# CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE SURVEY

2.1 Introduction to Solid Oxide Fuel Cells

Nowadays, our need for sustainable energy resources increases causing that the fuel cells are currently attracting interest because of their good potential for power generation in stationary, portable and transport applications. The combination of high efficiency of fuel cells from direct conversion of chemical energy into electrical energy, low emissions of polluting substances such as sulfur, nitrogen oxides, hydrocarbons, a significant reduction of CO_2 emission confers the significant environmental advantages of fuel cells over conventional power generation [Ormerod R.M., 2003; Singhal S.C., 2007].

A fuel cell by definition is an electrical cell, which unlike storage cells can be continuously fed with a fuel so that the electrical power output is sustained indefinitely [Connihan M.A., 1981]. They convert hydrogen, or hydrogen containing fuels, directly into electrical energy plus heat through the electrochemical reaction of hydrogen and oxygen into water. The process is that of electrolysis in reverse.

$$\text{Overall reaction:} \quad 2H_2(g) + O_2(g) \rightarrow 2H_2O + \text{energy} + \text{heat} \qquad \text{(Eq. 2.1)}$$
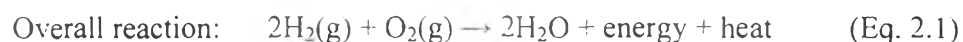
Because hydrogen and oxygen gases are electrochemically converted into water, fuel cells have many advantages over heat engines. These include: high efficiency, virtually silent operation and, if hydrogen is the fuel, there are no pollutant emissions. If the hydrogen is produced from renewable energy sources, then the electrical power produced can be truly sustainable [Cook B., 2001]. Instead of hydrogen, any hydrocarbon fuel can be used as fuel and the formation of water and carbon dioxide is altered during the reactions in the burning, but fuel cells are still very low levels of NOx and SOx emissions [Singhal S.C., 2004; Minh N.Q., 1993].

The concept of the fuel cell was first demonstrated by William Grove (1839). The principle was discovered by accident during an electrolysis experiment. While investigating the electrolysis of water, Grove observed that when the current

was switched off, a small current flowed through the circuit in the opposite direction which is as a result of a reaction between the electrolysis products, hydrogen and oxygen catalyzed by the platinum electrodes. Grove recognized the possibility of combining them in series to form a gaseous voltaic battery, and also made the crucially important observation that there must be a "notable surface of action" between the gas, the electrode and the electrolyte phases in a cell. Maximizing the area of contact between the gaseous reagent, the electrolyte and the electrode (the electrocatalytic conductor), the "three-phase boundary", remains at the forefront of fuel cell research and development [Cook B., 2001; Ormerod R.M., 2003].

2.1.1 Types of Fuel Cells

There is now a whole range of different types of fuel cells, which have been developed and differ in the nature of the electrolyte. However, the basic operating principle of all types of fuel cell is the same as shown in Eq. 2.1 and Fig. 2.1. At the *anode*, a fuel, such as hydrogen, is oxidized into protons and electrons, while at the *cathode*, oxygen gas is reduced to oxygen ions. Protons and oxygen ion then react to form water. Depending on type of the electrolyte, either protons or oxygen ions are transported through an *ion conducting*, but electronically insulating *electrolyte*, while electrons travel around an external circuit delivering electric power. Practical fuel cells are usually not operated as a single unit, but rather are connected in electrical series to build voltage. A series of cells is referred to as a stack. A component, variously called a bipolar separator or an interconnect, connects the anode of one cell to the cathode of the next cell in a stack, as shown in Fig. 2.2. Fuel cell stacks can be configured in series, parallel, both series and parallel, or as single units, depending on the particular application.
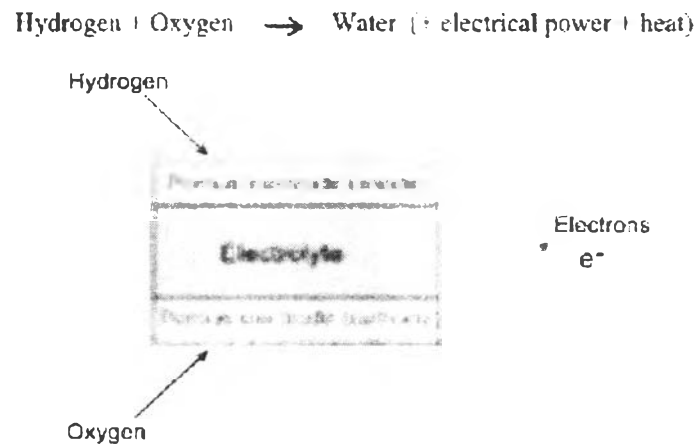
Hydrogen + Oxygen —→ Water (+ electrical power + heat)

