  $f_{c \ min}$  (Hz), the maximum value of converter capacitance can be obtained:

$$C \leq \left( \frac{1}{2\pi \cdot f_{c \ min} \cdot \sqrt{L}} \right)^2 \quad (2.116)$$

On the other hand, the capacitance is also used to filter the converter output voltage ripple. Normally the DC/DC converter output voltage ripple should be less than 1% of the output voltage:

$$\Delta V_{O \ max} \leq 1\% \cdot V_{O \ max} \quad (2.117)$$

Thus the minimum capacitance value can be obtained:

$$C > \frac{\Delta V_{O \ max} \cdot T_{PWM}^2}{8 \cdot L \cdot \Delta V_{O \ max}} \quad (2.118)$$

The buck converter (IGBT switch) is controlled by a classic PI (Proportional Integral) closed loop with an anti-windup feedback. The controller coefficient,  $K_p$ ,  $K_i$  and  $K_t$  (anti-windup) are adjusted during experimentation using the Ziegler-Nichols tuning rule.

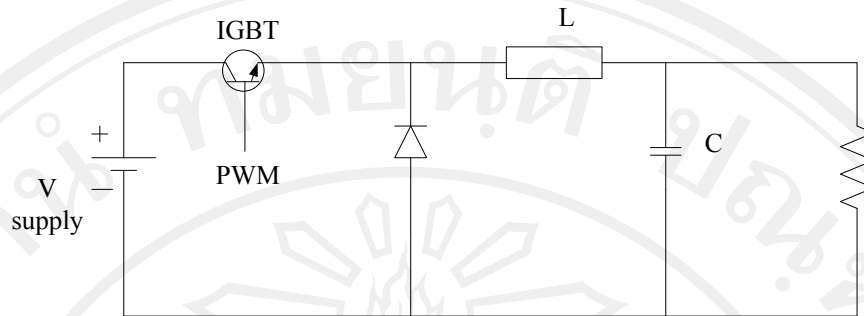


Figure 2.6 Schematic diagram of the buck converter

## 2.5 Hybrid Technology

Hybrid power system generally integrates two or more energy sources. The most commonly energy source uses to provide electric power is internal combustion engine generator (electric generator) combined with renewable energy sources, such as batteries, photovoltaic, wind turbine, and fuel cell. The role of integrating renewable energy in a hybrid power system is primarily to save fuel. There are generally two accepted hybrid power system configurations:

- Systems based mainly on electric generators (Energy source #1) with renewable energy (Energy source #2) used for reducing fuel consumption as shown in Figure 2.7; and
- Systems relying on the renewable energy source with an electric generator used as a backup supply for extended periods of low renewable energy input or high load demand.

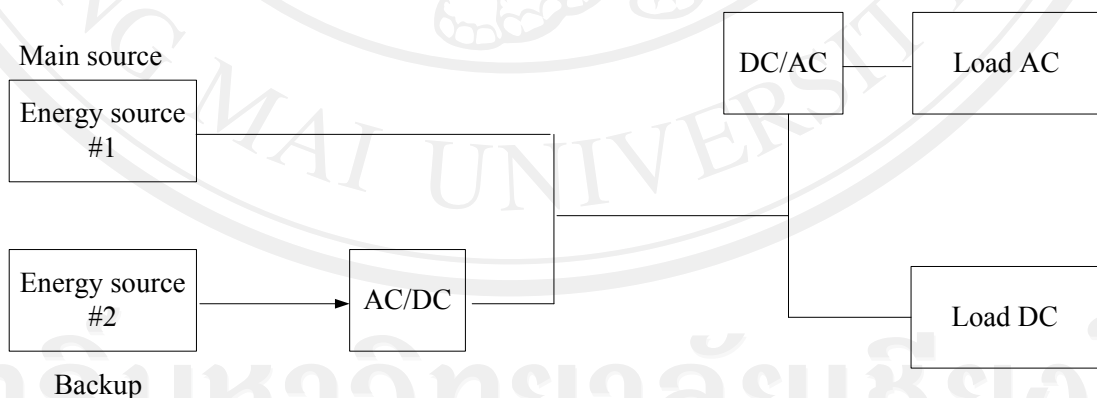


Figure 2.7 Diagram of hybrid system with two power sources connected to electronic load

The application of fuel cell technologies to advanced power generation systems signifies the most significant advancement in energy conservation and environmental protection for the next decade. Fuel cells represent the most important new power generation technology of this decade and the technology's successful emergence is constrained in the absence of an institutional magnet that can attract and coalesce the

various stakeholders into an integrated effort to pursue technical development and raise awareness of fuel cells. One example of a major new fuel cell technology is the Hybrid System where a fuel cell is combined with another power generation device to create a synergy with attributes that exceed the sum of the two when combined.

