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CHAPTER 2

THEORIES

2.1 Fuel cells

Fuel cell is an electrochemical device that generates electrical energy from chemical energy without combustion [FT, 2005]. Its principle concept was first demonstrated by William R.Grove in 1839, as called gaseous voltaic battery. The name 'fuel cell' was invented by Ludwig Mond and Charles Langer in 1889. After that, several types of fuel cell were developed for different applications. In 1959, the truly workable fuel cell –which was a 5 kW alkaline fuel cell (AFC) – was established by Francis Thomas Bacon. The first step in developing fuel cell technology was started by The National Aeronautics and Space Administration (NASA) in 1960s. The oil crisis and worldwide concern about global warming problem were the main force for the continued improvement of the fuel cell. In 1990s, the first fuel cells vehicle was presented by the Canadian company, Ballard.

2.1.1 Advantages of fuel cells

- Low environment impact.
- High efficiency
- Continuous operating
- Low noise

2.1.2 Disadvantage of fuel cells

- High investment cost compared with other generator system
- Fuel accessibility and storage
- Material duration of the fuel cell components.

2.2 Types of Fuel Cells

During 1960s, several types of fuel cells had been originally developed. They can be classified according to their different electrolytes, electro-catalysts, operating conditions, anode and cathode reactions, and the dominant moving ion through the electrolyte. The different types of fuel cell are summarized in Table 2.1 [FC handbook, 7th].

Table2.1 Summary of different types of fuel cell technology

Fuel cell type	Abbreviation	Electrolyte	Operating temperature (°C)
Alkaline	AFC	Potassium hydroxide	50-90
Proton Exchange Membrane	PEMFC	Hydrated polymeric ion exchange membrane	50-125
Phosphoric acid	PAFC	Phosphoric acid	190-210
Molten carbonate	MCFC	Molten carbonate	630-650
Solid oxide	SOFC	Ceramic	700-1100

The Alkaline Fuel Cell (AFC): this type of fuel cell has been developed by NASA for the Apollo moon spaceship module. The common electrolyte is potassium hydroxide (KHO). Hydrogen is oxidized by hydroxide to provide electrons and also produce CO_2. Since CO_2 is not rejected by KOH solution, electro-catalytes are easily poisoned. However, the AFC are the cheapest fuel cells.

Proton Exchange Membrane Fuel Cell (PEMFC): for this type of fuel cell, the electrolyte is solid polymer membrane. The performance of this electrolyte depends on the amount of water. If humidity of the feed gas is too high, content of steam can flood the membrane. On the other hand, the low content of steam can dry the cell. In both cases, power output will drop. PEMFC is the top candidate fuel cell for transportation or mobile applications. Currently, methanol can also be fed directly into PEMFC without reforming unit, so it is called direct methanol fuel cell (DMFC). However, the performance of this type is still low due to an unresponsive dynamic behavior and high methanol permeation (though membrane). Furthermore, methanol is also poisonous for membrane and electrodes.

Phosphoric acid fuel cell (PAFC): PAFC is the first commercial fuel cells with a phosphoric acid as the electrolyte with an operating range from 150°C to 220°C. It was continuously developed by UTC Fuel Cells in U.S. and Fuji Electric Corporation, Toshiba Corporation, and Mitsubishi Electric Corporation in Japan.

Molten carbonate fuel cell (MCFC) and **Solid oxide fuel cell (SOFC)**: both types of fuel cells are operated at high temperature (600-1000°C). For MCFC, molten alkaline carbonate is used as electrolyte which formed the carbonate ion (instead of oxygen ion) at the positive electrode. Although CO_2 is poisonous for the fuel cells, it needs to be supplied to the cathode together with oxygen in order to convert to the carbonate ion. SOFC, which is the main focus in this research, is described in the next section.

2.3 Solid Oxide Fuel Cells (SOFCs)

SOFCs are the systems which directly convert chemical energy to electrical energy. Each cell consists of porous ceramic electrodes, an anode and a cathode separated by a solid ceramic electrolyte. SOFC are developed for stationary applications with an output from 1 kW to 2 MW. They are operated at high temperature (700-1100°C) [Park *et al.*,2002] and atmospheric or elevated pressures. During operation, oxygen ions from the cathode transmit through the solid electrolyte to the anode in order to chemically react with the fuel. This reaction also produces water and carbon dioxides while liberates electrons flow block to the interface of the cathode and electrolyte via an external circuit. The overall reaction is exothermic. The electrochemical reactions are showed in Table 2.2.

Table 2.2 Electrochemical reactions in a SOFC [Park, 2002]

Anode reaction	Cathode reaction	Overall reaction
$H_2 + O^{2-} \rightarrow H_2O + 2e^-$	$O^2 + 4e^- \rightarrow 2O^{2-}$	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$
$CO + O^{2-} \rightarrow CO^2 + 2e^-$		$CO + \frac{1}{2} O_2 \rightarrow CO_2$

Since only H_2 and CO can be utilized in the fuel cell, primary fuel feed stock has to be reformed to hydrogen rich gas phase. The perform method for hydrogen production is catalytic stream reforming. Because of this process is endothermic reaction, a reformer is thermodynamically favored at high temperature. In addition, the reformer may be located separately or internally from a fuel cell stack, called "external and internal reforming".

2.3.1 Principle of SOFC Operation

As well as battery and internal combustion engine, the final product of fuel cell is electricity. In case of internal combustion engine, chemical energy has to be converted to mechanical engine before generating electricity whereas the chemical energy is converted directly to power in the case of the fuel cells. According to the principle mechanism of fuel cell, fuel is oxidized to generate electricity. As you can see in Fig.2.1, hydrogen and air are used as fuel and oxidant, respectively. At anode, hydrogen rich gas is separated to hydrogen's positive charges (protons) and electrons over electrocatalyst.

