CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Fuel Cell

A fuel cell is usually defined as an electrochemical device that converts the internal chemical energy of supplied reactants (both fuel and oxidant) to electrical energy directly and continuously, as long as reactants are supplied to the cell, yielding direct current.

2.1.1 Fuel Cell Types and Applications

The different types of fuel cell are usually distinguished by the electrolyte used. The data of basic information for different fuel cell types is summarized in Table 1.

Table 2.1 Data of different fuel cell types (Larminie, 2003)

Fuel Cell type	Mobile ion	Operating temperature	Applications and notes
Alkaline (AFC)	OH^+	50-200°C	Used in space vehicles
Proton Exchange Membrane(PEM)	H^+	30-100°C	Vehicle and mobile applications
Direct methanol (DMFC)	H^+	20-90°C	Suitable for portable electronic systems
Phosphoric acid (PAFC)	H^+	220°C	Large numbers of 200 KW CHP systems in use
Molten carbonate (MCFC)	CO_3^{2-}	650°C	Suitable for medium to large-scale CHP
Solid oxide (SOFC)	O^{2-}	500-1000°C	Suitable for all sizes of CHP systems,

2.1.2 Advantages of Fuel Cells

Fuel cells have various advantages depending on their types, and lead to different applications. However, the typical advantages, compared to other energy conversion technologies, are:

- Efficiency; fuel cells are generally more efficient than combustion engines, whether piston- or turbine-based, due to the combined heat and power system (CHP system).

- Simplicity; few moving parts leads to highly reliable and long-lasting systems.

- Low emissions; fuel cells can be referred to as "zero emission" due to the fact that the by-product is water when pure H_2 is used as a fuel.

- Silence; this is important for portable applications and local power generation.

2.2 High-temperature Fuel Cells

Above 800°C, the theoretical maximum efficiency of a fuel cell is actually less than a heat engine. Therefore, it might seem unwise to operate fuel cells at high temperature. However, this problem is outweighed by the additional advantages of higher temperature. The high temperature of the outlet gases means that there is high-quality waste heat which can be used further in the bottoming cycle to generate additional electricity or become a valuable heat source for buildings, processes or facilities near the fuel cell. Moreover, a noble metal catalyst is also not required due to the electrochemical reaction rate being fast at their operating conditions. One of the two high-temperature fuel cells is the SOFC.

The SOFC was developed with the intention of operating on coal-derived gases. Hence, no problem is encountered with the presence of CO and CO_2. In fact, CO becomes a fuel directly in addition to H_2. It is typically operated at 800°-1000°C. At this condition, an internal reforming is enabled. These provide opportunities for greater flexibility in the use of hydrocarbon-based fuels, especially natural gas. However, the major problems of SOFCs are all associated with the material used in constructing the cell, where the most difficult issue is to match the thermal expansion coefficients of the cell structure, including the anode, cathode, electrolyte and interconnects.

2.3. Solid Oxide Fuel Cells (SOFCs)

2.3.1 Principle and Electrochemical Reactions

The SOFC is a complete solid-state fuel cell that uses an oxide ion-conducting ceramic material as an electrolyte. The typical operating condition is 800°C-1000°C. Fig.2.1 shows the operating principle of a single solid oxide fuel cell using H_2 and CO as fuels and O_2 as oxidant.
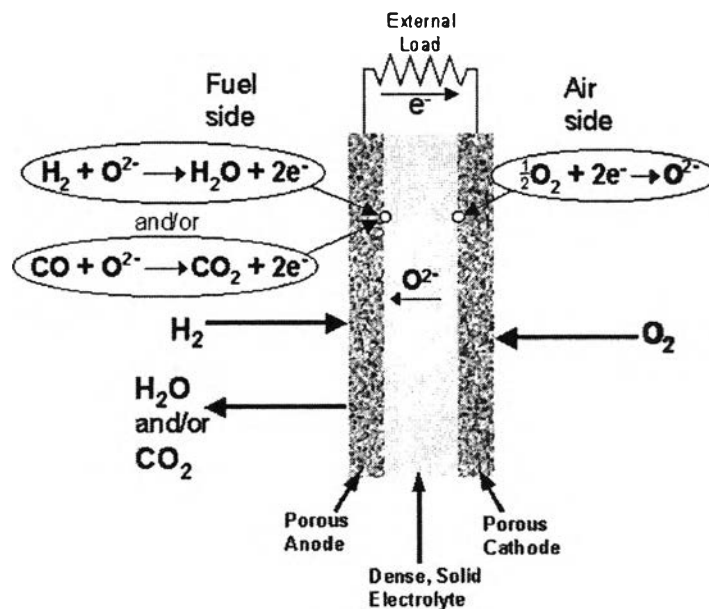
Figure 2.1 Operating principle of an SOFC using CO and H_2 as fuels and O_2 as the oxidant. (http://www.thirdorbitpower.com)

