CHAPTER 2

Theory

2.1. Fuel Cell

Fuel cells are promising and clean technology which can generate electrical energy by converting electrochemical reactions from their fuels. Because the electricity is generated without combustion or mechanical work from fuel cells, the efficiency of fuel cells is greater than that of conventional systems that use fossil fuel as a raw material. Typically, the main components of fuel cells are an electrolyte set up between a positive and negative electrode (anode and cathode, respectively). The components of the fuel cell are similar to a battery but the fuel cell principle is different. That is, fuel cells can generate electricity until their fuel is depleted. This differs from a battery, as when the charge from electrochemical reaction of the battery is completely consumed, the battery can no longer generate the electricity.

There are five common types of fuel cells, solid oxide fuel cells (SOFCs), molten carbonate fuel cells (MCFCs), phosphoric acid fuel cells (PAFCs), alkaline fuel cells (AFCs) and PEMFCs. These are classified by their individual electrolyte, electrode and supplied fuel. For example, the electrolyte usually used in SOFCs is solid non-porous metal oxide, Y_2O_3-stabilized ZrO_2 (YSZ), where oxygen ions are conducted during electrochemical reactions. These fuel cells operate at a temperature around 800–1000 ºC. MCFCs use combined alkali (Li, Na, K) bonded carbonyl group retained in a $LiAlO_2$ ceramic matrix as electrolyte. In the electrochemical reaction, the carbonate ions are conducted in the electrolyte to generate electricity. Since MCFCs are operated at high temperatures of 600 and 700ºC, they do not require noble metal catalysts to accelerate the electrochemical reaction. PAFCs use phosphoric acid with a concentration of around 100% as electrolyte, usually retained in a matrix of SiC. During electrochemical reaction, hydrogen ions are driven in the electrolyte.

Table 2.1 Classification of fuel cells [43]

Fuel cell type	Electrolyte	Electrode	Catalyst	Operating temperature	Charge carrier	Product
SOFC	Perovskites (Ceramics)	Perovskite and perovskite / metal cermet	Electrode material	800 – 1000ºC	O^-	Gaseous product
MCFC	Immobilized Liquid molten carbonate in $LiAlO_2$	Nickel and Nickel oxide	Electrode material	600 – 700ºC	CO_3^-	Gaseous product
PAFC	Immobilized liquid phosphoric acid in SiC	Carbon	Platinum	150 – 220ºC	H^+	Evaporative water
AFC	Mobilized or immobilized potassium hydroxide in asbestos matrix	Transition metals	Platinum	65 – 220ºC	OH^-	Evaporative water
PEMFC	Hydrated polymeric ion exchange membranes	Carbon	Platinum, platinum alloy, non-precious metals	40 – 80ºC	H^+	Evaporative water

A platinum catalyst is used in both the anode and cathode. Typically, PAFCs are operated at temperatures of 150–220ºC. AFCs use KOH as electrode maintained in the matrix (usually asbestos). A high concentration (85 wt.%) and lower concentration (35–50 wt.%) of KOH are used to operate at high temperature (250ºC) and low temperature

(<120ºC), respectively. The ions carried in the electrolyte are hydroxide ions. Their electrode is composed of a wide range of catalysts, such as Ni, Ag, metal oxides, and noble metals. AFCs are not tolerant of CO_2 from their fuel or oxidant. PEMFCs use thin proton conductive polymer (<50 μm), typically fluorinated sulfonic acid polymer or another similar polymer, as the electrolyte membrane. The electrocatalyst is generally platinum (Pt) supported on various types of carbon particle. Pt alloy or non-precious metal can be used instead of Pt in order to keep down the cost of the electrocatalyst. Hydrogen and oxygen or air are the anode and cathode reactant gases for this fuel cell, respectively. During electrochemical reaction, positive hydrogen ions (protons) released from the oxidation reaction (anode) are conducted through a polymer electrolyte membrane that allows only protons to pass. The electrons that cannot pass are conducted through electrically conductive components to be utilized as electricity. Protons and electrons are reacted with oxidant gas at the cathode to complete the reduction and then water is generated as the byproduct of this fuel cell. The operating temperature of this fuel cell is around 40–80ºC. Major different types of fuel cells are summarized in Table 2.1.

