CHAPTER II

OUTLINES OF FUEL CELL

2.1 Fuel Cell Description

Fuel cells are electrochemical devices to convert the chemical energy of a reaction directly into electrical energy. The basic physical structure of a fuel cell consists of an electrolyte layer in contact with a porous anode and cathode on either side. In a typical fuel cell, gaseous fuels are fed continuously to the anode (negative electrode) compartment and an oxidant (i.e., oxygen from air) is fed continuously to the cathode (positive electrode) compartment; the electrochemical reactions take place at the electrodes to produce an electric current.

A fuel cell is similar to a typical battery; however, it differs in several aspects. The battery is an energy storage device and the maximum energy available is determined by the amount of chemical reactant stored within the battery itself. The battery will cease to produce electrical energy when the chemical reactants are consumed (i.e. discharged). In a secondary battery, the reactants are regenerated by recharging, which involves storing energy into the battery from an external source. The fuel cell, on the other hand, is an energy conversion device. Theoretically, it has the capability to generate electrical energy for as long as the fuel and oxidant are supplied to the electrodes. In reality, degradation, primarily corrosion, or malfunction of components limit the practical operating life of fuel cells.

An electrolyte used in the fuel cell can be either proton or oxygen ion conducting types. The fuel and oxidant gases are fed to the anode and the cathode, located on the opposite side of the electrolyte. There are various types of fuel cell which are at different stage of development.

The most common classification of fuel cell is by the type of electrolyte used in the cells. The following fuel cells are listed in the order of operating temperature. (Hirschenhofer *et al.*, 1998)

1) proton exchange membrane fuel cell (PEMFC), polymer electrolyte fuel cell (PEFC)
2) alkaline fuel cell (AFC)
3) phosphoric acid fuel cell (PAFC)
4) molten carbonate fuel cell (MCFC)
5) solid oxide fuel cell (SOFC)

A brief description of various electrolyte cells is as follows.

2.1.1 Polymer electrolyte fuel cell (PEFC)

The electrolyte in this fuel cell is an ion exchange polymer membrane. A common is sulphonated fluoro polymer, usually fluoroethylene that is an excellent proton conductor. The only liquid in this fuel cell is water; thus, corrosion problems are minimal. Water management in the membrane is critical for an efficient performance. The polymer must be highly hydrophilic and sufficient water content inside, then H^+ ions can move quite free giving a good conductivity. However, if there are too much water content which are bonded to the electrolyte, flood, blocking the pores of electrode may occur. So the water balance should be taken into account. The other problem, PEFC tolerance for CO in only low ppm level so H_2-rich gas with minimal or no CO is needed.

2.1.2 Alkaline fuel cell (AFC)

The electrolyte in this fuel cell is 35-50 wt% KOH and operated at temperature about 120°C. The electrolyte is hydroxyl ion conductor and water is produced at the anode. The fuel supply is limited to pure hydrogen (purity > 99.99 %). CO is a poison, and CO_2 will react with the KOH, thus altering the electrolyte. Even a small amount of CO_2 in air must be considered with the alkaline cell. The AFC is in progress of space application, while terrestrial applications begin to be investigated.

2.1.3 Phosphoric acid fuel cell (PAFC)

The PAFC works in a similar fashion to PEFC, the electrolyte is proton conductor. Concentrated 100% phosphoric acid is used as the electrolyte because it it is only common inorganic acid that has good enough thermal and chemical stability and low enough volatility at 150 to 220 °C of operating temperature. The severe problem is CO poisoning of the Pt electrode. The fuel has to be reformed external of the cell. The level of tolerance for CO is dependent on temperature, the higher temperature, the greater of tolerance for CO. These limitation lead the development to high temperature fuel cell such as MCFC and SOFC.

2.1.4 Molten carbonate fuel cell (MCFC)

As mention above, CO poisoning is not a problem of MCFC as in low temperature fuel cells, in fact, CO is a directly usable fuel. The electrolyte in this fuel cell is usually a combination of alkali carbonates or combination (Na and K), which is retained in a ceramic matrix of $LiAlO_2$. The fuel cell operates at 600 to 700 °C where the alkali carbonates form a highly conductive molten salt, with carbonate ions providing ionic conduction. As high operating temperatures in MCFC, Ni (anode) and nickel oxide (cathode) are adequate to promote reaction, noble metals are not required.

2.1.5 Solid oxide fuel cell (SOFC)

The solid oxide fuel cell (SOFC) is an all-solid-state power system which usually use Y_2O_3-stabilized ZrO_2 as an electrolyte. The cell operates at 700 to 1000°C where an ionic conduction by oxygen ions takes place. Typically, Ni-ZrO_2 cermet and Sr-doped $LaMnO_3$ are used as the anode and cathode, respectively.

