

Chapter 2

Literature Review

2.1 Principles of Fuel Cells

A fuel cell is an electrochemical device which converts energy from a fuel (such as hydrogen, natural gas or other hydrocarbon-based fuels) directly into electricity. The first fuel cell was reported by a Welsh lawyer/scientist Sir William Robert Grove in 1839. Platinum was used as electrodes in dilute sulfuric acid electrolyte, and it was operated at room temperature as shown in Figure 2.1. The electrolysis process is being reversed such that hydrogen and oxygen recombine, and an electric current is generated.

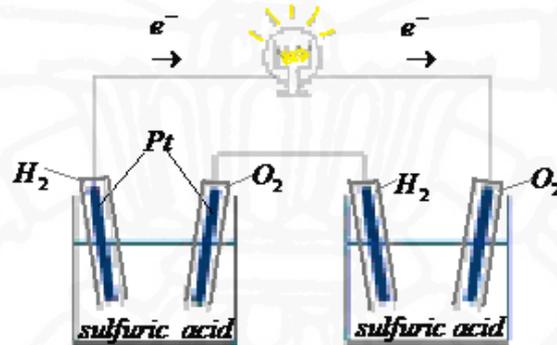


Figure 2.1 Grove's fuel cell is one of the simplest examples (Grove, 1839).

A fuel cell has electrochemical mechanisms similar to a battery but it is different in the fuel supply management. A fuel cell uses externally supplied fuels, while a battery uses internal fuels to produce electricity. There are two main fuel cell operating mechanisms. The conducting ions are supplied either from the cathode or the anode.

At the anode of an acid electrolyte fuel cell, hydrogen gas ionizes, creating electrons and H^+ ions (or protons).



At the cathode, oxygen reacts with electrons taken from the electrode and H^+ from the electrolyte to form water.



The net reaction is similar to the combustion reaction:



2.2 Types of Fuel Cell

Fuel cells are typically classified according to their electrolyte material. Today, there are five main types of fuel cells, i.e. Proton Exchange Membrane Fuel cells (PEMFCs), Alkaline Fuel Cells (AFCs), Phosphoric Acid Fuel Cells (PAFCs), Molten Carbonate Fuel Cells (MCFCs), and Solid Oxide Fuel Cells (SOFCs). Table 2.1 summarizes the main differences between these fuel cell types.

Table 2.1 Different types of fuel cells (U.S. Department of Energy, 2002; Larminie and Dicks, 2003)

Type of fuel cell	Electrolyte	Charge Carrier	Operating Temperature	Fuel	Oxidant
PEMFC	Polymer: proton exchange membrane	H^+	50-80°C	Hydrogen	O_2 /Air
AFC	Potassium hydroxide (KOH)	OH^-	65-220°C	Pure hydrogen or hydrazine liquid methanol	O_2
PAFC	Phosphoric Acid	H^+	~220°C	Hydrogen	O_2 /Air
MCFC	Molten salts such as CO_3	CO_3^{2-}	~650°C	Hydrogen, CO, natural gas, propane, marine diesel	CO_2/O_2 /Air
SOFC	Ceramic such as YSZ or GDC	O^{2-}	600-1000°C	Natural gas or propane	O_2 /Air

2.2.1 Proton Exchange Membrane Fuel cells (PEMFCs) (Larminie and Dicks, 2003)

A polymeric membrane is used as the electrolyte in PEMFCs. A stream of hydrogen is delivered to the anode side of the membrane-electrode assembly (MEA). At the anode side, it is catalytically divided into protons and electrons. This oxidation process is represented by:



The formed protons permeate through the polymer electrolyte membrane to the cathode side. The electrons travel along an external load to the cathode side of the MEA as shown in Figure 2.2. Hence, the current output of the fuel cell was created. A stream of oxygen is delivered to the cathode side of the MEA. At the cathode side, oxygen molecules react with the protons permeating through the polymer electrolyte membrane and the

electrons arriving through the external circuit to form water. This reduction process is represented by:

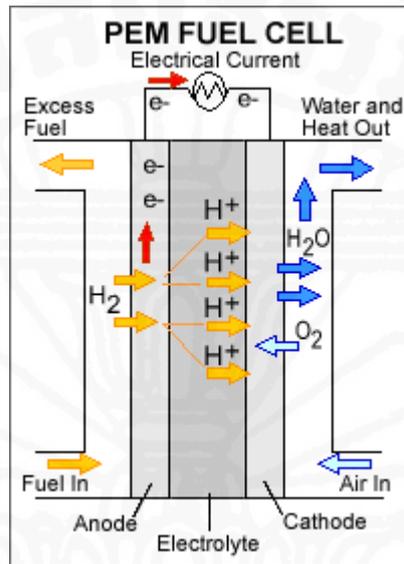
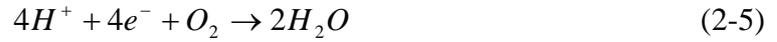


Figure 2.2 Proton Exchange Membrane Fuel cells (U.S. Department of Energy, 2008).

A perfluorosulfonic acid membrane called Nafion is typically used as an electrolyte in PEMFC and Platinum (Pt) or Pt alloy is used as catalyst at low operating temperature. The noble metal alloys are the main cause of the high cost of PEMFCs. The poisoning of Pt by carbon monoxide (CO) is one disadvantage of this low operating temperature fuel cell. Furthermore, the byproduct heat cannot be used for cogeneration due to the low operating temperature and water management becomes a problem. The main advantage which makes PEMFCs suitable for the automotive market is the low operating temperature which allows a quick start-up.