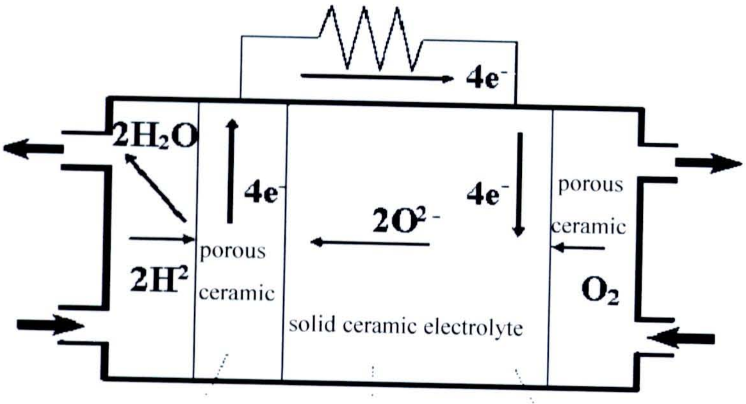
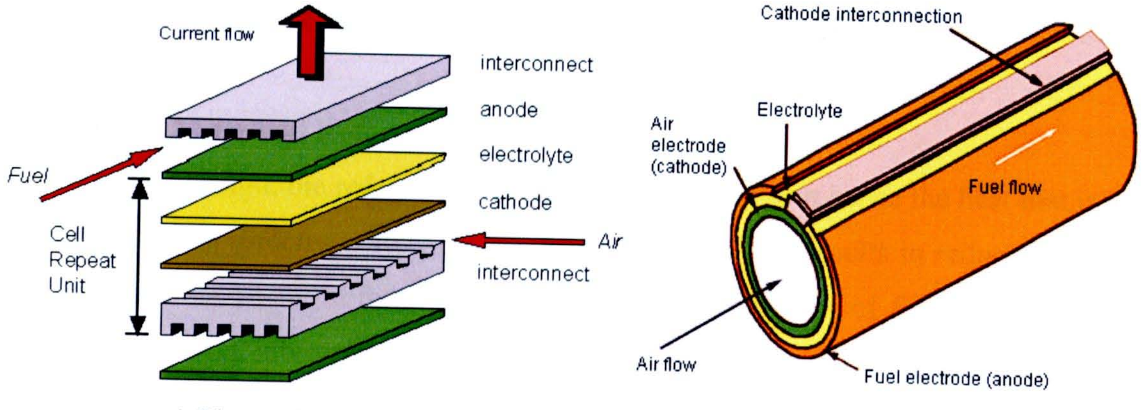


Figure 2.1 SOFC operation

Oxygen is reduced to oxygen ions at cathode. Then oxygen ions migrate though the electrolyte to combine with protons, to form water. Electron is moved by the difference of potential of two electrodes. Since electrons can not pass though electrolyte to cathode, they travel via external circuit, resulting in electric current [Larminie and Dicks, 2000].

2.3.2 Solid Oxide Fuel Cell Stack Design

For the actual power usage, it is necessary to combine single cells together in muti-cell or stack. Typically, the SOFC is fabricated into two geometries: planar and tubular (Fig. 2.2).



a) Planar design b) Tubular design

Figure 2.2 Typical designs for solid oxide fuel cell stacks: a) Planar design b) Tubular design

2.3.3 Solid Oxide Fuel Cell Reforming Concept

Since only H_2 and CO are benefit for power generation of SOFC technology, the primary fuels (hydrocarbon compounds) have to be reformed into hydrogen rich gas before being fed into the cell. Normally, a reformer is separated from the cell. In the case of high temperature fuel cell, the reformer is integrated with the cell in order to transfer the liberated heat from the cell to the reformer, as known autothermal operation. Therefore, the possible reforming concepts of SOFC are external and internal reforming configuration

2.3.3.1 External Reforming

In this design, the reformer is separated from the fuel cell stack. Thus, fuel [Eguchi, 2003] is converted to hydrogen in the reformer before being introduced to the fuel cell chamber. According to this operation, the heat liberated from fuel cell stack is not utilized so it is necessary to supply the heat toward the reformer. In order to use the waste heat, the fuel recycling anode gases system is developed. But the inlet fuel maybe diluted by the anode exit gases that lead to reduce the open circuit voltage [Richard, 1998; Larminie and Dicks, 2000].

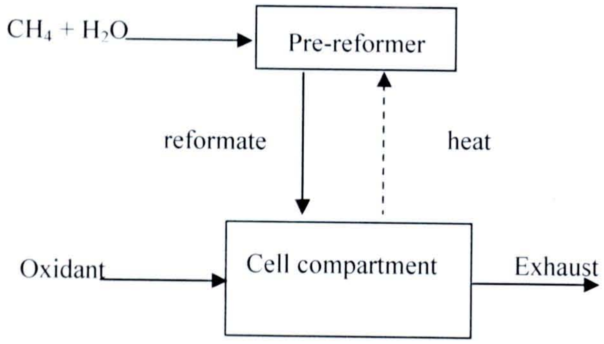


Figure 2.3 Basic designs of external SOFCs [Eguchi, 2003]

2.3.3.2 Internal Reforming (IR)

In this design, the reformer is located in fuel cell system hence the heat that is released from the stack is directly utilized in the reforming unit. This results in reducing the external heat requirement of the reformer and the cooling requirement of fuel cells. Compared to external reforming, internal reforming has many advantages: reduced system complication, as explained above, reduced system cost, increased system efficiency. [Larminie and Dicks, 2000] However, several key parameters must be considered i.e. type of fuel, electro-catalysts activity, reactivity of production gases and efficiency of respective fuel direct reaction of hydrocarbon on the electrode, carbon formation, and thermal management.

The internal reforming of a SOFC has two alternative procedures: Direct Internal Reforming (DIR-SOFC) and Indirect Internal Reforming Internal Reforming (IIR-SOFC).