At the anode, H_2 and CO are fed and diffused through a porous structure to the anode/electrolyte interface where they are oxidized in combination with oxygen ions (O^{2-}), resulting in water, CO_2 and electrons as products. The released electrons are delivered to the cathode via an external circuit and produce direct-current electricity. The anode reactions are:

$$H_2 + O^{2-} \longrightarrow H_2O + 2e^- \qquad (2-1)$$

$$CO + O^{2-} \longrightarrow CO_2 + 2e^- \qquad (2-2)$$
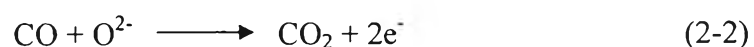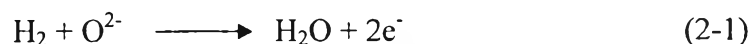
Since CO and water vapor are present as the fuel and product of the electrochemical reaction, respectively, carbon formation and a water-gas shift reac-

tion (WGS) can take place at the anode. (More details about these two reactions are given in the next section.)

At the cathode, oxygen is introduced and accepts the released electrons from the external circuit to produce oxygen ions which are transferred through an electrolyte to the anode. The cathode reaction is

$$O_2 + 4e^- \longrightarrow 2O^{2-} \tag{2-3}$$

2.3.2 Water-gas Shift (WGS) and Carbon Formation Reactions

If the water is in a vapor phase, the WGS reaction (Equation 2-4) is slightly exothermic:

$$CO + H_2O \longrightarrow CO_2 + H_2. \tag{2-4}$$
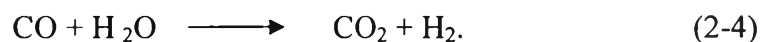
Because the WGS reaction is exothermic, at high temperature, it produces more reactants (CO and H_2O), while at low temperature, it produces more products (CO_2 and H_2). However, at high temperature, the reaction rate is higher.

In carbon formation, the carbon is formed from the disproportionation of CO via the Boudouard reaction, Equation 2-5:

$$2CO \longrightarrow C + CO_2. \tag{2-5}$$
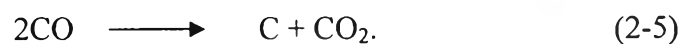
This reaction is catalyzed by metal, such as Ni, and therefore there is a high risk of its occurrence on an anode catalyst containing Ni or on Ni-containing stainless steel used for fabricating the cell stack. Fortunately, there is a simple approach to reduce the risk-by adding steam to the fuel stream. The principle effect is to promote the water gas shift reaction by reducing the partial pressure of the CO in the fuel steam.

2.3.3 SOFC Cell Components and Materials

An SOFC consists of two porous electrodes-an anode and a cathode-which are connected to each other by means of gas-tight electrolytes. The anode/electrolyte/cathode assembly is referred to as a single cell.

The porous anode serves to provide electrochemical reaction sites for oxidation of the fuel. A Ni/YSZ (yttria-stabilized zirconia) cermet is currently the most common anode material for SOFC applications because of its low cost, stability in the reducing environment, close thermal expansion coefficient with YSZ electrolyte, and low charge transfer resistance (Zhu and Deevi, 2003).

The electrolyte is the gas-tight central part of an SOFC cell. Within the electrolyte, the oxygen ions (O^{2-}) are transported and react with fuel at the anode. Nowadays, the most-used electrolyte material is zirconia (ZrO_2). By adding stabilizing agents like yttria, YSZ can be stabilized even at ambient temperature (http://www.fz-juelich.de).

Currently, $La_xSr_yMnO_{3-\delta}$, a complex oxide with a perovskite structure, is used as a cathode; typically strontium-doped lanthanum manganite (($La_{0.84}Sr_{0.16}$)MnO_3). This material fulfills the requirements with respect to processing and to chemical stability during operation as the fuel cell cathodes. The coefficient of thermal expansion also matches well to that of the electrolyte. Nevertheless, $La_xSr_yMnO_{3-\delta}$ exhibits high electronic conductivity and the ionic conductivity is nearly zero.