2.2.2 Alkaline Fuel Cells (AFCs) (Larminie and Dicks, 2003)

An AFC contains an alkaline electrolyte such as potassium hydroxide (KOH) and sodium hydroxide (NaOH), which are the lowest cost and not excessively corrosive. The fuel cell produces power through a redox reaction between hydrogen and oxygen as shown in Figure 2.3.

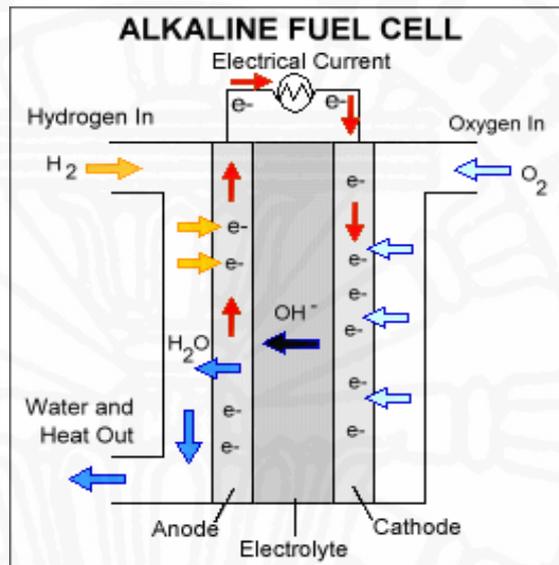


Figure 2.3 Alkaline Fuel Cells (U.S. Department of Energy, 2008).

At the anode, hydrogen is oxidized according to the reaction:



At the cathode, oxygen reacts with electrons taken from the electrode, and water in the electrolyte, forming new OH^- ions.



However, CO_2 in the oxidants and fuels could react with the electrolyte forming carbonate which in turn reduces the OH^- mobility. Therefore, the requirement of AFC is no CO_2 present in the oxidants and fuels.

2.2.3 Phosphoric Acid Fuel Cells (PAFCs) (Larminie and Dicks, 2003)

A PAFC shown in Figure 2.3 works in a similar way as a PEMFC in that it utilizes a proton conducting electrolyte. A PAFC uses phosphoric acid (H_3PO_4) as an electrolyte with Pt as a catalyst. The reactions which occur on the anode and cathode sides are:

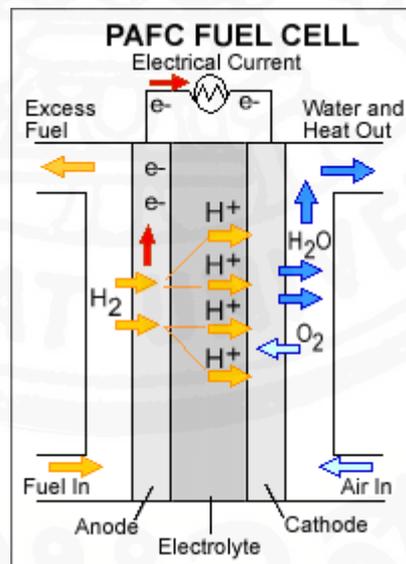
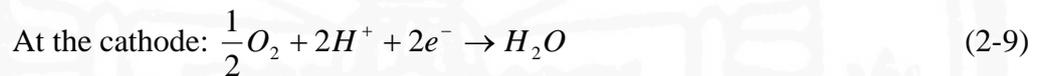


Figure 2.4 Phosphoric Acid Fuel Cells (U.S. Department of Energy, 2008).

The acid is used as an electrolyte therefore components in the cell need to be corrosion resistant, which increase the cost. In addition, although CO_2 does not react with

the electrolyte but dilute the electrolyte. However, the CO poisoning of Pt catalyst remains a problem.

2.2.4 Molten Carbonate Fuel Cells (MCFCs) (Larminie and Dicks, 2003)

An MCFC is another type of high temperature fuel cell. A molten salt of alkali carbonate such as lithium, sodium, potassium carbonate retaining in a ceramic matrix is used as the electrolyte. The MCFC operates with CO_2 containing fuel at high temperatures to yield sufficiently high CO_3^{2-} mobility. Nickel (Ni) and nickel oxide (NiO) are used as the anode and cathode, respectively as shown in Figure 2.5.

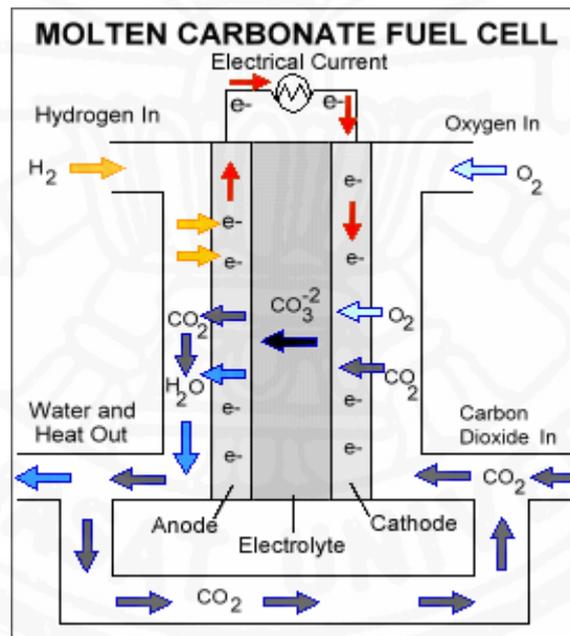
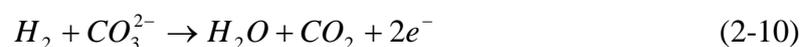


Figure 2.5 Molten carbonate fuel cells (U.S. Department of Energy, 2008).