The details of SOFC technology will be described in the next section because it is the main target in this thesis.

2.2 Solid Oxide Fuel Cell

SOFC technology is the most demanding from a materials standpoint and is developed for its potential market competitiveness arising from: (Stambouli and Traversa, 2002)

- SOFC is the most efficient (fuel input to electricity output) fuel cell electricity generators currently being developed world-wide.
- SOFC is flexible in the choice of fuel such as natural gas.

- SOFC has a modular and solid state construction and does not present any moving parts, thereby is quiet enough to be installed indoors.
- SOFC does not have problems with electrolyte management. There is no liquid electrolyte with its attendant material corrosion and electrolyte management problems or flooding in the electrodes.
- The high operating temperature of SOFC allows internal reforming, promotes rapid kinetics without precious or noble metals.
- The high operating temperature of SOFC produces high quality heat by product which can be used for co-generation, or for use in combined cycle applications.
- Normal SOFC has extremely low emissions by eliminating the danger of carbon monoxide in exhaust gases.
- The solid state character of all SOFC components means that there is no fundamental restriction on the cell configuration.

However, nowadays, SOFC is the best suited for provision of power in utility applications due to the significant time required to reach operating temperatures.

2.2.1 Principle of SOFC

The operating principle of SOFC with an oxygen ion conductor is schematically shown in Figure 2.1. SOFC consists of two electrodes sandwiched on both sides of a hard ceramic electrolyte such as the remarkable ceramic material called zirconia. Hydrogen or carbon monoxide fuel is fed into the anode of the fuel cell and oxygen, from air, enters the cell through the cathode.

When the circuit is connected or an external load is applied to the cell which allows electrons to flow from the anode to the cathode, oxygen is reduced at the porous air electrode to produce oxygen ions. These ions migrate through the solid electrolyte to the fuel electrode, and they react with the fuel, H_2 or CO, to produce H_2O or CO_2.

