

CHAPTER II

THEORY

2.1 Fuel Cell

2.1.1 General Characteristics of Fuel Cell

A fuel cell is an electrochemical device which is able to convert the free-energy of an electrochemical reaction into electrical energy from a variety of fuels. In fact, the fuel cell is a kind of galvanic cells like a battery that produces electricity from a gaseous fuel. Unlike custom power generators, the fuel cell bypasses the step of the conversion of chemical energy to mechanical energy. Consequently, its efficiency is not restricted by thermodynamic limitations found in a Carnot engine. The fuel cell possesses higher power efficiency than that of the conventional power generation; i.e. the efficiency as high as 45 to 60% can be achieved. In addition to the high conversion efficiency, the fuel cell offers several advantages (Mogensen, 2001):

- Low pollutant emission and low noise levels, which allows location in populated areas. The NO_x emission of gas turbines and diesel engines is typically 10 and 100 times higher, respectively, than that of the fuel cells. Generally, this makes combustion systems less attractive for location in urban areas;
- Modularity which allows optimum adaption to the energy use requirements and cheap mass production;
- Fuel cells such as molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC) produce high temperature waste heat which is suitable for cogeneration in both buildings and industry;
- Low maintenance costs due to low number of moving parts and to autonomous operation.

Especially for high temperature fuel cells, besides the attributes above, hydrocarbon fuels can be internally reformed without the need of prereformer, and, through the solid electrolyte of the high temperature fuel cell, the material corrosion and liquid electrolyte management problems are eliminated.

2.1.2 Type of Fuel Cell

Fuel cell can be categorized into several types according to a selected variable such as type of electrolyte, type of fuel, operating temperature, primary and regenerative systems, and direct or indirect systems. Traditionally, the type of electrolyte is used for classification; that is, alkaline (normally KOH), acid (mainly phosphoric acid), molten carbonate (KLiCO_3), solid oxide (generally yttria-stabilized zirconia), and solid proton conductor (polymer H^+ -conductor). They are called corresponding to their electrolytes; that is, alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), solid oxide fuel cell (SOFC), and solid polymer proton conductor fuel cell (SPFC).

Nevertheless, the operating temperature is frequently used as criteria for the classification of the fuel cell. The fuel cells are grouped into low-temperature and high-temperature fuel cells. The low-temperature fuel cells are AFC, PAFC and SPFC, whereas the high-temperature fuel cells are MCFC and SOFC. Some essential data for the five main types of the fuel cells are listed in Table 2.1 and the principle basic structure of these major types is illustrated in Figure 2.1.

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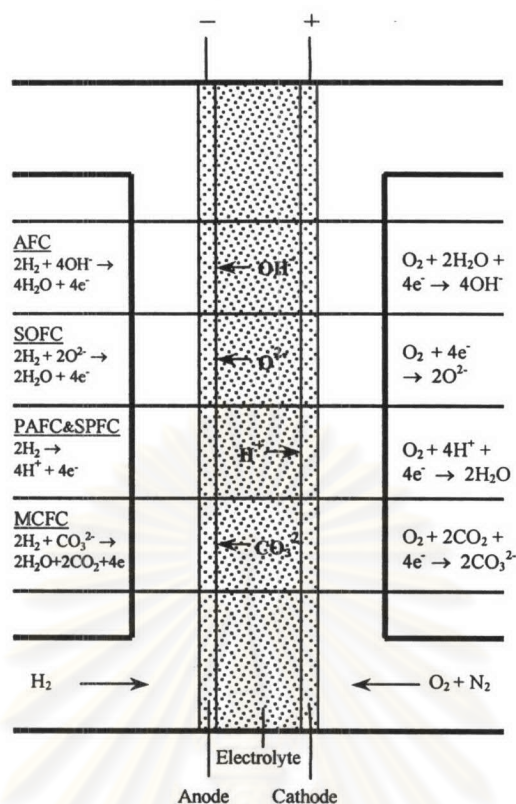