At the anode, hydrogen reacts with the carbonate ions to produce water, electrons and carbon dioxide.



The electrons are transported away via an external circuit to the cathode. Oxygen from air and carbon dioxide from the anode react with electrons at the cathode to form water and carbonate ions.



The carbonate ions migrate through the electrolyte to the anode, and complete the electrical circuit. CO_3^{2-} is used up at the anode while CO_2 is consumed at the cathode. Therefore, the disadvantages of MCFCs are the corrosive nature of the components and the need for an extra source of CO_2 at the cathode.

2.2.5 Solid Oxide Fuel Cells (SOFCs) (Minh and Takahashi, 1995; Larminie and Dicks, 2003)

Ceramic fuel cells are also known as Solid Oxide Fuel Cells (SOFCs). Ceramic components are used as SOFC electrodes and electrolyte as shown in Figure 2.6.

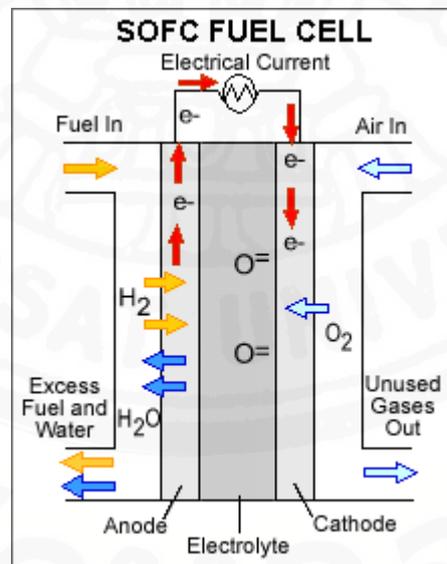


Figure 2.6 Solid Oxide Fuel Cells (U.S. Department of Energy, 2008).

At the cathode, the reduction of oxygen occurs via



At the anode, O^{2-} reacts with hydrogen producing water:



SOFCs are operated at very high temperature, around 1000°C. The high operating temperature helps to eliminate the water management problem because water is evaporated at high temperature. Moreover, it can also be operated with a variety of fuels and the byproduct heat can be used to generate additional electricity. However, the main disadvantage of SOFC is its high operating temperature, which causes thermal expansion mismatch and limits the material choices of SOFC components. The high operating temperature also results in a slow start up.

At present, SOFC technology is still in its development. Because of the high degradation rates and materials costs incurred at 1000°C, it is economically more favorable to operate SOFCs at lower temperatures (600-800°C). The need for low-cost materials which are durable at high temperatures and low temperature operation are the main technical and economical challenges.

2.3 Advantages/Disadvantages of Fuel Cells (Larminie and Dicks, 2003)

2.3.1 Advantages

The most attractive feature of fuel cells is its ability to produce electricity, in an environmentally-friendly manner. In addition, there are many advantages as follows:

1) **High conversion efficiency:** fuel cells are generally more efficient than combustion engines. The fuel cell produces high quality byproduct heat suitable for use in cogeneration (simultaneous production of electrical power and heat) or bottoming cycles (the use of byproduct heat to generate additional electricity) as shown in Figure 2.7.

2) Low emission: no undesirable products such as NO_x and SO_x are produced during operation. The byproduct of the fuel cell is water when hydrogen is used as a fuel. It means a fuel cell can be operated with zero emission.

3) The fuel cell operation is quiet because it has no moving parts. Moreover this can lead to long lasting systems.

4) Fuel cell systems can be designed to match the load requirements. It is easily scalable.

5) Fuel cells can work as long as fuel and oxidants are supplied.

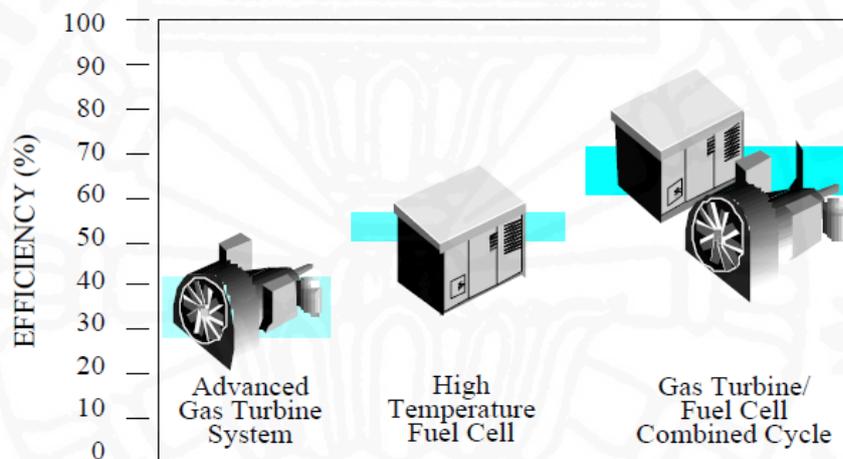


Figure 2.7 Combination the SOFC with a gas turbine engine to improve efficiency (U.S. Department of Energy, 2002).

2.3.2 Disadvantages

1) The main disadvantage of a fuel cell is its cost. The materials and system production are of high cost.

2) The volumetric power density of fuel cells is lower than batteries and combustion engines.

3) Most fuel cells work best with hydrogen gas, which is not widely available. Currently, hydrogen storage cannot contain high hydrogen density/pressure.

4) A high operating temperature fuel cell such as an SOFC encounters problems with durability upon cyclic on-off heating.

2.4 Solid Oxide Fuel Cell Components (Minh and Takahashi, 1995; Singhal and Kendall, 2003)

An SOFC single cell consists of two porous electrodes (cathode and anode), on either side of an electrolyte, which is made of a ceramic material as shown in Figure 2.8.