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2.3.3.2.1 Direct Internal Reforming [Park *et al.*,2002; EG&G,2006]

The reforming reaction is carried out directly at the anode. Hydrogen is consumed continuously that results in high methane conversion and more uniform temperature distribution. However, this approach has suffered from two main problems. Firstly, the catalysts deactivation, coke formation, leads to decrease the system efficiency. Secondly, the large temperature gradient across the cell is resulted of the extremely endothermic reaction, as known as the cooling effect. Thus, high carbon resistant and high durability are required for the anode material.

2.3.3.2.2 Indirect Internal Reforming [Park *et al.*,2002, Eguchi,2003]

The catalytic reformer is not inside the fuel cell system but it is in close thermal contact with the anode. Thus, the released heat from the stack can be used for the reforming reaction and the reforming catalyst and anode material can be optimized individually. Although the reformer is adjacent to the cell stack, in this approach, their physical environments do not get the direct influence to each other. [EG&G,2006]. However, its location causes the mismatch problem between the thermal loadings, associated with the rate of steam reforming at typical SOFC conditions, this problem can occur. Both planar and tubular designs are the possible geometry of IIR system. These had been proposed from several previous researchers. In IIR-planar configuration, the plate reformer is alternated with small cell packages so that the inlet fuel from each cell is fed to adjacent cells such as the integrated planner SOFC of Gardner *et al.* (2000). One of possible tubular design is the work of Aguiar *et.al* (2001). In this work, a reformer was the inner tube which was encircled with the fuel cell and the air channel was the outside.

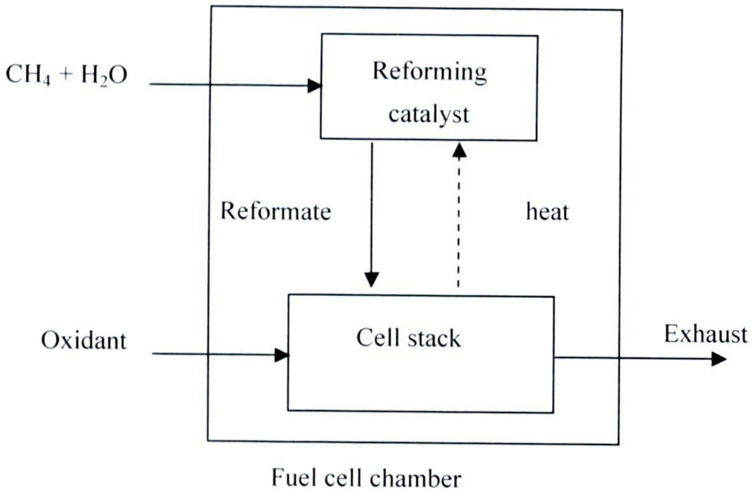

Figure 2.4 basic designs of IIR-SOFCs [Eguchi, 2003]

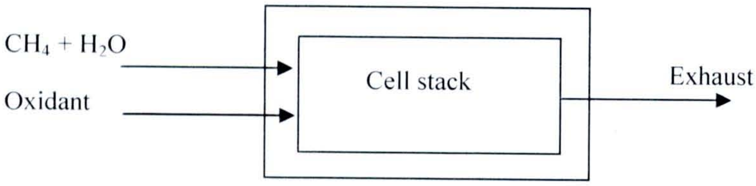

Figure 2.5 basic designs of DIR-SOFCs [Eguchi, 2003]

2.4 Autothermal operation

The autothermal operation has been of interest in education and industry during the last decade [Kolios *et al.*, 2000]. Integration of regenerative and recuperative heat exchanger and reactor within one part of the equipment is the main concept of this operation. Its advantages are heat loss minimization and less sensitivity to perturbations due to its natural adaptively [Frauhammera *et al.*, 1999]. The existing autothermal reactor contributions are based on different heat recovery systems: the reverse-flow reactor using direct or regenerative heat exchange and the counter-current fixed-bed reactor using indirect or recuperative heat exchange [Frauhammera *et al.*, 1999].The main application of these two designs is in the field of waste gas purification. The reverse-flow configuration is shown in Fig. 2.6a. An adiabatic catalytic fixed bed is used as the regenerative heat exchanger. The catalyst bed is heated up by the exothermic reaction, and then the feed temperature can be reduced to ambient. As the moving reaction front is developed, the bed is cooled by the cold feed and the feed is heated up by the hot bed. This is more interesting than conventional steady state reactor due to the fixed bed, which is clearly used as a regenerative heat exchanger, which is more efficient and simpler. Thus, autothermal operation of exothermic processes can be carried out at low temperature and fluctuating inlet reactant concentrations. Moreover, intensive energy trapping allows for efficient heat recovery for an exothermic reaction or a substantial decrease in energy consumption for an endothermic one and a reduction in the average reactor temperature with consequent decrease of pressure drops and heat losses. In counter-current reactors (Fig. 2.6c), the counter-current heat exchange can be either integrated into a catalyst bed or filled with catalyst (Kolios *et al.*, 2000). For the packing design, the counter-current reactors provide better heat transfer to the walls, and so enable a far denser, and possibly, less expensive design. Moreover, temperature sensitivity is reduced. Frauhammera *et al.* (1991) presented the new monolithic counter-current reactor concept for autothermal operation. They studied the thermal coupling efficiency between an endothermic high-temperature synthesis reaction and a combustion reaction.

The internal heat exchange was the key issue to optimizing the process. A decoupling of chemical conversion and local temperature is possible when the inert zone is introduced, which is necessary for an optimization of the temperature and conversion profiles. This concept is currently applied to the thermal coupling of the endothermic and exothermic reactions in an autothermal multifunctional reactor. According to the review of Kaiol *et al.*, (2000), the autothermal operation is possible only if the overall reaction is weak to moderate exothermic. This is a first limitation on the coupling of the two reactions. These are three ways to achieve this design. If the reactants for both (endo- and exothermic) reactions are mixed and all the reactions run more or less in parallel, it is called "simultaneous operation". If the reactants are separated, the feed directions of endothermic and exothermic reaction can be in parallel (co-current) or in opposite side (counter-current) as called asymmetric and symmetric operation, respectively.