2.4 SOFC Designs

2.4.1 Tubular Design

A tubular design of an SOFC is presented in Fig. 2. In this design, the cell is configured as a tube. In the most common tubular design, the tube is made of cathode material and is closed at one end. Electrolyte and anode layers are formed on the outside of the tube. The problems associated with the tubular design are its low power density and high fabrication cost. One great advantage, however, is that high-temperature gas-tight seals are eliminated.
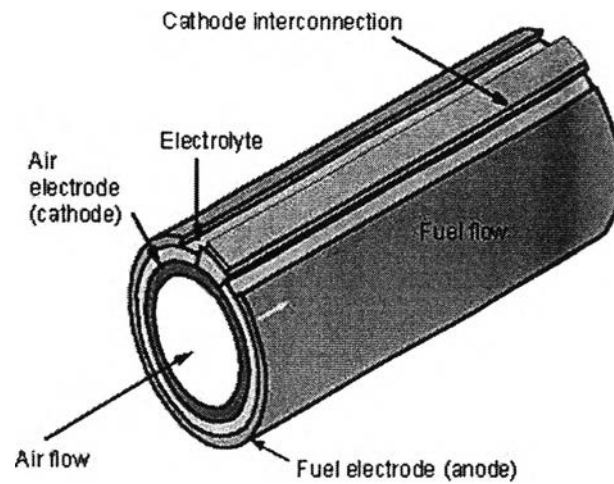
Figure 2.2 Tubular type SOFC (http://www.mech.gla.ac.uk).

2.4.2 Planar Design

In the planar design, the single cell is configured as flat plates, shown in Fig. 3. It can be fabricated by the low-cost method such as screen printing and tape casting. However, major disadvantages are the need for gas-tight seals around the edges of the cell components and the thermal stresses that tend to cause mechanical degradation.
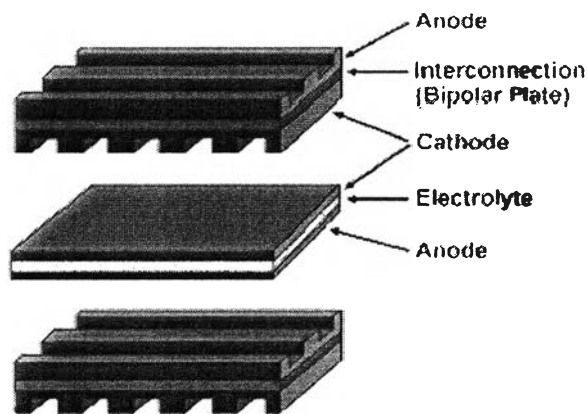
Figure 2.3 Planar type SOFC.

2.5 SOFC Performance

The performance of an SOFC is similar to that of any other power source whose performance is governed by actual cell potential, power density and cell

efficiency. The cell potential is calculated by subtracting all internal resistances from the reversible cell potential. The power density and cell efficiency are determined from the actual cell potential and current density. Detailed descriptions of all the important terms used to describe SOFC performance are explained in the next sections.

2.5.1 Reversible Cell Potential

The maximum possible corresponding electrical potential difference between cathode and anode is achieved when the fuel cell is operated under thermodynamically reversible conditions. This is called "the reversible cell potential" (E_r), expressed in terms of voltage. This potential depends on temperature, pressure and gas concentration and can be calculated by Nernst's equation which is derived from the thermodynamic aspect. The reactions and corresponding Nerst's equations of H_2 and CO fuels are expressed in Table 2, which considers both the effects of gas concentration and temperature.

Table 2.2 SOFC reactions and the corresponding Nernst's equations

Reaction	Equation	
$H_2 + 1/2O_2 \rightarrow H_2O$	$E_{rH_2} = -\dfrac{1}{2F}\left[\Delta G_{H_2} + RT\ln\left(\dfrac{P_{H_2O}}{P_{H_2}P_{O_2}^{0.5}}\right)\right]$	(2-6)
$CO + 1/2O_2 \rightarrow CO_2$	$E_{rCO} = -\dfrac{1}{2F}\left[\Delta G_{CO} + RT\ln\left(\dfrac{P_{CO_2}}{P_{CO}P_{O_2}^{0.5}}\right)\right]$	(2-7)

In these equations (2-6 and 2-7) R, T and F represent the universal gas constant, system temperature and Faraday's constant which equals to 96,487 Coulombs per mole, respectively. Pi is a partial pressure of each of the reactants and products. ΔG_r represents Gibb's free energy of each fuel cell reaction at arbitrary operating temperature.