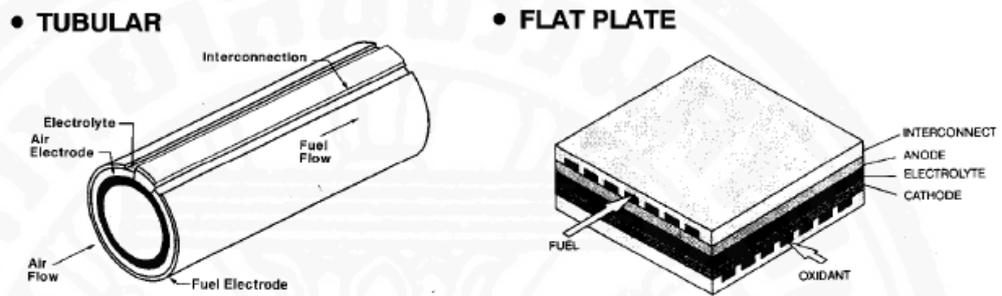


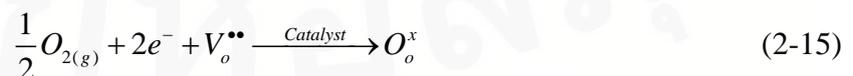
Figure 2.8 Solid Oxide Fuel Cell designs (U.S. Department of Energy, 1998).

For the half-cell reactions at the cathode, the oxidant (oxygen gas) in air is fed to the cathode, while fuels such as hydrogen or natural gas are fed to the anode. The net reaction is similar to the combustion reaction (2-14).

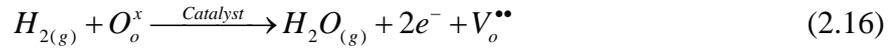


The electrolyte is also acting as a reaction separator. The combustion reaction is separated into two electrochemical half-cell reactions as shown in reactions (2-15)-(2-16).

A half-cell reaction at the cathode can be expressed as



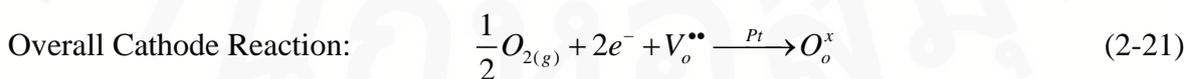
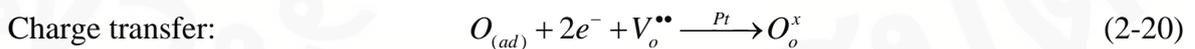
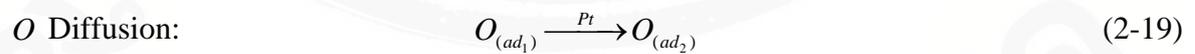
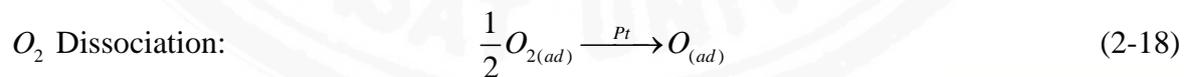
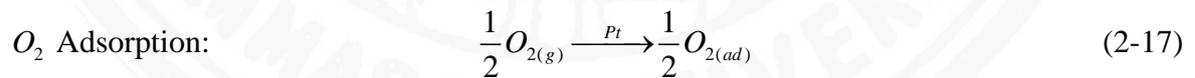
A half-cell reaction at the anode can be expressed as



2.4.1 Electrodes

1) Cathode (Minh, 1993)

The cathode material must be an electronic conductor in an oxidizing environment. Since the SOFC operates at high temperatures (600-1000°C), the cathode must be chemically and thermally compatible with the other cell components, from room temperature to those operating temperatures and to the even higher temperatures at which the fuel cell is fabricated. Hence, a stable oxide or noble metals are the material of choices. Doped $LaMnO_3$ has been extensively used as cathode material in the SOFC such as $La_{1-x}Sr_xMnO_3$ (Minh and Takahashi, 1995). This material has high electronic and ionic conductivity. However, at low temperature (250-600°C), the material becomes an inactive catalyst. To improve the cathode catalytic activities, Pt is an interesting choice (Xiong and Manthiram, 2005; Xu, Ruban, and Mavrikakis, 2004). The different reaction steps of half-cell with Pt used as a catalyst are shown in reactions (2-17)-(2-21).



The requirements of cathode are the following:

1) **Stability:** The cathode must be chemically, morphologically, and dimensionally stable in the oxidant environment. The cathode must maintain its desired microstructure in long-term operation; significant microstructural changes cause degradation in the cell performance.

2) **Conductivity:** The cathode must possess sufficient electronic conductivity to support electron flow in the oxidizing environment at the operating temperature.

3) **Thermal expansion:** The thermal expansion of the cathode must match that of other cell components from room temperature to operation and fabrication temperatures to avoid cracking.

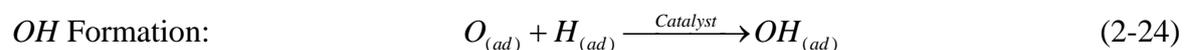
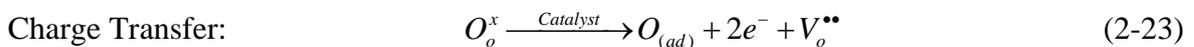
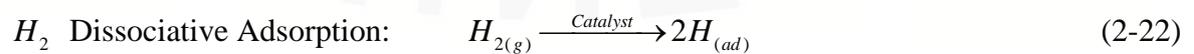
4) **Compatibility:** The cathode must be compatible with other components, not only at the operating temperature, but also at the higher temperature at which the fuel cell ceramic structure is fabricated.