### 2.5.1 Components of Hybrid Power System

A typical hybrid power system may contain a combination of:

- Renewable energy sources (PV, fuel cell, and wind turbine)
- Internal combustion generators (gasoline engine or diesel engine)

Many of researchers study in hybrid system with different type of energy power sources, such as Praya (2008) shows the hybrid system of wind and solar energy. The hybrid system consists of PV solar–wind and conventional backup source i.e. diesel or grid as shown in Figure 2.8

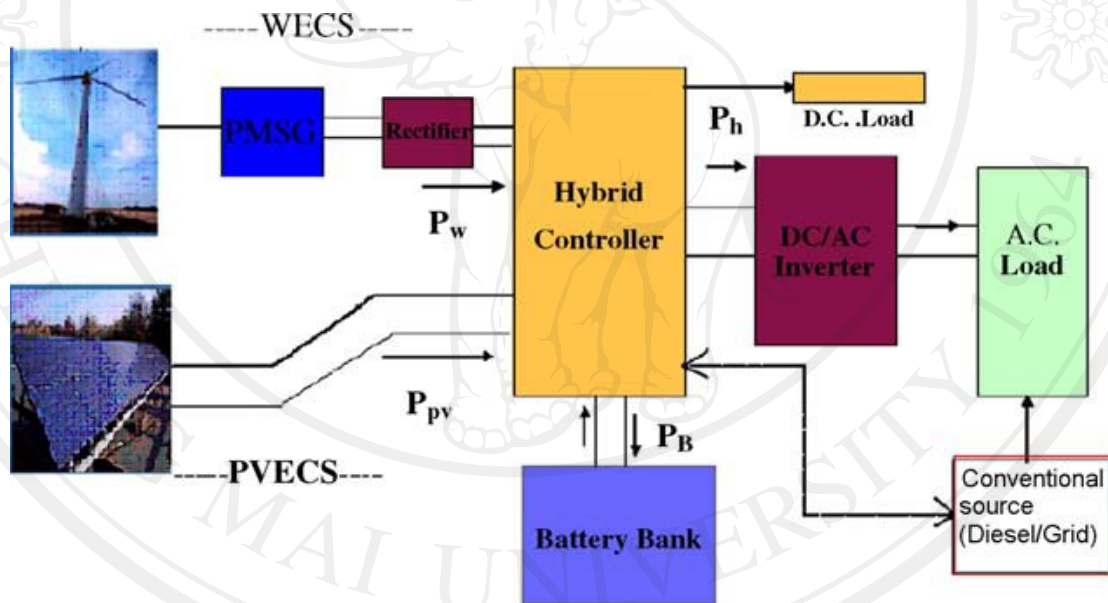


Figure 2.8 Concept diagrams of hybrid energy systems (Praya et al, 2008)

Andrew F. Burke (2007) studied hybrid system for vehicles. The objectives of this research is to study how to improve driveline efficiency or to provide for the use of energy sources other than fossil fuel for road transportation, engine powered hybrid-electric and fuel cell powered cars are being developed by auto companies. The drivelines of the vehicles utilize electric motors and electrical energy storage to supplement the output of the engine during vehicle acceleration and cruise and for energy recovery during braking. The energy storage technology being utilized is rechargeable batteries and ultra-capacitors. The energy storage units can be recharged from the engine or fuel cell or from the renewable energy much like an electric vehicle. The different design approaches are evaluated using detailed simulation results and when available, vehicle test data. The characteristics of the energy storage