In 1999, the autothermal operation was also applied to electrochemical oxidation of SOFC by Neophytides *et al.*, (1999). They investigated the dynamic operation of the electrochemical oxidation of H2 in planer monolithic SOFCs operating under forced periodic reverse- flow with different flow-patterns. They found that this reverse flow reactor provided the more uniform concentration and temperature distribution than did the co-current flow.

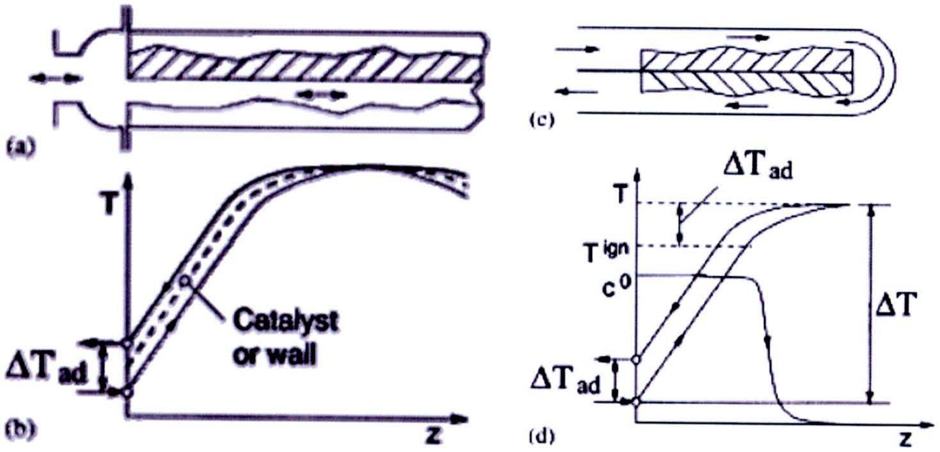

Figure 2.6 Analogy between fast flow reversal and countercurrent operation: (a) scheme of a reverse-flow reactor. The catalyst is the shaded area; (b) temperature profiles in the gas phase (—) and in the solid phase (---) in the reverse-flow reactor for short switching periods ("sliding regime"); (c) scheme of a countercurrent reactor with geometric and catalytic properties equivalent to (a); (d) temperature and conversion profiles in the countercurrent reactor. [Kolios *et al.*, 1998; Frauhammer & Eigenberger, 2000]. Based on the literatures, the following phenomenon has been compiled: kinetic, thermodynamic, and electrochemical behaviors, which take place in the SOFC system, in order to predict the autothermal operation.

2.5 System Modeling

2.5.1 Kinetic of Stream reforming

Transformation of each gas component in the SOFC system is kinetically controlled by reforming reaction and electrochemical reaction. Firstly, the primary fuel is reformed to hydrogen and carbon compound gases via reforming reaction. However, the kinetic behavior depends on type of primary feed and reforming catalysts. Hydrogen and carbon monoxide are consumed via electrochemical reaction, section 2.5.3.

2.5.2 Thermal Model

Heat transfer phenomena in the SOFC system involve conduction along the stack materials, convection from the heat flow through the system, and radiation between gray bodies. However, the heat transfer mechanism relies on the system is geometry.

2.5.2.1 Conduction

This phenomenon is investigated by using Fourier's law, Eq. 2.1

$$\vec{q}_{cond} = -k_{cond} \nabla T \tag{2.1}$$

where q_{cond} is the heat flux (W/m^2) from conduction, and k_{cond} is thermal conductivity (W/m^2.K).

2.5.2.2 Convection

The effect of convective heat transfer is obtained from the Newton's law, Eq.2.2

$$\vec{q}_{conv} = h_{conv}(T_1 - T_2) \tag{2.2}$$

where q_{conv} is the heat flux (W/m^2) from convection, and h_{conv} is convection heat transfer coefficient (W/m^2.K).

2.5.2.3 Radiation

The net heat flux from heat radiation between two grey bodies is defined on Eq.2.3

$$Q_{rad} = \frac{\sigma(T_1^4 - T_2^4)}{\left(\frac{1-\varepsilon}{\varepsilon A}\right)_1 + \frac{1}{A_1 F_{12}} + \left(\frac{1-\varepsilon}{\varepsilon A}\right)_2} \tag{2.3}$$

where Q_{rad} is the heat flux (W) from convection, σ is Stefan-Boltzmann coefficient ε is emittance, A is area (m^2), and F_{12} is grey-body transfer factor from surface 1 to surface 2

2.5.3 Electrochemical Model

In order to investigate the fuel cell system, all parameters, which influence the efficiency of the fuel cell, must be considered. The operating parameters of fuel cell consist of pressure, temperature, fuel concentration, and current density.