2.5.2 Actual Cell Potential

For practical applications, the electrical power output is obtained when a reasonably large current is drawn from the cell, which is defined as:

$$\text{Power} = E_{actual} \times I \quad \text{or} \quad \text{Power density} = E_{actual} \times J, \qquad (2\text{-}8)$$

where E_{actual} represents the actual potential, Volts, and I and J represent current and current density, respectively.

In reality, the actual cell potential is less than the reversible one because of the energy losses that occur during the operation, which can be referred to as "irreversibility". The difference between the reversible potential and actual cell potential is called "overpotential" or "overvoltage". The related equation is:

$$E_{actual} = E_r - \eta, \qquad (2\text{-}9)$$

where η represents the total energy losses, or overpotential. The processes that give rise to the overpotential is known as "polarization". Hence, the plot between the actual cell potential and current or current density is called the "polarization curve", which is shown in Fig. 2.4.
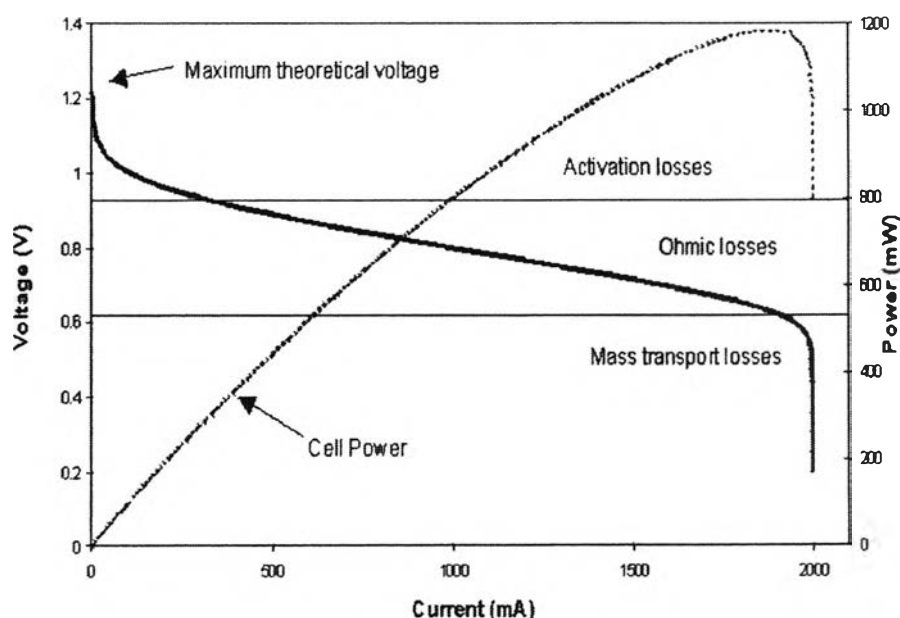
Figure 2.4 Polarization curves. (http://www.corrosion-doctors.org)

The polarization curve shows that the actual cell potential is smaller than the reversible cell potential and decreases as the current drawn is increased due to the three polarizations-activation, ohmic, and concentration or mass-transport polarizations.

Activation polarization, η_{act} , arises from the slow rate of electrochemical reactions, and a portion of the energy is spent on driving up the rate of electrochemical reaction in order to meet the rate required by the current demand.

Ohmic polarization, η_{ohm} , arises from the electrical resistance in the cell; including ionic resistance to the flow of ions in the electrolyte and the electronic resistance to the flow of electrons in the rest of the cell components.

Concentration polarization, η_{conc} , is caused by the slow rate of mass transfer resulting in the depletion of reactants in the vicinity of active reaction sites and the over-accumulation of reaction products which block the reactants from reaching the reaction sites.