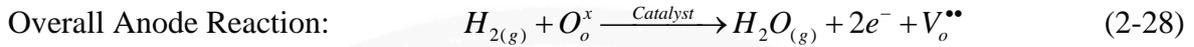
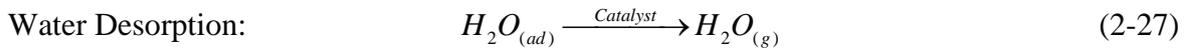
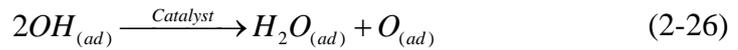
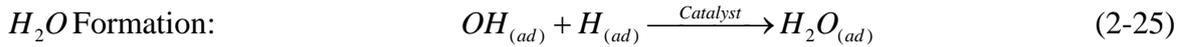
5) **Porosity:** The cathode must have sufficient porosity to allow gas transport to the reaction site.

6) **Catalytic activity:** The cathode must have high catalytic activity for the electrochemical reduction of the oxidant.

2) Anode (Minh, 1993)

An anode is located on the fuel supply side of SOFC. Nickel is mixed with yttria-stabilized zirconia, a cermet (Ni/YSZ) used as the anode (Minh and Takahashi, 1995; Sammes, 2006). YSZ has high ionic conductivity while Ni has reasonably high electronic conductivity. Therefore, the cermet can be both the electrode and catalyst in SOFC. In addition, this cermet has an effective thermal expansion closer to that of the electrolyte. The anode reaction steps are shown in the following reactions:





The key requirements for an anode in the SOFC are the followings:

1) Stability: The anode must be chemically, morphologically, and dimensionally stable in the fuel (reducing) environment.

2) Conductivity: The anode must possess sufficient electronic conductivity to support electron flow in the reducing environment at the operating temperature.

3) Compability: The anode must be chemically compatible with other components, not only at the operating temperature, but also at the much higher temperature at which the fuel cell ceramic structure is fabricated.

4) The thermal expansion: The thermal expansion of the anode must match (from room temperature to operation and fabrication temperatures) that of other cell components to avoid cracking and delamination during fabrication and operation, including thermal cycling. The coefficient of thermal expansion of the anode must remain unchanged despite changes in oxygen partial pressure of the fuel atmosphere during operation.

5) Porosity: The anode must have sufficient porosity to allow gas transport to the reaction sites. The lower porosity is set by mass transport considerations. (The porosity limit may be less critical for mixed conducting anode materials.) The upper limit is based on consideration of mechanical strength of the component.

6) Catalytic activity: The anode must have sufficient catalytic activity, thus low polarization, for the electrochemical oxidation of the fuel. The anode must be tolerant to certain levels of contaminants (e. g., sulfur) commonly present in fuel gas.

3) Electrolyte

A solid electrolyte for use in SOFCs must fulfill certain criteria apart from the high oxygen ion conductivity. It must be a pure oxygen ion conductor, close to zero electronic conductivity and chemically stable with respect to other cell components. The material must be 100% dense, to prevent a direct mixing of the fuel and the air. If the fuel and air are mixed, the combustion rather than an electrochemical oxidation of the fuel occurs. The electrolyte not only transports dissolved reactants to the electrode, but also conducts ionic charge between the electrodes and thereby completes the cell electric circuit.

Zirconia-based electrolyte such as Yttria Stabilized Zirconia (YSZ) is the most popular electrolyte material for solid oxide fuel cells (SOFCs) because it conducts only oxygen ions over a wide range of oxygen partial pressures. Yttria (Y_2O_3) introduces high concentrations of oxygen vacancies into the zirconia crystal structure as shown in Figure 2.10. This high oxygen vacancy concentration allows YSZ to exhibit high ionic conductivity.

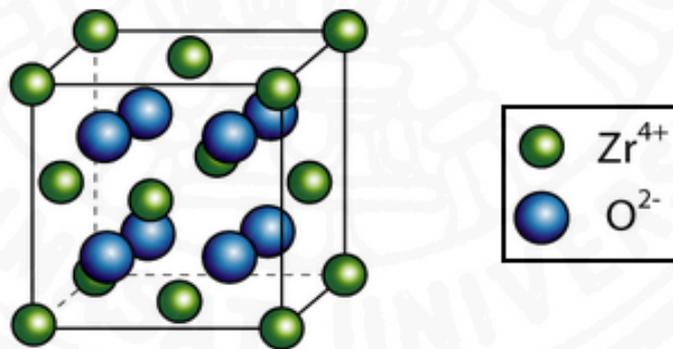


Figure 2.9 Cubic fluorite structure of zirconia (Skinner and Kilner, 2003).

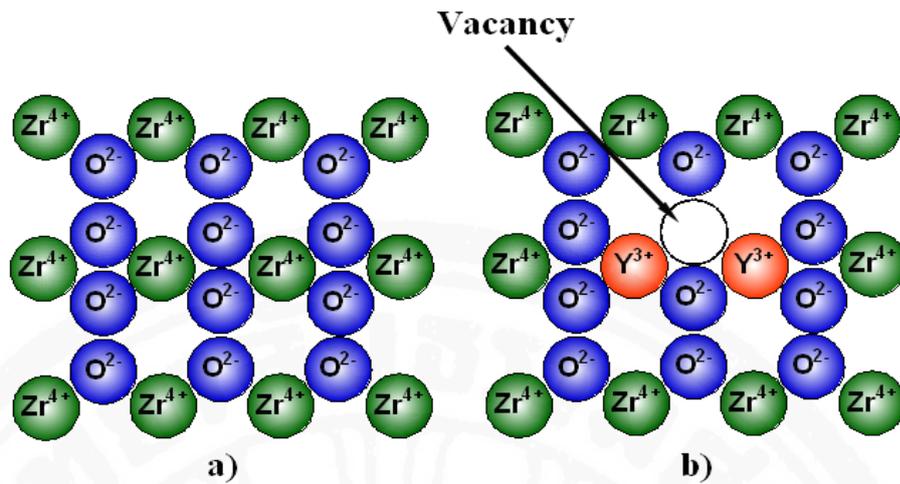


Figure 2.10 Stabilization of zirconia using yttria, a) pure ZrO_2 , and b) YSZ (Skinner and Kilner, 2003).

