Chapter 1 Introduction

There has been an increasing interest in developing other sources of energy for many years since the oil crisis in the middle east. In conventional power generators, electric power from fossil fuel including coal, oil and natural gas has three major problems. First, the efficiency of fossil fuel combustion is fairly low regarding the limit of energy conservation. Second, the atmospheric pollution from the inefficiency of heat engines to generate power is a major concern for environmental problems. Emissions of carbon dioxide, oxides of sulfur, oxides of nitrogen including particulate matters harm both environmental and people health. The build-up of carbon dioxide from fossil fuel combustion appears to cause the greenhouse effect. Oxides of nitrogen and sulfur combine with atmospheric moisture and return to the earth as acid rain which cause a great damage to forests, lakes and buildings. Third, the alternative energy is necessary because of the depletion of fossil fuel resources. The devastating oil shortage, especially in the these few years, caused the economic problems in many countries. A better idea to resolve these problems is to develop the less polluting and higher efficiency method to generate electricity. Electric power generation from fuel cells is potentially one of the best candidates as it has been proved to be economically comparable to conventional cost.

Fuel cells have emerged in the last decade as one of the most promising new technologies for the power generating applications. They generate electric power together with water and heat by means of electrochemical reactions combining a variety of fuels and an oxidant gas⁽¹⁻³⁾. The most common fuel is hydrogen. Other fuels containing hydrocarbons can be used by hydrogen extracting in reforming process. The basic unit of fuel cell is composed of anode, cathode and electrolyte. Hydrogen as fuel gas is oxidized at the anode and electrons are released to the external circuit. Oxidant gas (air or oxygen) is reduced at cathode and electrons are derived from external circuit. The electrolyte conducts ions between the two electrodes. The moving electrons via external circuit create electricity. Like battery, fuel cell can generate electricity electrochemically and it is combined into groups, called stacks, and so joined by the interconnectors to obtain a usable voltage. However, fuel cell does not release energy stored in cell and then run down when energy is used up which happened in battery. On the other hand, it keeps generating electricity as long as both fuei and oxidant are supplied to electrodes⁽¹⁻³⁾.

The most attractive feature of fuel cell is its high energy conversion efficiency regardless of size and load, up to 40-60 percent⁽¹⁾. This is because it converts the chemical energy of fuel and oxidant into electrical energy directly. Emission of pollution of fuel cell is extremely lower than that of the conventional power systems. Fuel cell is inherently modular that can be stacked to various sizes to accommodate capacity needs. It also operates so quietly that it can be sited wherever power is needed. In addition, it offers fuel flexibility and a high potential for cogeneration application.

There are many types of fuel cells. It is convenient to classify them into 5 types⁽¹⁻²⁾ according to the electrolyte material which plays an important role to the operating temperatures of each type⁽¹⁻²⁾.

1. Polymer Electrolyte Fuel Cell (PEFC)

This type uses a solid polymer as the electrolyte. The operating temperature is about $80^{\circ}C^{(1)}$. Pure hydrogen as fuel gas is required for this type. Since there is no other liquid except water in cells, the corrosion problems are minimal. PEFC is practically used for transportation applications⁽²⁾.

2. Alkaline Fuel Cell (AFC)

Potassium hydroxide (KOH) is used as the electrolyte in this type of fuel cell. The fuel gas must be pure hydrogen only because a small amount of carbon dioxide can react with KOH to form potassium carbonate which degrades the fuel cell performance. The operating temperature is approximately 100°C⁽¹⁾. AFC was developed to provide electric power for Apollo space vehicle in 1960⁽¹⁻⁴⁾.

3. Phosphoric Acid Fuel Cell (PAFC)

PAFC uses phosphoric acid as the electrolyte. It operates approximately at $200^{\circ}C^{(1)}$ and uses the same gas as PEFC and AFC. The major problem is the corrosion from the acid electrolyte. PAFC is now in the stage of commercialization⁽⁵⁾.

4. Molten Carbonate Fuel Cell (MCFC)

The carbonate salt is used as the electrolyte in MCFC. The exhaust heat can be used for combined-cycle applications. MCFC uses air and a variety of fuels such as pure hydrogen, hydrocarbons and even carbon monoxide. At high operating temperature, up to 650°C⁽¹⁻²⁾, hydrocarbon fuel can be reformed internally in the cell. However, using carbonate salt brings about severe corrosion problem. MCFC is cost effective and now being tested in the large-scale demonstration plant in Japan and U.S.A.

5. Solid Oxide Fuel Cell (SOFC)

The ceramic electrolyte, usually yttria-stabilized zirconia is used in SOFC. This ceramic electrolyte eliminates the corrosion problems. The operating temperature of SOFC is in the range of 650-1000 $^{\circ}C^{(1-2)}$ which allows internal reforming of fuel, more fuel flexibility and a higher potential for cogeneration or bottom-cycling than MCFC^(1,2,4).

SOFC is apparently the most interesting technology since it offers such the highest efficiency compared to all types of fuel cells. The high operating temperature up to 1000°C promoted rapid electrochemical reaction. Thus, the efficiency of SOFC approaches 60 percent for simple cycle system and 85 percent when the by-product heat is utilized in cogeneration system⁽⁶⁾. The fuel flexibility and the internal reforming of fuel are allowed in SOFC. Another attractive characteristic of SOFC is its solid state nature which eliminates the corrosion problems and the electrolyte management. Furthermore, the oxides of ceramics can be fabricated into flexible shapes such as tubular, planar or monolithic^(1,3,7) by the existing technologies.

The reactions involving the present SOFCs are the oxidation of fuel at anode and the reduction of the oxidant at the cathode. The oxygen ions are conducted from the anode to the cathode and the electrons are circulated via the external circuit.

At the anode, the reaction is $H_{2(g)} + O^{2-} \rightarrow H_2O + 2e'$ At the cathode, the reaction is $\frac{1}{2}O_{2(g)} + 2e' \rightarrow O^{2-}$ Thus, the overall reaction is $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O$

The most frequently used SOFC system^(1,3,7) employs yttria stabilized zirconia (YSZ) as an electrolyte, cermet or Ni-YSZ as an anode and lanthanum strontium manganite as a cathode.

SOFC has many advantages over other technologies as mentioned above. However, there are material-selection problems regarding high temperature operation. To promote SOFCs towards commercialization, there have been many attempts to develop the suitable materials for operating at the temperature below 800°C without impeding their performances. This thesis has studied the possible cathode materials for SOFC which concentrate on lanthanum strontium manganite doped with the selected ions such as cobalt and iron into the system.

The objectives of this thesis are the followings:

- To study the effect of iron or cobalt addition into lanthanum strontium manganite system whether either ion can improve the electrical property compared to the currently used systems.
- 2. To characterize crystal structure, phase, thermal expansion coefficient and electrical property of the modified compositions.