and fuel cell components used in the vehicle simulations correspond to the present status of those technologies as well as projected future improvements in their performance. The vehicles can use both liquid or gaseous fuels and grid electricity. One of the attractive features of the plug-in hybrid vehicle is that it permits the use of grid electricity generated using energy sources other than petroleum. This study is concerned with the design and performance of electric battery powered, charge sustaining and plug-in hybrid vehicles using engines, and fuel cell powered vehicles using hydrogen. The characteristics of the energy storage and fuel cell components used in the vehicle simulations correspond to the present status of those technologies as well as projected future improvements in their performance. The application of batteries and ultra-capacitors in electric energy storage units for battery powered (EV) and charge sustaining and plug-in hybrid-electric (HEV and PHEV) vehicles have been studied in detail. The use of both IC engines and hydrogen fuel cells as the primary energy converters for the hybrid vehicles was evaluated and compared. The study focused on the use of lithium-ion batteries and carbon/carbon ultra-capacitors as the energy storage technologies most likely to be used in the future vehicles. Figure 2.9 shows schematic of a fuel cell vehicle driveline.

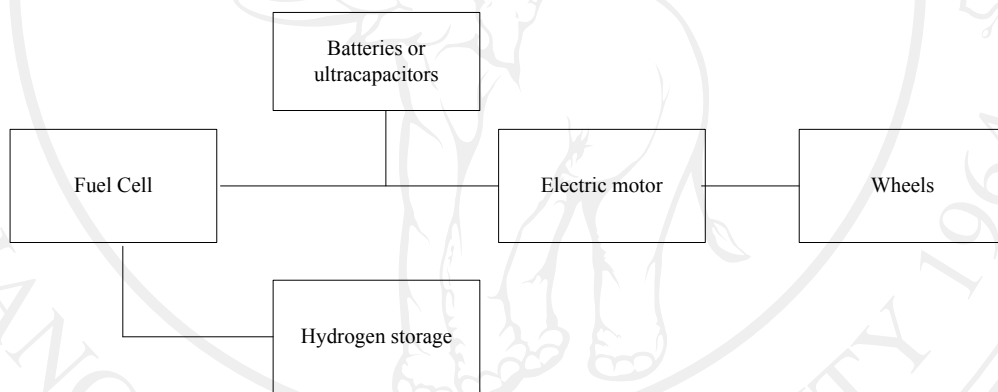


Figure 2.9 Schematic of a fuel cell vehicle driveline

Yong et al (2001) studied a hybrid system which combined a 2 kW air blowing PEM fuel cell and lead-acid battery system for lightweight electric vehicle application. Hybrid electric vehicle (HEV) has arisen globally due to the pressing environmental concerns and skyrocketing price of oil. Representing a revolutionary change in vehicle design philosophy, hybrid vehicles surfaced in many different ways. However, they share the hybrid power-train that combines multiple power sources of different nature, including conventional internal combustion engines (ICE), batteries, ultra-capacitors, or hydrogen fuel cells (FC). This vehicle with onboard energy storage devices and electric drives allows braking power to be recovered and ensures the ICE to operate only in the most efficient mode, thus improving fuel economy and reducing pollutants. As a product of advanced design philosophy and component technology, the maturing and commercialization of HEV technologies demand extensive research and developments. This research intends to address many key issues in the development of HEV. A fuel cell hybrid electric vehicle operates solely on electric power. The fuel cells continuously produce electrical power while energy storage devices buffer the power flow in the electric power train. A fuel cell system is

an electric power-generating plant based on controlled electrochemical reactions of fuel and oxidant. In principle, fuel cells are more efficient in energy conversion and produce zero emission. HEV Classifications by drive-train Architectures One of the most common ways to classify HEV is based on configuration of the vehicle drive-train. In this section, three major hybrid vehicle architectures introduced are series, parallel and series-parallel. Until recently, many HEV in production are either series or parallel. In terms of mechanical structure, these two are primitive and relatively simple. A series-parallel power-train brings in more degrees of freedom to vehicle engine operation with added system complexity. Series Hybrid is one of the basic types of HE. In this configuration, the ICE is used to generate electricity in a generator. Electric power produced by the generator goes to either the motor or energy storage systems. The hybrid power is summed at an electrical node, the motor. The series hybrid configuration tends to have a high efficiency at its engine operation.

From the fundamental theory and basic equations of both proton exchange membrane fuel cell and hybrid technologies, they will be used to develop the mathematical model of the proton exchange membrane fuel cell and hybrid system.

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