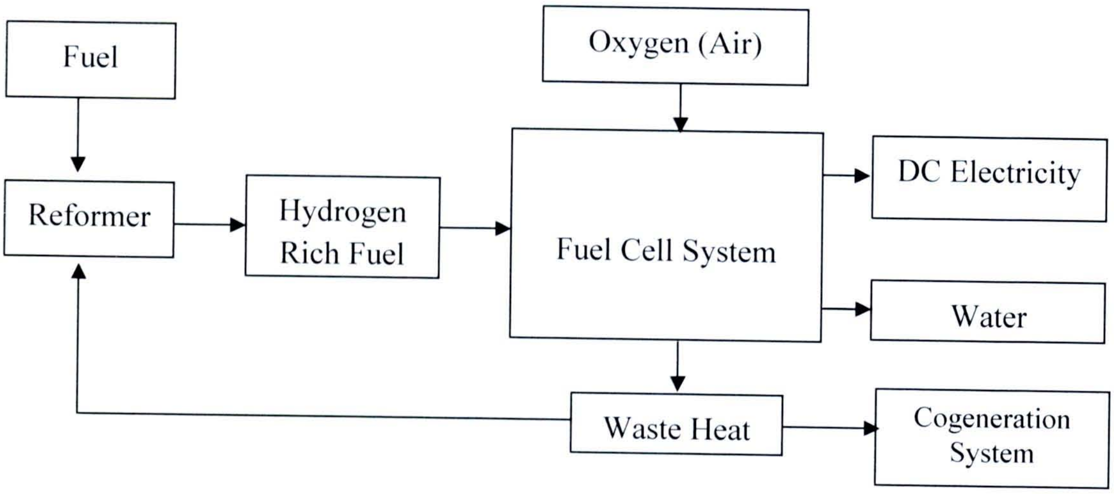

Figure 2.7 Simplify operational fuel cell

The basic energy generation of a fuel cell is the conversion of chemical energy to electrical energy. At input, the chemical energy is thermodynamically considered in terms of enthalpy and Gibb free energy which provide heat potential and work potential of fuel cell, respectively.

The basic electrochemical reactions of a fuel cell are:

Anode: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$ (2.4)

$CO + O^{2-} \rightarrow CO_2 + 2e^-$ (2.5)

Cathode: $\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$ (2.6)

Overall: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ (2.7)

$CO + \frac{1}{2} O_2 \rightarrow CO_2$ (2.8)

The liberated heat is given from the internal energy of fuel. Since SOFCs are generally operated at constant pressure, the maximum heat energy can be obtained from change in enthalpy of reactions.

$$\Delta H_{rxn} = \Delta H_f \text{ of products} - \Delta H_f \text{ of reactants} \tag{2.9}$$

$$= \Delta H_{f,H_2O} - \Delta H_{f,H_2} - \tfrac{1}{2}\Delta H_{f,O_2} \tag{2.10}$$

The work potential is calculated from the difference of Gibb free energy of the reaction, Eq.2.11.

$$\Delta G_{rxn}(T) = \Delta H_{rxn}(T) - T\Delta S_{rxn}(T) \tag{2.11}$$

If the losses in the fuel cell are neglected and the processes are "reversible" (or open circuit cell) and all the Gibbs free energy is converted into electrical energy, the amount of electrical energy will depend on the number of electrons that pass round the external circuit, n. The electrical work at the load is:-

Electrical work done = charge x voltage $= -nFE$ Joules (2.12)

where n is amount of electrons that pass though the external circuit, E is the voltage of the fuel cell (Volts),and F is Faraday's constant or the charge on one mole of electron, 96,485 C.

Thus: $\Delta G_{rxn} = -nFE$ (2.13)

where ΔG_{rxn} is the change in Gibb free energy of formation.(kJ)

Under standard state condition (STD), only one mole of hydrogen input is considered, then n = 2

$$\Delta g^{o}_{rxn} = -2FE^{o} \qquad (2.14)$$

Thus, $E^{o} = \Delta g^{o}_{rxn} / 2F$ (2.15)

where E^{o} is the voltage of the fuel cell (Volts) at STD, and Δg^{o}_{f} the change in Gibbs fee energy of formation per mole(kJ/mole) at STD

Since temperature and reactant status (liquid, gas) are influential in the Gibbs free energy of reaction, it is important to consider the changes in Gibbs free energy with reactant's pressure and concentration, as known "Nernst Equation", Eq. 2.16.

$$E = E^{o} - \frac{RT}{2F} \ln\left(\frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}}\right) \qquad (2.16)$$

where E is operating voltage (Volt), E^{o} is electro-motive-force at standard condition (Volt), Δg^{o}_{f} is the change in Gibbs fee energy of formation at STD (kJ/mole), R is universal gas constant and T is temperature (K).

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2.5.3.1 Operational Fuel Cell Voltages

If fuel cell is actually operated, its electrochemical reaction is irreversible. Thus, the actual voltage is less than the theoretical value of the open circuit voltage. This is the result of ohmic, activation and concentration overpotential. The typicality of the high temperature fuel cell is shown in Fig. 2.8.

2.5.3.1.1 Potential losses

Ohmic overpotential is the effect of electrode and electrolyte resistance to the electron and ion flow. The simplified equation for evaluating the size of the voltage drop is shown below.

$$V_{ohmic} = j.R_{ohm} \tag{2.17}$$

where V_{ohmic} is voltage drop caused by ohmic losses (Volt), j is current density (mA.cm^{-2}), and R_{ohm} is ohmic resistant per unit area (kΩ.cm^{2})

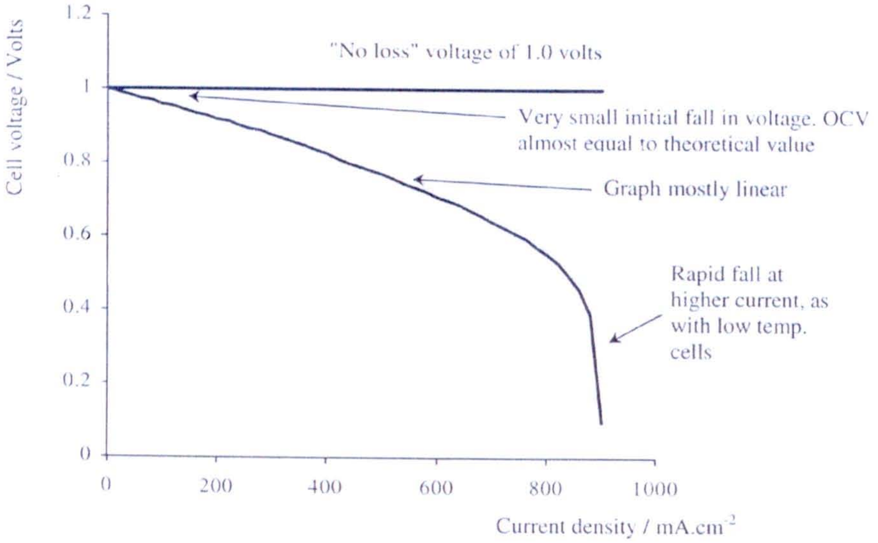

Figure 2.8 The voltage of a typical air pressure fuel cell operating at about 800°C [Larminie and Dicks, 2000]

2.5.3.1.2 Activation Overpotential

Activation loss is the effect of activation barrier of electrochemical reaction at electrode. This effect is significant at low current density. The overpotential can be evaluated by the Butler-Volmer equation [Larminie and Dicks, 2000]. Several literatures of SOFC model suggested this equation was suitable to explain the activation behavior without error [Hernández-Pacheco *et.al.*, 2004., Sánchez *et.al*, 2006].