Figure 2.1 An Illustration of the Basic Structure of a Fuel Cell

Table 2.1 Some Typical Data for Important Fuel Cell Types (Mogensen, 2001)

Fuel Cell Type	Alkaline	Solid proton conductor	Phosphoric acid	Molten carbonate	Solid oxide
Abbreviation	AFC	SPFC	PAFC	MCFC	SOFC
Electrolyte	Aq. KOH	Polymer H^+ Conductor	H_3PO_4	KLiCO_3	Zr(Y)O_2
Anode material	Porous Ni	Grafite + Pt	Grafite + Pt	Porous Ni	$\text{Ni} + \text{Zr(Y)O}_2$
Cathode material	Porous Ni or Ag	Grafite + Pt	Grafite + Pt	Porous NiO	$\text{La(Sr)MnO}_3 + \text{Zr(Y)O}_2$
Possible fuel	Pure H_2	H_2 (CO free)	H_2 (low CO)	H_2 , CO, Natural gas	H_2 , CO, Natural gas
App. Operation temperature	373 K	373 K	473 K	923 K	1273 K
App. Efficiency*	40%	40%	40%	60%	60%

* % of HHV of natural gas.

2.1.3 Solid Oxide Fuel Cell (SOFC)

SOFC is a solid state energy conversion device that produces electric power by an electrochemical reaction. Its mechanism is based on the electrochemical combustion of the fuel. In fact, the overall reaction is the same as that of the combustion but the reaction is separated into two electrochemical reactions, that is, an oxidation reaction on the anode side and a reduction reaction on the cathode side.

For the oxidative coupling of methane (OCM) reaction, the electrochemical reaction consists of the oxidation of methane at the anode and the reduction of oxygen at the cathode. The overall reaction, like the OCM reaction, yields C₂₊ hydrocarbons, carbon dioxide, carbon monoxide and water as the reaction products. In the operation of a SOFC, methane is fed to the anode, where it is oxidized and electrons are released to the external circuit. Oxygen is fed to the cathode, where it is reduced and the electrons are accepted from the external circuit. The electron flow (from the anode to the cathode) through the external circuit produces direct-current (DC) electricity. The electrochemical transformation of the methane and oxygen in the SOFC is almost isothermal; i.e. the fuel cell directly uses the available free energy in the fuel as electric power at the operating temperature. The fundamental operation is shown in Figure 2.2.