An addition of yttria to zirconia introduces oxygen vacancies due to charge compensation effects. Pure ZrO_2 forms an ionic lattice consisting of Zr^{4+} ions and O^{2-} ions, as shown in Figure 2.10a), an addition of Y^{3+} ions to this lattice upsets the charge balance. As shown in Figure 2.10b), for every two Y^{3+} ions taking the place of Zr^{4+} ions, one oxygen vacancy is created to maintain the overall charge neutrality as in reaction (2.29). Figure 2.11 shows a phase diagram of a ZrO_2 - Y_2O_3 system. It can be seen that the addition of Y_2O_3 to ZrO_2 reduces the temperature of the tetragonal/monoclinic transformation, and the transformation temperature decreases with increasing Y_2O_3 content. A further increase in Y_2O_3 content results in a homogeneous cubic solid solution. The minimum Y_2O_3 amount required to fully stabilize the cubic phase of ZrO_2 is approximately 8 to 10 mol% (Stubican, 1988).



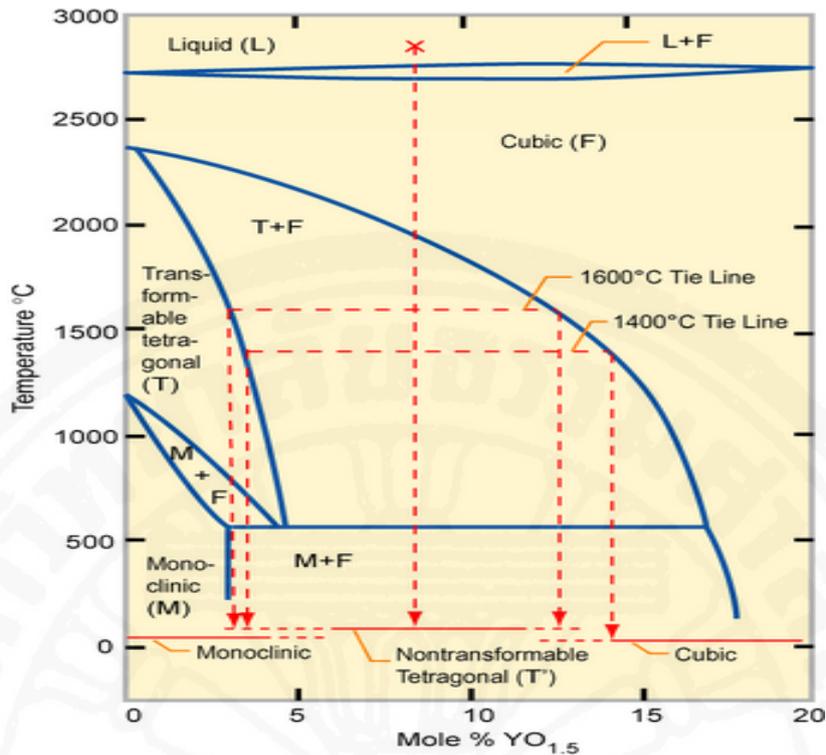
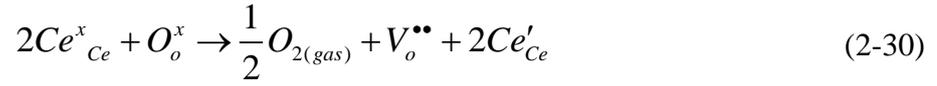
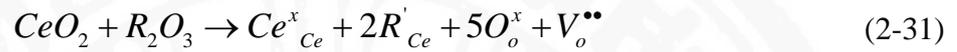


Figure 2.11 Phase diagram of ZrO₂-Y₂O₃ system (Miller, 1977).

Ceria-based electrolytes are attractive for low temperature SOFCs (Steele, 1989) because the electrical conductivity and diffusion constants of various fluorite compounds are compared and those of ceria-based oxides are almost the highest among these fluorite oxides (Inaba and Tagawa, 1996). Cerium oxide (CeO₂) has a fluorite structure which is similar to zirconia-based electrolyte and it is important for an application such as electrolyte for SOFCs because the ceria lattice contains a high concentration of highly mobile oxygen vacancies. However, ceria has been known not to be easily used with hydrogen and wet hydrocarbon fuels because of its structural change (Ce⁺⁴→Ce⁺³) which causes a decline in mechanical strength under reduction atmosphere. The equilibrium in reaction (2.30) describes the reduction of Ce⁺⁴ to Ce⁺³ via the creation of oxygen vacancies. CeO₂ is reduced at high temperature and low oxygen partial pressure resulting in oxygen deficiency. When CeO₂ is reduced to CeO_{2-y}, defects are formed in the form of oxygen vacancies, and the Kröger-Vink notation for such a reduction reaction may be written as



CeO₂ is not used as an electrolyte for an SOFC because its ionic conductivity is not particularly high from a low concentration of oxygen vacancies. Therefore, introducing the aliovalent ions into CeO₂ formed the oxygen vacancies. The process of incorporating the trivalent ions of the dopant is described by the reaction:



The conductivity of doped ceria systems depends on the kind of dopant (Ln) and its concentration. Yahiro et al. (1988) reported a typical dopant concentration dependence of the electrical conductivity. Moreover, the conductivity of the CeO₂–Ln₂O₃ system depends on the dopant ionic radius resulting in the binding energy of the electrolyte structure. The binding energy is closely related to the conductivity as shown in Figure 2.12. The dopant with low binding energy exhibits higher conductivity as reported by Butler et al. in 1983. Table 2.2 lists conductivity data for various doped CeO₂ materials.