The Butler-Volmer equation: $j = j_0\left\{\exp\left(\alpha_a \frac{n_e F\Delta V_{act}}{RT}\right) - \exp\left(\alpha_c \frac{n_e F\Delta V_{act}}{RT}\right)\right\}$ (2.18)

where j is current density (mA.cm^{-2}), j_0 is exchange current density (mA.cm^{-2}), $\alpha_{a,c}$ is charge transfer coefficient of anode and cathode, F is Faraday's constant, and V_{act} is voltage drop caused by activation losses (volts).

2.5.3.1.3 Concentration Overpotential

Concentration overpotential is the result of the drop in pressure or partial pressure of reactant gases along the electrodes at the reaction sites. This pressure drop is occured from the gas diffusion resistant through the porous media. However, this overpotential is normally reduced at high current density. Generally, gas diffusion behavior will be explained by three mathematical models: Fick's model, Dusty gas model, and Stefan-Maxwell model. These three models were compared the performance to predict the concentration overpotential in a SOFC by Suwanwarangkul *et.al.* (2003). The dusty gas model was suggested for an anode SOFC system. This recommendation was confirmed by Hernández-Pacheco *et.al.*(2004). Nevertheless, Fick's model and Stefan-Maxwell model are still applied in the model.

Mass diffusion by obey Fick's low

$$\frac{1}{A}\frac{\partial N_i}{\partial t} = -D_{i,k}\nabla x_i \qquad (2.19)$$

where $\frac{1}{A}\frac{\partial N_i}{\partial t}$ is the flux of particle, $D_{i,k}$ is the binary diffusion constant (m^2/s), C is total molar concentration (mol/L) = $\frac{P}{RT}$, and x_i is the mole fraction of gas.

Dusty gas model includes the effect of molecular diffusion and Knudsen which is presented in the first two terms of Eq. 2.20, respectively.

$$\sum_{i=1,i\neq k}^{n}\frac{x_i N_k^D - x_k N_i^D}{D_{i,k}^e}-\frac{N_i^D}{D_i^{ks}}=\frac{\nabla p_i}{RT} \tag{2.20}$$

where x_i, x_k is the mole fraction of component i, k, respectively. N_i^D is the bulk molar diffusive flux of gas component u (mol/m.s), $D_{i,k}^e$ is the effective molecular diffusivity (m^2/s), D_i^{ks} is the Kundsen diffusivity (m^2/s), and p_i is the partial pressure of component i.

Stefan-Maxwell model concerns only the influence of molecular diffusion of dusty gas model. Thus, the collisions of particle phenomena are not investigated.

$$\sum_{i=1,i\neq k}^{n}\frac{x_i N_k^D - x_k N_i^D}{D_{i,k}^e}=\frac{\nabla p_i}{RT} \tag{2.21}$$

In conclusion, when the fuel cell is operated, the electrochemical reaction is irreversible. Therefore, the operating voltage of the fuel cell at a current density "i" is

$$V_{call} = E - V_{ohmic} - V_{act} - V_{con} \tag{2.22}$$

2.5.3.2 Faraday's law and Fuel Cell Performance Factors

This section presents the dependence of the electrochemical variables on the gas streams properties. Furthermore, the parameters which are useful in accessing the overall performance of the cell are included in this section

The relation between the flux of reactants and products and the electric current drawn is determined by Faraday's law. According to this law, when H_2 oxidation is presented, the local amount of H_2 and O_2 are consumed and H_2O is produced. This is related to the local electric current density, j or j_{H_2}, produced in the cell.

$$R_{elect} = \frac{j_{H_2}}{2F} \tag{2.23}$$

where R_{elect} is the hydrogen oxidation reaction rate (mol/m^{2}s), j_{H_2} is current density from hydrogen oxidation reaction (A/m^2)

As mentioned before, not only electricity is generated but heat is also produced from the cell. The heat is generated because of the inefficiency of the cell to convert all the Gibbs free energy change into electricity. The local heat generated is obtained by

$$Q_{gen} = (-\Delta H_{elect})R_{elect} - P_{SOFC} \qquad (2.24)$$

where Q_{gen} is the local generated heat (W/m^2), P_{SOFC} is the local power density (W/m^2).

With referrence to the operation of fuel cells, it is usual to specify the average current density, the fuel utilization factor, the air ratio, the cell power and the fuel cell efficiency. These parameters are defined in the next sections.