2.6 SOFC Developments and Challenges

Recently, the SOFC has received more attention in many applications due to its high efficiency, high waste-heat utilization, and high fuel flexibility. Nonetheless, SOFCs still have a number of drawbacks in their application to actual power systems. The reliability and cost competitiveness of an SOFC system are recognized as key technical barriers that hinder the entry of SOFCs into the commercial marketplace. Therefore, most research and development activities on SOFCs are focused mainly on the development of commercially viable SOFC technology with high electrochemical performance and long-term stability (Jung *et al.*, 2005). One way to step over these cost, reliability and efficiency barriers is to reduce the operating temperature to 500°C-700°C, which is becoming one of the technical trends of SOFC development nowadays (Faghri and Guo, 2005). Furthermore, the development of cell components and materials has been changed: to thinner electrolytes, to anode-support cells, to the use of metallic interconnects and more conductive material for the electrolyte to provide higher performance. Therefore, many different designs, including

the cell configuration and the flow type, of intermediate fuel cells are being developed, stability tested and published (Nishiwaki *et al.*, 2006 and Yoshida *et al.*, 2005).

This marketable-SOFCs challenge entails an increased research effort for industry and research institutions in order to develop advanced numerical models and computer codes that can be used for fuel cell design and development. This could yield a better understanding of the physical process and help fuel cell designers to define more promising strategies.

2.7 Fuel Cell Modeling

Fuel cell modeling is a useful tool to gain better insight into the inner working mechanism so that fuel cell design can be improved (Faghri and Guo, 2005). Plus, it is faster to run a "modeled fuel cell" than a real one. Thus, modeling can speed up the design process and play an important role in fuel cell development and research in modeling SOFCs, which has also increased the last few years.

2.7.1 SOFC Mechanistic Models

The levels of the mechanistic models can be divided into two categories: cell/stack models and microstructure models. The purpose of the cell/stack models is to simulate the characteristics of fuel and air flows, as well as predict cell/stack performance for various operating and designed conditions (Leah *et al.*, 2004). The microstructure models are aimed at relating cell performance as a function of microstructural parameters, such as porosity, pore size and composition of the ionic/electronic conductor (Costamagna *et al.*, 2004). The incorporation of these models into the cell/stack model is expected to improve the accuracy of model prediction over the cell/stack model since the information of the microstructure is added. Unfortunately, no previously-published model considered cell/stack and microstructure models together. Therefore, there is a need for developing cell-level models coupled with microstructure models.

To answer questions related to the design and operation of an SOFC for achieving the highest performance, a model with detailed mechanistic relations of momentum, heat- and mass-transfer phenomena, and chemical reactions is required. Most of the proposed mechanistic models are based on tubular and planar geometries.

For the planar design, the anode-supported type is the most considered since it allows low operating temperature and is easy to fabricate. For example, to predict the concentration polarization in the anode-supported SOFC, Yakabe *et al.* (2000) simulated the flow phenomena using the finite volume method. The model assumed that the gas flow in the porous structure is governed by Darcy's law and the reactants are transported mainly by diffusion. The calculated concentration polarization was found to be comparable to the experimental results. Lehnert *et al.* (2000) developed one-dimensional numerical simulation program in order to describe the transport of gases inside an SOFC anode, by diffusion and permeation, for the internal reforming reaction. The transport of gases was described in the frame of the mean transport pore model (MTPM). In this model, Darcy's law is used for permeation and the Stefan-Maxwell equation for diffusion. The simulated results show that the ratio of porosity to tortuosity has a high effect on methane conversion in the anode.

Because of the high fuel flexibility of an SOFC, a number of models and studies on SOFC operation with various fuels were developed. In 2005, Inui *et al.* investigated in detail the influence of the mixing ratio of H_2 and CO in the fuel on the cell performance of the SOFC. They developed a model based on a single cell plate of a co-flow planar cell. They found that the electromotive force of the H_2 rich fuel gas is slightly higher than that of CO rich fuel gas and the internal voltage drop in the cell decreases as the CO fraction becomes high. In the same year, Hernandez-Pacheco *et al.* (2005) developed a model that was used to analyze the performance of the SOFC under different gasifier compositions. The model was integrated by an electrochemical module and a thermal module. The results showed that high initial concentration of H_2 fuel and H_2O provided the best performance. In 2007, an analytical model was developed by Aloui *et al.*, 2007 to study fuel type (pure H_2 and syngas produced by biomass gasification) effect on polarization and performance of an SOFC. Analysis showed that a fraction of about 23% CO in syngas improved the performance of the SOFC compared to that obtained using pure H_2.