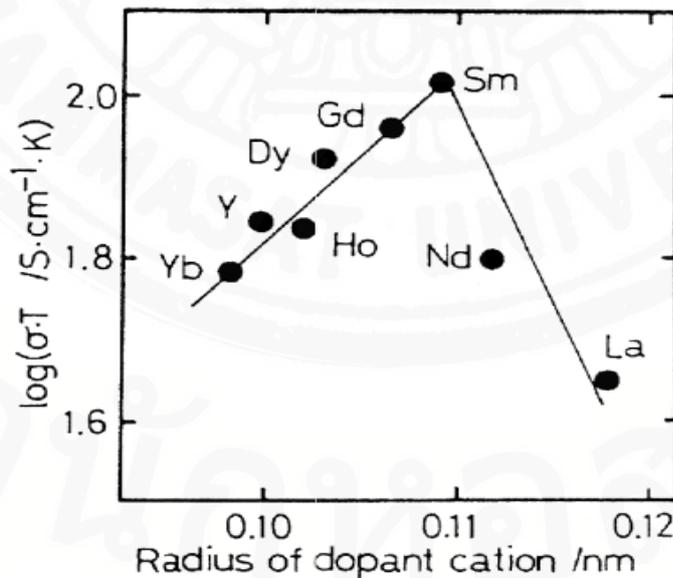


Figure 2.12 Influence of ionic radii of dopants over the ionic conductivity of CeO₂-based electrolytes (Yahiro, 1988)

Table 2.2 Ionic conductivity of Doped CeO₂

Dopant	Content (mol%)	Ionic conductivity at 800°C (10 ⁻² Ω ⁻¹ cm ⁻¹)	Ref.
La ₂ O ₃	10	2.2	Takahashi et al. (1965)
Y ₂ O ₃	20	5.5	Yahiro et al. (1989)
Gd ₂ O ₃	20	8.3	Yahiro et al. (1989)
Sm ₂ O ₃	20	11.7	Yahiro et al. (1989)
CaO	10	3.5	Tuller and Nowick (1975)
SrO	10	5.0	Yahiro et al. (1986)

Of all these dopants, Gd₂O₃ and Sm₂O₃-doped ceria were found to have the highest conductivity (Steele, 1989). However, there are many reports showing that the CeO₂ –Gd₂O₃ system have the highest conductivity (Mogensen, 1994 and Steele, 2000). Hence, Gd₂O₃-doped CeO₂ (Gadolinia doped Ceria: GDC) is chosen for an intermediate temperature solid oxide fuel cell (IT-SOFC).

2.5 Electrical Property of Electrolyte in SOFC

The electrical properties of electrolytes for SOFC application can be characterized using a complex impedance measurement which evaluates the conductivities. The ionic conductivity behavior of the electrolyte is influenced by several factors such as dopant and dopant concentration, temperature, atmosphere, grain boundary, and time.

The complex impedance measurement is a well established technique to measure an ionic conductivity of electrolytes and ceramics in general. It depends on the microstructure, especially grain boundaries, of the material. Much work on correlating the microstructure and electrical properties can be directly traced to the pioneering study of Bauerle (1969). The complex impedance has also been used to separate the contributions of grain boundaries to the total conductivity. Equivalent circuits are used to analyze the impedance data elucidating the contributions of grain boundaries. Most of us are familiar with the common form of Ohm's law,

$$V = IR \quad 2.1$$

Where V is the voltage (volts, V), I is the current (amps, A), and R is the resistance (ohms, Ω) to the current flow. This law is the basis in an investigation of electrolyte conductivity. The resistance (R) of a resistor is a characteristic of the size, shape, and properties of the materials used at that particular temperature.

$$R = \rho \frac{l}{A} = \frac{l}{\sigma A} \quad 2.2$$

Where l is the length (cm), A is the cross-sectional area (cm^2), ρ is the electrical resistivity ($\text{ohm}\cdot\text{cm}$ or $\Omega \cdot\text{cm}$), and σ , which is the reciprocal of ρ , is the electrical conductivity ($\text{ohm}^{-1} \cdot\text{cm}^{-1}$).

The complex impedance plot of an electrolyte of an SOFC consists of three equivalent circuits that the first semicircle represents the bulk resistance (R_b), the second represents the grain boundary resistance (R_{gb}) and the last one is the electrode resistance (R_e). Figure 2.13 shows a complex impedance plot of the imaginary (Z'') vs. the real (Z') components for these circuits over a wide range of frequencies. The diameter of each semicircle is the resistance of the corresponding circuit element. The high-frequency semicircle provides the bulk resistance and capacitance of the interior of grains; the intermediate-frequency semicircle provides the grain boundary resistance and capacitance; and the low-frequency semicircle provides information on the oxygen ion transfer at the electrodes.