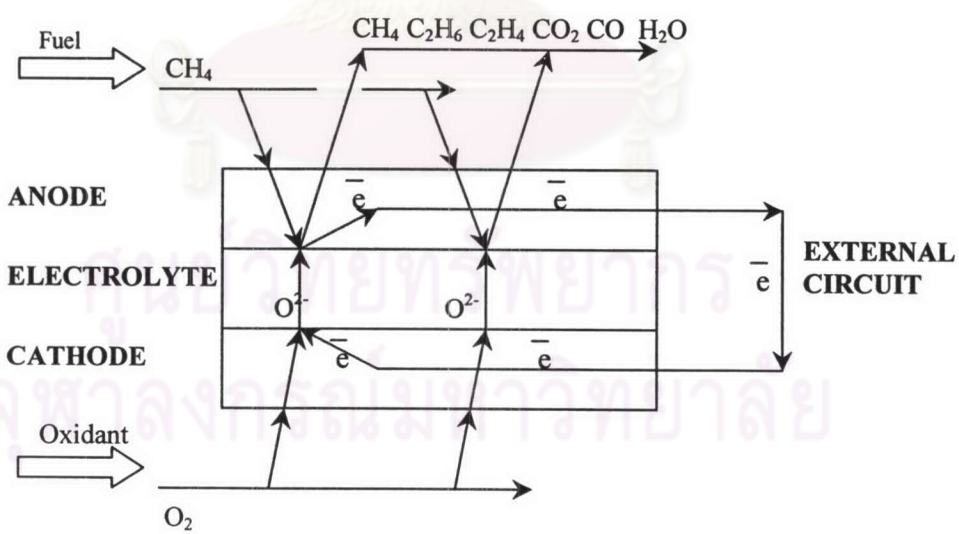


Figure 2.2 Fundamental Operation of a SOFC

2.2 Principle of Operation of Fuel Cell

2.2.1 Thermodynamic Principles

SOFC generates the electric power through an electrochemical reaction, which is separated to two reactions, that is, the reduction of the oxidant at cathode and the oxidation of the fuel at anode. For the OCM reaction, the electrolyte is an oxygen ion conductor, so that the reaction at the cathode is the reduction of oxygen and that at the anode is the oxidation of oxygen ion described by following reactions:



where the subscripts (c), (a) and (e) represent cathode, anode and electrolyte, respectively. The SOFC is, therefore, able to be considered as an oxygen concentration cell, and the electromotive force or reversible (thermodynamic) voltage, E_r , is expressed by the Nernst's equation

$$E_r = \frac{RT}{4F} \ln \frac{P_{\text{O}_{2(c)}}}{P_{\text{O}_{2(a)}}} \quad (2.3)$$

where R is the gas constant, T the temperature, F the Faraday constant, $P_{\text{O}_{2(c)}}$ and $P_{\text{O}_{2(a)}}$ the partial pressure of oxygen at the cathode and the anode, respectively.

Furthermore, because a fuel cell converts the chemical energy directly to electrical energy, the electromotive force can be calculated from the balance of the chemical energy and the electrical energy as the following equation:

$$E^\circ = -\frac{\Delta G^\circ}{4nF} = -\frac{\Delta H^\circ - T\Delta S^\circ}{4nF} \quad (2.4)$$

where ΔG° is the standard Gibbs free energy change of the combustion reaction of the fuel, ΔH° the standard enthalpy change, ΔS° the standard entropy change, and n

the number of oxygen required to oxidize one mole of fuel. Table 2.2 lists ΔG^0 , ΔH^0 , E^0 and ϵ_T for the combustion of several fuels (when the fuel cell reaction products are in gaseous state).

2.2.2 Thermodynamic Efficiency

In a fuel cell, the Gibbs free energy change of the reaction may be totally converted to electrical energy. Consequently, a maximum thermodynamic efficiency is defined as follow

$$\epsilon_T = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H} \quad (2.5)$$

For hydrogen, carbon monoxide and hydrocarbons, the values of ΔH and ΔS are negative and, consequently, the thermodynamic efficiency is less than 1. The value higher than 1 is possible for the reaction whose ΔS is negative. The thermodynamic efficiency of some reactions is shown in Table 2.2.

Table 2.2 Thermodynamic Data and Thermodynamic Efficiencies for Several Reactions modified from (Minh, 1995).

Reactions	T (K)	ΔG^0 (kJ)	ΔH^0 (kJ)	E^0 (V)	ϵ_T
$H_2 + 1/2O_2 = H_2O$	1000	-192.5	-247.3	0.997	0.78
	1250	-178.2	-249.8	0.924	0.71
$CH_4 + 2O_2 = CO_2 + 2H_2O$	1000	-802.5	-800.4	1.039	1.00
	1250	-802.9	-801.2	1.039	1.00
$CH_4 + 1/2O_2 = CO + 2H_2O$	1000	-603.1	-518.6	1.042	1.16
	1250	-625.0	-521.6	1.079	1.20
$CH_4 + 1/4O_2 = 1/2C_2H_6 + 1/2H_2O$	1000	-60.3	-87.5	0.625	0.69
	1250	-53.6	-87.8	0.555	0.61
$CH_4 + 1/2O_2 = 1/2C_2H_4 + H_2O$	1000	-152.5	-139.7	0.790	1.09
	1250	-155.6	-140.7	0.806	1.11
$CH_4 + 1/2O_2 = 1/3C_3H_8 + H_2O$	1000	-150.4	-202.0	0.779	0.74
	1250	-149.3	-202.5	0.774	0.74