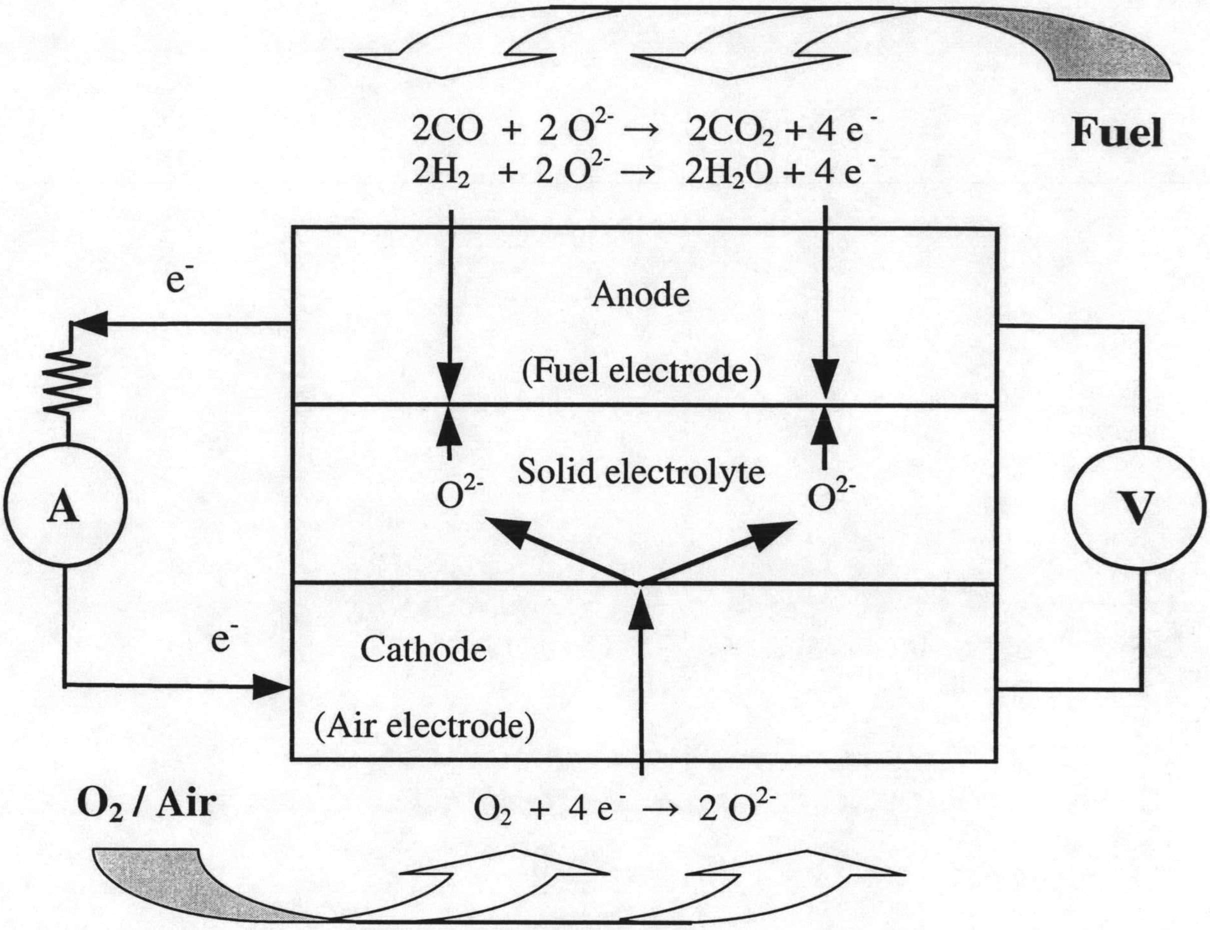


Figure 2.1 Principle of operation of SOFC

Alternatively, a proton conducting solid electrolyte can be used, where H_2 is oxidized to produce protons which subsequently react with oxygen to form water. In some cases, CH_4 can be oxidized directly on the anode to form CO_2 and H_2O. The open-circuit voltage, E_{OCV}, of the cell can be calculated from the free energy change, ΔG, of the electrochemical reaction

$$E_{\mathrm{OCV}} = \frac{-\Delta G}{nF}$$

In this equation, T is the absolute temperature, F the Faraday constant, and n the electron equivalent of oxygen.

However, when a fuel cell is operated, the voltage is less than this theoretical value. The difference or the voltage drop was resulted from four major irreversibilities or losses. (Larminie and Dicks, 2000)

- Activation losses

These are caused by the slowness of the reactions taking place on the surface of the electrodes. The slow step could be from many possibilities such as adsorption of reactant to the surface of electrode catalyst or desorption of product. Because of high operating temperature of SOFC, the reaction rate is rapid, the activation loss is usually small.

- Ohmic losses

This voltage drop is the resistance to the flow of electrons through the material of the electrodes and the various interconnections and the resistance to the flow of ions through the electrolyte and also by contact resistance between cell components. This voltage drop is essentially linear and proportional to current density called "ohmic" losses.

- Mass transport or concentration losses

Mass transport or concentration losses appear when the electrode reaction is hindered by mass transport effects. These result from the change in the concentration of reactants at the surface of the electrodes and become severe as the degree of conversion increase. This loss can be minimized with increasing feed velocity of reactant and/or the removing velocity of reaction product.

- Fuel crossover and internal currents

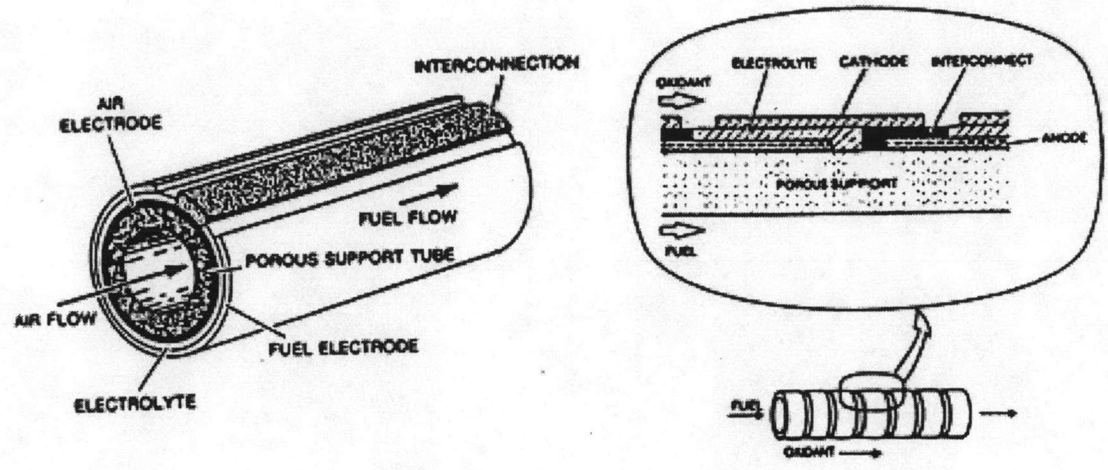
This loss results from the waste of fuel passing through the electrolyte, and, to a lesser extent, electron conduction through the electrolyte. The electrolyte should only transport ions through the cell, however, a certain amount of fuel diffusion and electron flow will be possible. The fuel loss and current are usually small.