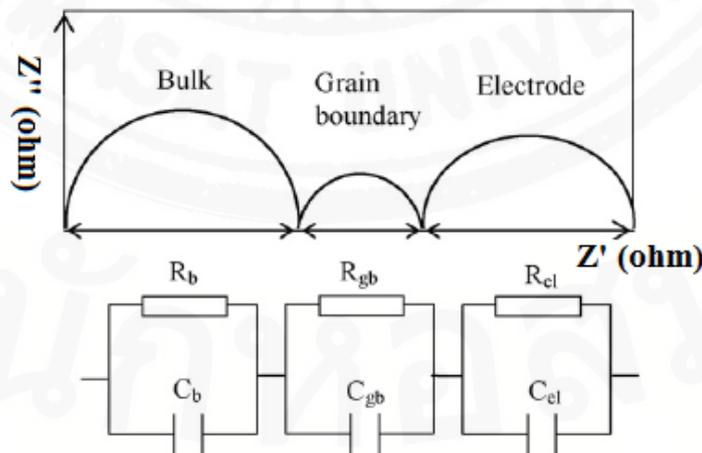


Figure 2.13 Schematic complex plot and equivalent circuit of polycrystalline (Barsoukov and Macdonald, 2005).

The electrolyte conductivity is investigated from the first two semicircles which are bulk and grain boundary resistances. The bulk properties are sensitive to the chemical composition, internal porosity and the presence of additional phases. The grain boundary contribution is influenced by the sample purity, doping concentration, aging, grain size, porosity and space charge (Macdonald, 1953). The total resistance (R_{total}) of the electrolyte can be obtained from the impedance data according to

$$R_{total} = R_b + R_{gb} \quad 2.3$$

The calculation of the electrolyte conductivity is based on Equations 2.4 and 2.5. According to the Arrhenius equation, the conductivity of electrolyte can be expressed as:

$$\sigma_T = \left(\frac{A}{T}\right) \exp\left(\frac{-Ea}{RT}\right) \quad 2.4$$

$$\ln \sigma_T T = -\frac{Ea}{RT} + \ln\left(\frac{A}{T}\right) \quad 2.5$$

Where Ea is the activation enthalpy for ionic conductivity (J/mol), T is absolute temperature (K), R is a gas constant (8.314 J/K mol), and A is the pre-exponential factor.

The electrical conductivity of the electrolytes as a function of temperature typically follows Arrhenius-type behavior. Figure 2.14 shows several Arrhenius conductivity plots of selected oxygen ion conductor which were considered as electrolytes for SOFC.

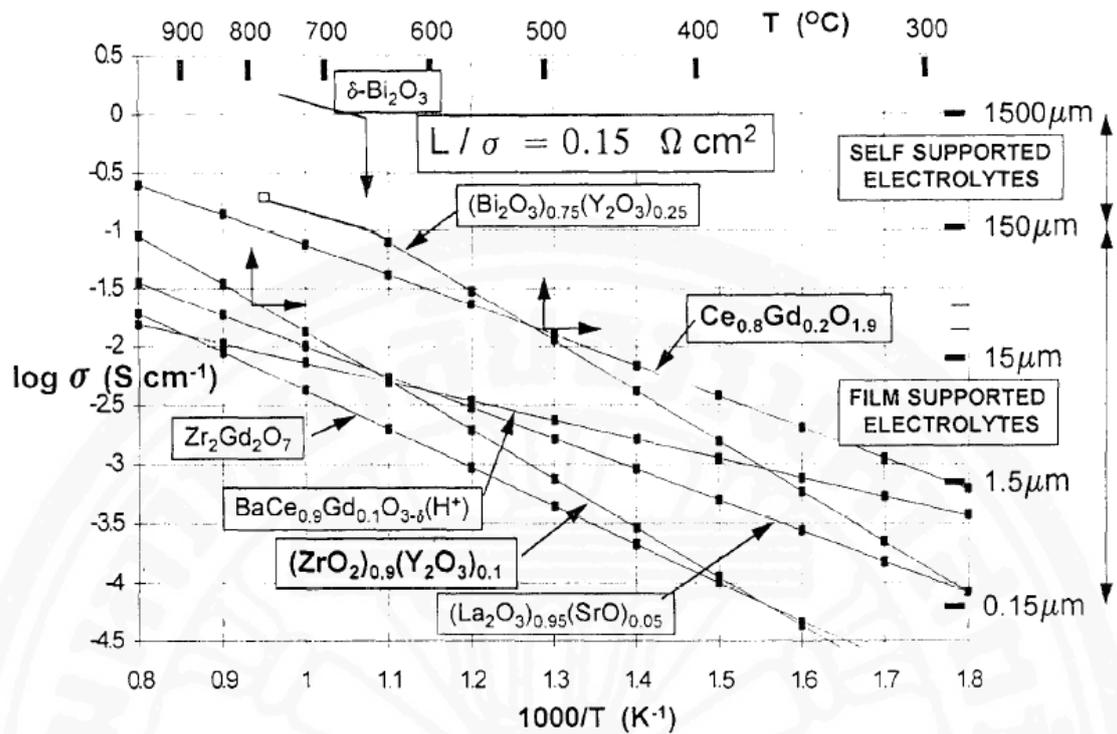


Figure 2.14 Specific ionic conductivity values for selected oxide electrolytes as a function of reciprocal temperature (Steele, 1995).

This work represents the manufacturing and characterizations of a number of electrolytes for SOFCs consisting of both single material electrolytes, i.e., YSZ, TZP, GDC and mixtures of TZP/YSZ and GDC/YSZ as composite electrolytes. To investigate the suitability of the materials used as electrolytes for SOFCs, the electrical properties, microstructure, phases, and mechanical properties of YSZ, TZP and GDC as well as TZP/YSZ and GDC/YSZ composites were characterized.