2.5.3.2.1 Fuel Utilization Factor

Since the quality of generated electricity is depended on amount of hydrogen which is consumed, this factor is known as currency efficiency. Normally, it is given by

$$Ueff = \frac{\text{fuel}_{\text{inlet}}\,(\text{mol/s}) - \text{fuel}_{\text{outlet}}\,(\text{mol/s})}{\text{fuel}_{\text{inlet}}\,(\text{mol/s})} \qquad (2.25)$$

2.5.3.2.2 Air Ratio

The heat in a SOFC is normally removed with the flowing fuel and oxidant gases but the fuel gas cannot carry heat out of the cell chamber. Thus, excess air is normally used as a coolant (Hirano *et al.*, 1992). The air ratio is defined as the relation between excess air and theoretical:

$$\lambda_{air} = \frac{\text{oxygen supplied (mol/s)}}{\text{oxygen theoretical (mol/s)}} \qquad (2.26)$$

2.5.3.2.3 The Local Power Density

This parameter is defined as the relation between current density (j) and operating voltage (V_{cell})

$$P_{SOFC} = jV_{cell} \qquad (2.27)$$

2.5.3.2.4 Cell Efficiency

Because a fuel cell converts chemical energy directly to electricity, the common definition of efficiency is the comparison of the electrical energy produced or cell power output with the heat that would be released by burning the same quantity of fuel.

$$\eta_{SOFC} = \frac{\text{power (W)}}{\text{enthapy of inlet fuel (W)}} \qquad (2.28)$$

2.6 Heating up option

As mentioned earlier, hydrogen can be produced from various hydrocarbon compounds. However, this section is concerned with primary fuel as methane. Their properties and produce processes are expressed in the following sections. Heat-up gas is not te same as fuel of SOFC but it is not damage porous media component of SOFC.

2.6.1 Nitrogen

Nitrogen is a colorless, odorless, tasteless and mostly inert gas at standard conditions and constituting 78.08% by volume of Earth's atmosphere.

2.6.2 Hydrogen

Hydrogen gas is highly flammable and will burn in air at a very wide range of concentrations between 4% and 75% by volume. The enthalpy of combustion for hydrogen is −286 kJ/mol

Hydrogen gas forms explosive mixtures with air in the concentration range 4–74% (volume per cent of hydrogen in air) and with chlorine in the range 5–95%. The mixtures spontaneously detonate by spark, heat or sunlight. The hydrogen auto ignition temperature, the temperature of spontaneous ignition in air, is 500 °C (932 °F). Pure hydrogen-oxygen flames emit ultraviolet light and are nearly invisible to the naked eye

H_2 reacts with every oxidizing element. Hydrogen can react spontaneously and violently at room temperature with chlorine and fluorine to form the corresponding hydrogen halides, hydrogen chloride and hydrogen fluoride, which are also potentially dangerous acids.

Hydrogen is main fuel of fuel cell that occurred reaction on anode of fuel cell. Electrochemical by hydrogen on anode side of fuel cell is gives heat that shown below.

Electrochemical reaction: $H_2O+\frac{1}{2}O_2 \rightarrow H_2O$ $\Delta H^\circ = 286$ kg/mol

2.6.3 Methane

Methane (CH_4) is an odorless and colorless gas. It is the major component of natural gas; containing about 75% methane, 15% ethane , and 5% other hydrocarbons, such as propane and butane. It is the gas phase at ambient temperature. It melts at –183°C and boils at –164°C. It is not very soluble in water. Natural gas has a heat value (HHV) of 38.3 MJ/m^3. Methane is combustible, and mixtures of about 5 to 15 percent in air are explosive. Although methane is not toxic when inhaled, it can produce suffocation by reducing the concentration of oxygen inhaled.

2.6.3.1 Methane Production Process

Methane is, generally, given from natural gas. However, it can be produced from organic-materials, animal wastes, via anaerobic fermentation or digestion process, as called bio-gas. [http://www.ext.colostate.edu/pubs/farmmgt/05002.html].

In the digestion process, methane is produced by anaerobic bacteria. The process is divided into two parts. The first part is the breakdown of complex organic matter (manure) into simple organic compounds by acid-forming bacteria. Then these simple compounds are digested to methane and carbon dioxide by the methane-formers. Normally, biogas usually contains about 60 to 70 % methane and 30 to 40 % carbon dioxide, and other gases, including ammonia, hydrogen sulfide, mercaptans, other noxious gases and some water vapor. The heat value (HHV) of bio-gas is 21.814 MJ/m^3.

2.6.3.2 Reforming of Methane

Generally, hydrogen can be produced from methane via several processes, as expressed below:

Steam reforming: $CH_4 + H_2O \leftrightarrow 3H_2 + CO$;$\Delta H^o = 206$ kJ/mol (2.29)
Water-gas shift reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$;$\Delta H^o = -41$ kg/mol. (2.30)
Dry Reforming: $CH_4 + CO_2 \rightarrow 2H_2 + 2CO$;$\Delta H^o = 247$ kJ/mol (2.31)
Partial Oxidation: $CH_4 + 0.5O_2 \rightarrow 2H_2 + CO$;$\Delta H_o = -38$ kJ/mol (2.32)

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2.6.4 Methanol

Methanol (CH_3OH) is the simplest chain of all alcohol compounds. It is a light, volatile, colorless, flammable and poisonous liquid .Methanol melts at -97 °C, boils at 64.7°C, and has a density of 0.7918 g/cm3 at ambient temperature. The heat value (HHV) of methanol is 22.7 MJ/m^3. Energy density of methanol [Edinger, 2003] is 50% as compared to gasoline and 200% as compared to liquid hydrogen (by mass); 58% as compared to gasoline and 350% as compared to liquid hydrogen (by volume).Although methanol is attractive to use a final energy carrier, it is important to remember that it is poisonous. Its metabolites formic acid and formaldehyde can because blindness and death. Methanol goes into the body via ingestion, inhalation, or absorption though the skin. Therefore, a person who is always exposed to its vapors or in contact with its liquid without skin protection would be in danger.

2.6.4.1 Methanol Production Process

Methanol can be produced from either renewable or non-renewable feedstock via both chemical and biological processes.