2.2.2 Cell components

SOFC single cell consists of an oxide electrolyte sandwiched between an anode and a cathode. Under typical operating conditions (with hydrogen fuel and oxygen oxidant), a single cell produces less than 1 V. Thus, practical SOFCs are not operated as single units; rather, they are connected in electrical series to build up voltage and/or in electrical parallel to build up current to achieve workable power outputs. Single cells are combined to multi-cell units, referred as a stack. A component, variously called an interconnect or a bipolar separator, connects the anode of one cell to the cathode of the next cell in a stack.

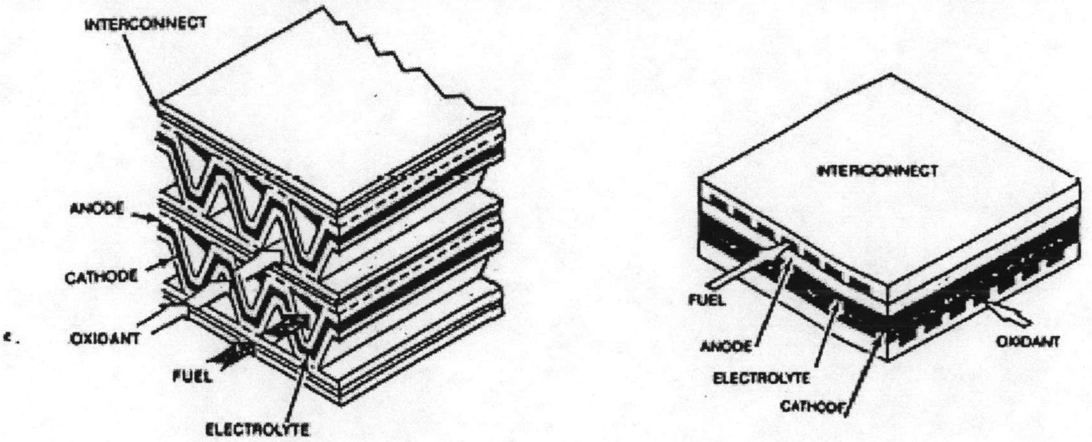
The developments of suitable low cost materials and fabrication of ceramic structure are presently the key technical challenges of SOFC. Each component in the SOFC stack must meet certain requirements and also conjunction with the other cell component. Each component must have the proper stability (chemical, phase, and microstructure) in oxidizing and/or reducing environments, and compatibility with other components. Structural components should have reasonable strength and toughness at the cell operating temperature, as well as reasonable thermal shock resistance. The thermal expansion mismatch between various cell components should be minimized to reduce stresses arising and to avoid separation or cracking during fabrication and operation. The electrolyte and interconnect must be free of porosity to prevent gas mixing, while the anode and cathode must be porous to allow gas transport to the reaction sites. The requirements for the various cell components are summarized in Table 2.1.

Since all the components are solid, the SOFC stack can be casted into flexible shapes which are unachievable in other types of fuel cells. The cell configurations can respond to other design prerequisites. At present, four common stack configurations have been proposed and fabricated for SOFC: tubular design, segmented-cell-in-series design, monolithic design, and flat-plate or planar design. Each design may have several variations; for example, the tubular design can be in the form of a sealless tube closed at one end or a microtube open at both ends (Minh, 2004). Figure 2.2 shows the schematic diagrams of the various SOFC stack designs (Minh, 1993; Minh and Takahashi, 1995).



Seal-less Tubular Design

Segmented-Cell-in-Series Design



Monolithic Design

Flat-plate Design

Figure 2.2 SOFC stack designs (Minh and Takahashi, 1995).

Table 2.1 Requirement for solid oxide fuel cell component (Minh and Takahashi, 1995).

Component	Requirements				
	Conductivity	Stability	Compatibility	Porosity	Thermal Expansion
Electrolyte	High ionic conductivity Negligible electronic conductivity	Chemical, phase, morphological, and dimensional stability in fuel and oxidant environments	No damaging chemical Fully interactions or interdiffusion with adjoining cell components	Fully dense	Thermal expansion match with adjoining components
Cathode	High electronic conductivity	Chemical, phase, morphological, and dimensional stability in oxidant environments	No damaging chemical Fully interactions or interdiffusion with adjoining cell components	Porous	Thermal expansion match with adjoining components
Anode	High electronic conductivity	Chemical, phase, morphological, and dimensional stability in fuel environments	No damaging chemical Fully interactions or interdiffusion with adjoining cell components	Porous	Thermal expansion match with adjoining components
Interconnect	High electronic conductivity Negligible ionic conductivity	Chemical, phase, morphological, and dimensional stability in fuel and oxidant environments	No damaging chemical Fully interactions or interdiffusion with adjoining cell components	Fully dense	Thermal expansion match with adjoining components