From Table 2.1, it can be seen that PEMFCs can generate electricity by releasing the lowest temperature from the reaction of H_2 and O_2/air compared with other fuel cells. Since the PEMFC operates in the low temperature range, heat losses are also small. This means that PEMFCs operate with high efficiency, fast heat-up and heat-down (fast startup and shutdown). Moreover, PEMFCs can be operated at atmospheric pressure. Due to these advantages of PEMFCs, they are widely applied as power sources for transportation, residential use, industry and electrical appliances.

2.2. Principle of PEM fuel cell

A single cell of the PEM fuel cell comprises three main components: flow field plates, GDLs and MEA, connected together with a tightening force. The MEA is set up at the center and respectively sandwiched by the GDLs and flow field plates on the anode and cathode as shown in Figure 2.1. Flow fields are characterized as electrical conductor plates that have flow field channels of various shapes, such as serpentine, parallel, pin-

type, interdigitated etc. [44], fully existing in the active area. GDLs are characterized as microporous plates which can be made from paper or cloth. The MEA is composed of catalyst layers or electrodes coated on both sides of the electrolyte membrane.

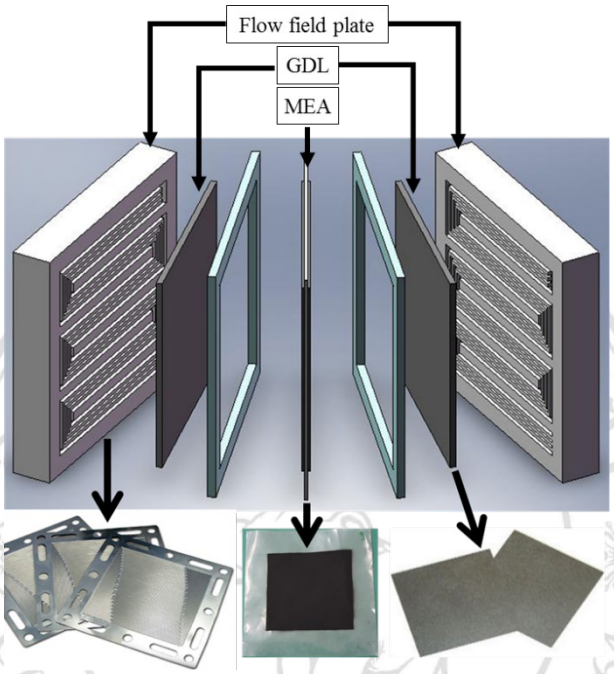

Figure 2.1 Schematic of a single cell's components in PEM fuel cell

The PEM fuel cell can generate electricity by the following processes. The reactant gas, typically hydrogen and oxygen or air, is fed into the cell at the anode and cathode, respectively. Both types of reactant gas are forced to flow in the flow field plates, which have flow channels as guidelines for them. While flowing on each side of the flow field plate, the reactant gas also simultaneously diffuses though the GDL which makes it disperse well. When the hydrogen gas from the anode is diffused to the center of the cell, at the MEA, it disintegrates into protons and electrons at the catalyst layers. This indicates the oxidation reaction (1). Protons released from the oxidation reaction are conducted through the electrolyte membrane, which allows only protons to pass. Electrons which cannot pass through the membrane are conducted through electrically conductive components to be utilized as electricity. The protons and electrons react with oxygen, the oxidant gas at the cathode, to complete the reduction and then water is generated as a byproduct (2). The overall reaction which takes place in the PEM fuel cell is presented in the third equation below (3).