Hydrogen

Electrolyte

Electrons
e⁻

Oxygen

Figure 2.1 Schematic diagram showing the general operating principles of a fuel cell [Ormerod R.M., 2003].

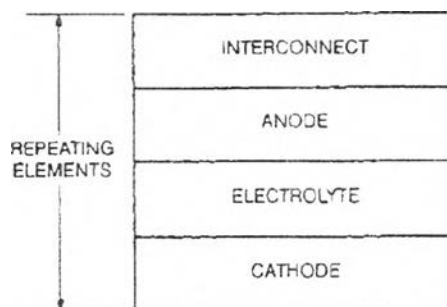| INTERCONNECT |
| ANODE |
| ELECTROLYTE |
| CATHODE |

REPEATING
ELEMENTS

Figure 2.2 Fuel cell components [Minh N.Q., 1993].

There are five main types of fuel cell, as shown in Fig. 2.3:

- Alkaline fuel cells (AFC)
- Phosphoric acid fuel cell (PAFC)
- Polymer electrolyte membrane (PEM) fuel cell
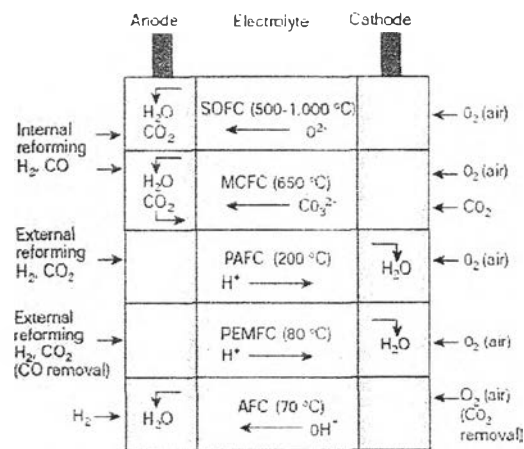- Molten carbonate fuel cell (MCFC)
- Solid oxide fuel cell (SOFC)

Figure 2.3 Summary of fuel cell types [Steele B.C.H. *et al.*, 2001].

Each type of fuel cell is characterized by the electrolyte. It is generally considered that the two types of fuel cells most likely to succeed in achieving widespread commercial application are the polymer electrolyte membrane fuel cells (PEMs) and the solid oxide fuel cell (SOFCs) [Ormerod R.M., 2003]. Differences in the operating temperature is the most obvious distinction between different types of the fuel cells, having a number of implications for the applications for which particular fuel cell types are most suited.