2.6.4.1.1 Biological Process

Metabolisms of microbes are the key process for renewable methanol production. The microbes produce specific enzymes as biological catalysts. The substances are converted to methanol over these catalysts. In 1999, Obert and Dave (1999) presented the conversion mechanism of CO_2 to methanol using enzymes. As shown in Fig. 2.9, CO_2 is first reduced to formate catalyst by formate dehydrogenase (FateDH), and then formate is reduced to formaldehyde by formaldehyde dehydrogenase (FaldDH). Reduction of formaldehyde to methanol by alcohol dehydrogenase (ADH) is the final step. In this process, decrease of nicotinamide adenine dinucleotide (NADH) plays a rule as a terminal electron donor for each dehydrogenase-catalyzed reduction. However, methanol production using enzymes is not economical or time-saving until a way to regenerate 40 NADH is more feasible, or a way is found to provide electrons to the synthetic biochemical pathway and to discerning the optimal conditions for large enzymatic production of methanol.

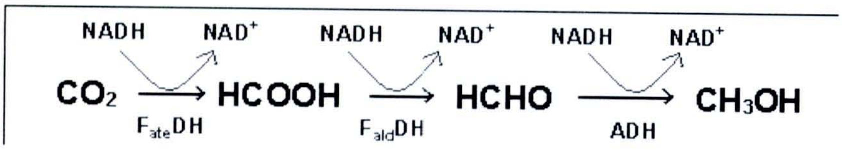

Figure 2.9 Reaction pathway of CO_2 conversion to methanol [Obert & Dave, 1999]

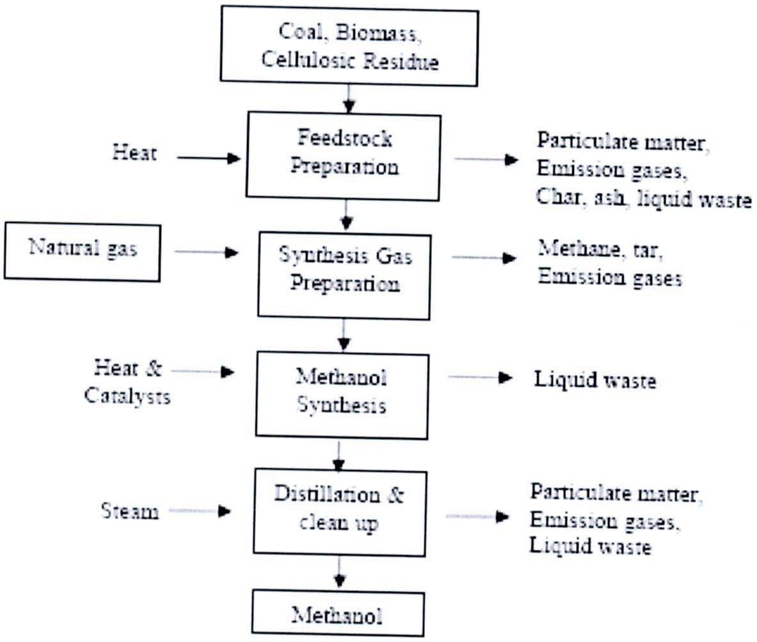

Figure 2.10 Chemical process of methanol production

2.6.4.1.2 Chemical Process

Production of methanol (wood alcohol) from biomass is a thermochemical conversion process to produce synthesis gases. Possible feedstock includes wood and agricultural residues. Synthesis gases can also be produced from coal. However, nearly all of the methanol produced now is made from natural gas. Methanol production flowchart is shown in Fig. 2.10. It is necessary to change the feedstock from solid state to gas state, which becomes the synthesis gases and then these are converted to liquid methanol.

2.8.2.2 Reforming Process of Methanol

As described, the reforming process is attractive for production of hydrogen from methanol. According to this process, the thermodynamics of the four key reactions are important to consider [Samms *et al.*, 2002].

Methanol decomposition: $CH_3OH \leftrightarrow CO + 2H_2$; $\Delta H_o = 90.64$ kJ/mol. (2.33)

Methanol steam reforming: $CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2$; $\Delta H_o = 49.47$ kJ/mol. (2.34)

Water gas shift: $CO + H_2O \leftrightarrow CO_2 + H_2$;$\Delta H_o = -41.17$ kJ/mol. (2.35)

Partial oxidation with air (in the case of adding some oxygen as autothermal reforming operation)

$$CH_3OH + 0.5(O_2+3.76N_2) \leftrightarrow CO_2 + 2H_2 + 1.88N_2 \quad ; \Delta H_o = -192.3 \text{ kJ/mol.} \quad (2.36)$$

The first two reactions are thermodynamically favored by low pressure [Johnson Matthey, 2005]. The last two reactions provide heat which is required for driving reactions 2.33 and 2.34.

2.6.5 Ethanol

Ethanol is a clear, colorless liquid. Ethanol's molecular structure consists of hydrogen-bonded pairs. Thus, viscosity and volatile properties of ethanol are less than polar organic compounds of similar molecular weight. Ethanol melts at −114.3 °C and boils at 78.4 °C. Its heating value is 29.7 MJ/m3.

2.6.5.1 Ethanol Production Process

Ethanol can be produced from many biomaterial sources which contain sugar or components that can be converted to sugar forms, such as, sugarcane, beet, forest residue and waste from agro-industry. As shown in Fig. 2.11, the biological feed stocks are converted to ethanol by using biochemical conversion. Firstly, sugar is extracted from grained feedstock and then fed into a microbial reactor. Sugar is then converted to ethanol and carbon dioxide by microbes.

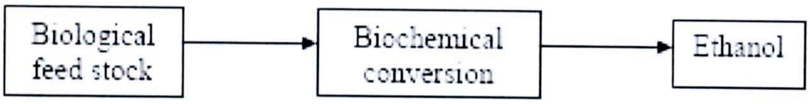

Figure 2.11 Ethanol production flow diagrams

2.6.5.2 Reforming of ethanol

The major reactions of ethanol steam reforming are mentioned in section 1.2.3. Additionally, hydrogen can be produced directly from the reaction of ethanol and oxygen at high temperature [Salge *et al.*, 2005].

Partial oxidation: $C_2H_5OH + 0.5\ O_2 \rightarrow CO + 3H_2 \quad ; \Delta H_o = 20 \text{ kJ/mol.} \quad (2.37)$