Oxidation reaction $H_2 \rightarrow 2H^+ + 2e^-$ anode process (1)

Reduction reaction $\frac{1}{2}O_2 + 2e^- + 2H^+ \rightarrow H_2O$ cathode process (2)

Overall reaction $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ (3)

2.3. PEM fuel cell current [43]

As the electrochemical reaction proceeds, there are charge and reactance transfers. Electrons released and consumed during the electrochemical reaction are proportional to the consumed reactance. This also relates directly to the electrical current generation, as described by Faraday's law:

$$i = nFj \tag{4}$$

where i is the current density (A/cm^2), nF is the charge transferred (coulombs/mol) and j is the flux of reactant per unit area (mol/s·cm^2).

In general electrochemical reactions, there are both oxidation and reduction reactions (forward and backward reactions, respectively) as instanced in Equation (1) and (2). The reactant consumption is proportional to the reactant surface concentration. The reactant flux is:

$$j = kC \tag{5}$$

where k is the reaction rate coefficient. It also represents the forward reaction rate coefficient (k_f) and backward reaction rate coefficient (k_b). C is the reactant surface concentration. It also represents the surface concentration of the oxidation reactant (C_{Ox}) and surface concentration of the oxidation reactant (C_{Rd}).

Substituting Equation (5) into (4) gives:

$$i = nFkC \tag{6}$$

2.3.1. Reaction rate

Arrhenius was the first person to recognize the relationship between the rate constant and temperature, as follows:

$$k = A\exp\left(\frac{-E_A}{RT}\right) \tag{7}$$

where E_A is the activation energy, which refers to energy obstructing the proceeding of the reaction. It is also well known as the standard internal energy, which relates to the standard enthalpy of activation (ΔH), and work change, Δ(PV). Since the work change in an electrochemical reaction is usually negligible, the standard enthalpy is equal to the standard internal energy. This also relates with the Gibbs free energy (ΔG) as follows:

$$k = A\exp\left(\frac{-\Delta H - T\Delta S}{RT}\right) k = A\exp\left(\frac{-\Delta G}{RT}\right) \tag{8}$$

The rate constant of Arrhenius is developed into the relationship of Boltzmann and Planck's constant as follows:

$$k = \frac{k_B T}{h}\exp\left(\frac{-\Delta G}{RT}\right) \tag{9}$$

where k_B is Boltzmann's constant (1.38049 $\times 10^{-23}$ J/K) and h is Planck's constant (6.621 $\times 10^{-34}$ Js).

Substituting Equation (9) into (6), the fuel cell current gives:

$$i = nF\frac{k_B CT}{h}\exp\left(\frac{-\Delta G}{RT}\right) \tag{10}$$

2.4. PEM fuel cell potential [43]

2.4.1. Effect of temperature on Gibbs free energy

According to reaction (3), if this reaction is combustion, the heats generated from this reaction are enthalpy. But in the fuel cell, the reaction is an electrochemical reaction. The heats cannot be completely converted into electricity due to an irreversible loss of energy called entropy. The enthalpy change and entropy change correspond to Gibbs free energy change as the following equation:

$$\Delta G = \Delta H - T\Delta S \tag{15}$$

where ΔH is the enthalpy change (kJ/mol) and ΔS is the entropy change (kJ/mol·K).

Gibbs free energy is also dependent on temperature because enthalpy and entropy are functions of temperature. At any temperature, the enthalpy, H_T and entropy, S_T can be found by the following equation:

$$H_T = H_{298} + \int_{298}^{T} C_P dT \tag{16}$$

$$S_T = S_{298} + \int_{298}^{T} \frac{C_p}{T} dT \tag{17}$$

where H_{298} is the enthalpy at standard temperature and S_{298} is the entropy at standard temperature.

The value of specific heat, C_P also varies with temperature as in the following equation:

$$C_P = a + bT + cT^2 \tag{18}$$

where *a*, *b*, and *c* are empirical constants.

In PEMFCs, the operating temperature is usually below 100°C, where the changes of C_p, ΔH, and ΔS are very small. Therefore, this value can be neglected.

2.4.2. Effect of pressure on Gibbs free energy

Gibbs free energy is a function not only of temperature but also of pressure, as in the following equation:

$$dG = V_m dP \tag{19}$$

where V_m is the molar volume, m^3/mol and P is the pressure, Pa
For an ideal gas:

$$PV_m = RT \tag{20}$$

where R is the gas constant (8.314 J/·K mol).