$\text{CO} + 1/2\text{O}_2 = \text{CO}_2$	1000	-195.4	-283.3	1.013	0.69
	1250	-173.2	-283.3	0.898	0.61
$\text{C} + \text{O}_2 = \text{CO}_2$	1000	-396.6	-396.2	1.027	1.00
	1250	-396.6	-396.6	1.027	1.00

2.2.3 Voltage Efficiency

During the SOFC operation, the electrochemical oxidation reaction takes place on the anode electrode yields the electrons which is then forced via the voltage difference through the anode electrode to the current collector and after that, to the cathode electrode, on which the electrons move through the cathode electrode to activate the oxygen molecules to form oxygen ions. Accordingly, the measured voltage during operation is less than the reversible voltage. In addition, due to the electrical current is produced from a chemical reaction, the diffusion of the reactants and products is also an important factor affecting the cell voltage. The reduction in the cell voltage under current load depends on current density and several factors such as temperature, pressure, gas flow rate and composition, and cell material. The voltage efficiency, ε_v , is defined as the ratio of the measured voltage under load, E , to the reversible voltage, E_r :

$$\varepsilon_v = \frac{E}{E_r} \quad (2.6)$$

Commonly, the reversible voltage is referred to as the open-circuit voltage, and may be different from the equilibrium voltage if there are side reactions, crossover leakage, etc.

The difference between the measured voltage and the expected reversible voltage is termed polarization, overvoltage, or overpotential presented as η . The total polarization, η , is the sum of the charge transfer or activation polarization (η_A), the diffusion or concentration polarization (η_D), and the resistance or ohmic polarization (η_Ω):

$$\eta = \eta_A + \eta_D + \eta_\Omega \quad (2.8)$$

Thus, it can be written as

$$E = E_r - \eta = E_r - \eta_A - \eta_D - \eta_\Omega \quad (2.9)$$

(a) Charge Transfer or Activation Polarization (η_A): The activation energy is an energy barrier of the electrochemical reactions, which must be overcome before the electrode reaction can take place. Therefore, during the fuel cell operation, the voltage difference (equilibrium voltage) is reduced because the electrostatic energy indicating by the difference in voltage is lost to overcome the barrier energy of the reaction. This loss of voltage is called charge transfer or activation polarization, η_A . Activation polarization is related to current density, j , by the following equation:

$$j = j_o \exp\left[\frac{\alpha \eta_A F}{RT}\right] - j_o \exp\left[\frac{(1 - \alpha) \eta_A F}{RT}\right] \quad (2.10)$$

where α is the transfer coefficient, and j_o is the exchange current density. The exchange current density is the electrode reaction rate at the equilibrium potential. The exchange current density can be determined experimentally by extrapolation the relation of $\log j$ and η to $\eta = 0$.

$$\eta_A = a \pm b \log j \quad (2.11)$$

where a and b are constants related to an electrode material and a type of electrode reaction. This relation is named as the Tafel equation.

Generally, the charge transfer or activation polarization is resulted from one or more rate-determining steps in the electrode reaction. The slow step could be adsorption of reactant, electron transfer, desorption of product, or other steps in the reaction. In a SOFC, the reaction rate is rapid due to high temperature, and as a result, the charge transfer or activation polarization is usually small.