Substituting Equation (20) into (19) and integrating gives:

$$G = G_0 + RT\, ln\left(\frac{P}{P_0}\right) \tag{21}$$

where G_0 is the Gibbs free energy at the standard temperature of 25°C and standard pressure of 1 atm and P_0 is the standard pressure, 1atm.

For any chemical reaction shown in Equation (22), the Gibbs free energy change is equal to Equation (23):

$$\alpha A + \beta B = cC + \delta D \tag{22}$$

$$\Delta G = cG_C + \delta G_D - \alpha G_A - \beta G_B \tag{23}$$

Substituting Equation (23) into Equation (21) yields the equation known as the Nernst equation:

$$\Delta G = \Delta G_0 + RT\, ln\left[\frac{\left(\frac{p_C}{p_0}\right)^c \left(\frac{p_D}{p_0}\right)^\delta}{\left(\frac{p_A}{p_0}\right)^\alpha \left(\frac{p_B}{p_0}\right)^\beta}\right] \tag{24}$$

$$\Delta G = \Delta G_0 + RT\, ln\left[\frac{(p_C)^c (p_D)^\delta}{(p_A)^\alpha (p_B)^\beta}\right]$$

For the electrochemical reaction of hydrogen and oxygen, substituting Equation (3) into Equation (21) yields the Nernst equation of the PEM fuel cell:

$$\Delta G = \Delta G_0 + RT\, ln\left[\frac{\left(p_{H_2O}\right)}{\left(p_{H_2}\right)\left(p_{O_2}\right)^{1/2}}\right] \tag{25}$$

Combining the effect of temperature in Equation (15) and the effect of pressure in Equation (25) on Gibbs free energy provides:

$$\Delta G = [\Delta H - T\Delta S] + \Delta G_0 + RT\, ln\left[\frac{\left(p_{H_2O}\right)}{\left(p_{H_2}\right)\left(p_{O_2}\right)^{1/2}}\right] \tag{26}$$

Substituting Equation (26) into Equation (14) gives the PEM fuel cell potential under the effects of temperature and pressure:

$$E = -\left[\frac{\Delta H - T\Delta S}{nF}\right] + \left[E_0 + \frac{RT}{nF} ln\left[\frac{\left(p_{H_2}\right)\left(p_{O_2}\right)^{1/2}}{\left(p_{H_2O}\right)}\right]\right] \quad (27)$$

$$\Delta E = -\left[\frac{\Delta H - T\Delta S}{nF}\right] + \left[\frac{RT}{nF} ln\left[\frac{\left(p_{H_2}\right)\left(p_{O_2}\right)^{1/2}}{\left(p_{H_2O}\right)}\right]\right]$$

At 25ºC and atmospheric pressure, the enthalpy change or the different heat between the product formation and reactants is equal to 268 kJ/mol, while the entropy change is approximately 0.178 kJ/mol·K. Therefore, the Gibbs free energy change as the effect of temperature is 273.34 kJ/mol. This makes the theoretical potential in the first term of Equation (27) equal to 1.23 V.

$$\Delta E = -\left[\frac{273.34 - 273(0.178)\ \text{J/mol}}{2 \times 96,485\ \text{As/mol}}\right] + \left[\frac{RT}{nF} ln[1]\right] \quad (28)$$

$$\Delta E = 1.23\ \text{Volts}$$

If air is used as the oxidant gas at the cathode instead of oxygen, the partial pressure is proportionally decreased by the concentration of oxygen in air (0.21). The PEM fuel cell potential yield is:

$$\Delta E = -\left[\frac{\Delta H - T\Delta S}{nF}\right] + \left[\frac{RT}{nF} ln\left[\frac{\left(p_{H_2}\right)\left(p_{O_2}\right)^{1/2}}{\left(p_{H_2O}\right)}\right]\right] \quad (29)$$

$$\Delta E = -[1.23] + \left[\frac{8.314\ (273)}{2 \times 96,485} ln\left[\frac{(1)(0.21)^{1/2}}{(1)}\right]\right] = 1.189\text{V}$$