(b) Diffusion or Concentration Polarization (η_D): The electrical energy is generated from a chemical reaction, so that the current density, which corresponds to the reaction, is limited by the diffusion effect of the reactants or products. When the reaction at the electrode is governed completely by diffusion, the current density is reached a limiting value, which is called as the limiting current, and at the limiting current, the voltage is decreased rapidly. This effect is the diffusion or concentration polarization. The limiting current can be calculated from the diffusion coefficient of the reacting ions, D , the activity of the reacting ions, a_M , and the thickness of the diffusion layer, δ , by applying Fick's law as

$$j_L = \frac{4nFDa_M}{\delta} \quad (2.12)$$

For an electrode process without activation polarization, the diffusion or concentration polarization is expressed as

$$\eta_D = \frac{RT}{4nF} \ln \left(1 - \frac{j}{j_L} \right) \quad (2.13)$$

The diffusion polarization is dependent on the mass transport properties of the system. Mass transport property is a function of temperature, pressure, concentration, and the physical properties of the system. In a SOFC, the reactants must diffuse through the porous anode and cathode so that electrode structure is important.

(c) Resistance or Ohmic Polarization (η_Ω): The ohmic polarization is caused by resistance to conduction of ions (through the electrolyte) and electrons (through the electrodes and current collectors), and resistance between cell components. The ohmic polarization is given as

$$\eta_\Omega = jR_i \quad (2.14)$$

where R_i represents the total cell resistance, including both ionic and electronic resistances. The resistance polarization is commonly separated from other type of polarization and referred to as the ohmic loss.

2.2.4 Power Generation

Operation of a SOFC is typically displayed by a relationship between voltage and current as shown in Figure 2.2. There are three regions, in which the different polarization predominates. At low current, the ohmic loss and the conversion are small, consequently, the major contribution to voltage losses is the activation polarization, as indicated by the sharp drop in voltage with increasing current. After this region, as the current is increased, the ohmic loss increases correspondingly and, therefore, the ohmic loss dominates as indicated by the declining straight line. When the current or the conversion increases, the diffusion or concentration polarization becomes important due to the mass transport limitation, resulting in a rapid decrease in cell voltage.

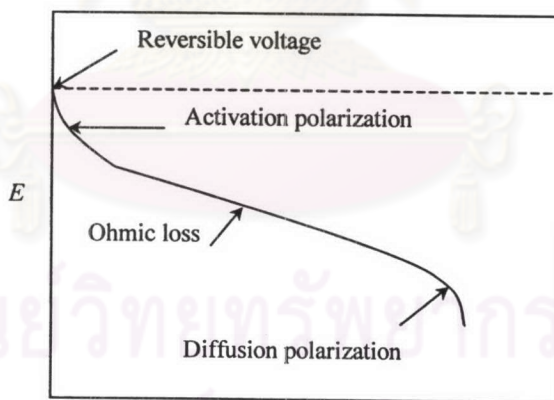


Figure 2.3 Typical Voltage/Current Relationship for a Fuel Cell Operation

The power output P_w of a fuel cell is expressed by the following equation.

$$P_w = EI \quad (2.15)$$

The power and current relationship can be predicted from the I - E curve. Because at low and high current, the voltage and the current approach to zero, respectively, the power also approaches to zero. Accordingly, there is a maximum power between two ends. The power curve tends to be parabolic as shown in Figure 2.4. In most typical fuel cell, due to the advance in construction of the porous electrodes, the current does not reach the limiting current point even at high current, resulting in the approximately linear relation.

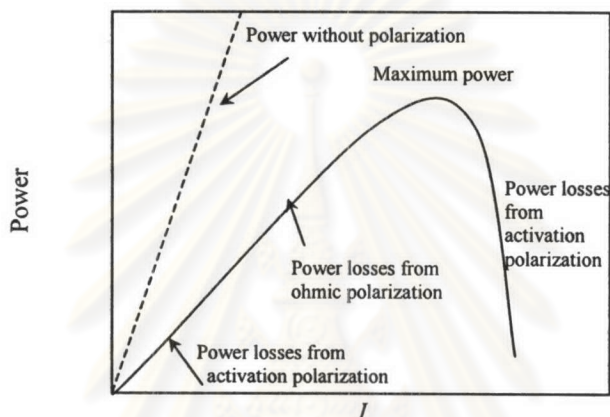


Figure 2.4 Typical Power/Current Relationship for a Hypothetical Fuel Cell

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