2.5. Current and potential relationship of PEM fuel cell [43]

According to Equation (10), if the activation energy is changed by increasing or decreasing, the potential will be changed by relating with the changing electron on the electrode by $-F\Delta E = -F(E - E_0)$; therefore, the Gibbs free energy performs in chemical and electrical terms because it occurs in the presence of an electrical field:

For a reduction reaction:

$$\Delta G = \Delta G_{ch} + \alpha_{Rd} FE \tag{30}$$

For an oxidation reaction:

$$\Delta G = \Delta G_{ch} - \alpha_{Ox} FE \tag{31}$$

where ΔG_{ch} is the chemical term of Gibbs free energy, F is Faraday's constant, E is the potential and α is the transfer coefficient. If the activation energy of the forward reaction is equal to the backward reaction, $\alpha = 0.5$, but if not, $0 \leq \alpha < 0.5$ or $0.5 < \alpha \leq 1.0$. The value of α depends on the activation barrier. For most electrochemical reactions, it is mostly in the range of 0.3–0.7. In the case of lacking actual measurements, it is approximately 0.5.

Therefore, the net current for forward and backward reaction is

$$i = nF\left[k_{0,f} C_{Ox} exp\left[\frac{-\alpha_{Rd} FE}{RT}\right] - k_{0,b} C_{Rd} exp\left[\frac{\alpha_{Ox} FE}{RT}\right]\right] \tag{32}$$

Due to the simultaneous forward and backward proceedings of the reaction, at equilibrium, the E_r and net current is zero. The rate at which these reactions proceed is called the exchange current density, i_0.

$$i_0 = nFk_{0,f} C_{Ox} exp\left[\frac{-\alpha_{Rd} FE_r}{RT}\right] = nFk_{0,b} C_{Rd} exp\left[\frac{\alpha_{Ox} FE_r}{RT}\right] \tag{33}$$

Combining Equation (32) and (33) obtains the relationship of current and potential for the PEM fuel cell. This is well known as the **Butler–Volmer Equation** as follows:

$$i = i_0 \left[exp\left[\frac{-\alpha_{Rd} F\left(E - E_r\right)}{RT} \right] - exp\left[\frac{\alpha_{Ox} F\left(E - E_r\right)}{RT} \right] \right] \tag{34}$$

where i is the current density, α_{Rd} is the transfer coefficient of oxygen reduction, α_{Ox} is the transfer coefficient of hydrogen oxidation, E_r is the reversible or equilibrium potential (0 V at the fuel cell anode, 1.229 V at the cathode with conditions of 25°C and atmospheric pressure) and E is the electrode potential. The difference between E and E_r is called the overpotential.

Normally, the exchange current density can be examined by extrapolating a plot of log i versus cell voltage at the activation loss region (V_{act}). The exchange current density relates to the speed of the electrochemical reaction proceeding in the electrode. It is similar to the rate constant in chemical reactions, but a small difference from the rate constant is the concentration dependence. A higher exchange current density leads to a lower barrier for the electrons to overcome, higher ECSA and consequently better fuel cell performance. At any temperature and pressure, the effective exchange current density can be determined by the following equation:

$$i_0 = i_0^{ref} a_c L_c \left(\frac{P_r}{P_r^{ref}} \right)^{\gamma} exp\left[-\frac{E_C}{RT}\left(1 - \frac{T}{T_{ref}}\right) \right] \tag{35}$$

where

i_0^{ref} is the exchange current density at 25 °C and 1 atm (A/cm^2)

a_c is the catalyst specific area (cm^2/mg)

L_c is the catalyst loading (mg/cm^2)

P_r is the reactant partial pressure (kPa)

P_r^{ref} is the reference pressure (kPa)

γ is the pressure coefficient (0.5 to 1.0)

E_c is the activation energy (66 kJ/mol for the reaction of oxygen on Pt)