2.1.2 Solid Oxide Fuel Cell

A solid oxide fuel cell was first conceived following the discovery of solid oxide electrolytes by Nernst (1899). A solid oxide fuel cell (SOFC) is characterized by having a solid ceramic electrolyte (hence the alternative name, *ceramic fuel cell*), which is a metallic oxide. A SOFC consists of three basic working parts: cathode, anode and ion conducting electrolyte. At the cathode, oxygen is reduced to oxygen ions, passing through the solid electrolyte under an electrical load, to the anode, where they react with the fuel, generally hydrogen and carbon monoxide, producing water and CO_2, as well as electricity and heat. This is shown schematically in Fig. 2.4. The theoretical maximum efficiency is very high, exceeding 80% [Ormerod R.M., 2003]. Eq. 2.2–2.5 show simple reactions that occur in a SOFC which a mixture of hydrogen and carbon monoxide was used as a practical hydrocarbon fuel with internal reforming and air was used as the oxidant:
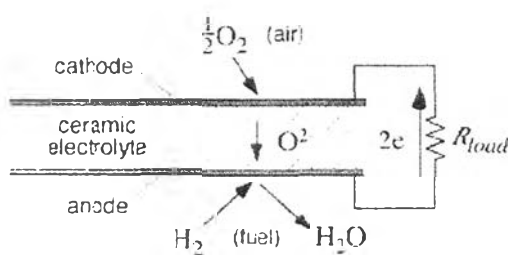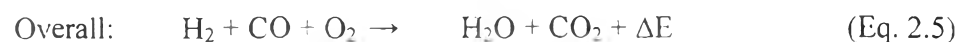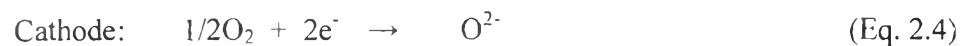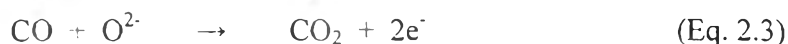
Anode:	$H_2 + O^{2-}$	$\rightarrow$	$H_2O + 2e^-$		(Eq. 2.2)
	$CO + O^{2-}$	$\rightarrow$	$CO_2 + 2e^-$		(Eq. 2.3)
Cathode:	$1/2O_2 + 2e^-$	$\rightarrow$	O^{2-}		(Eq. 2.4)
Overall:	$H_2 + CO + O_2 \rightarrow$		$H_2O + CO_2 + \Delta E$		(Eq. 2.5)

Figure 2.4 Schematic drawing of a SOFC showing the roles of anode, cathode, and electrolyte in a solid oxide fuel cell [Adler S.B., 2004].

A SOFC usually operates at elevated temperatures, conventionally between 800°-1000°C. The elevated operating temperature of SOFCs has a number of advantages. Firstly, high operating temperature allows the possibility of running the SOFC directly on practical hydrocarbon fuels without the need for a complex and expensive external fuel reformer as that is necessary for PEM fuel cells. The hydrocarbon fuel can be catalytically converted (*internally reformed*), generally to carbon monoxide and hydrogen (synthesis gas), within the actual SOFC. It is generally accepted that in order for SOFCs to ever be cost-effective, internal reforming of the fuel within the fuel cell is essential since this increases the efficiency and reduces the complexity of the system, and hence reduces costs. The reformed products, CO and H_2, are then electrochemically oxidized to CO_2 and water at the anode producing electrical power and high grade heat as the by–product. This high quality heat is not wasted, but can be used in various ways. for example, in combined heat and power systems, or to drive a gas turbine to generate more electricity. This significantly increases the overall efficiency of the SOFC compared to lower temperature types of fuel cell.

Beside the ability for internal reforming and the higher overall efficiency, another advantage of a SOFC compared to other types of fuel cells is that SOFCs show a great tolerance to impurities in the fuel and variation in fuel composition which makes the fuel processing requirement less demanding. For example, PEM fuel cells are highly susceptible to poisoning by CO, and thus require complex and expensive external processing of hydrocarbon feeds to convert all CO to CO_2, which is then removed to leave very pure hydrogen as the fuel.

The flexibility in the choice of fuel, with the ability to operate SOFCs directly on practical hydrocarbon fuels, such as, natural gas, methane, propane and butane, coupled with high efficiency makes the SOFC particularly suited to small-scale, stand-alone and remote applications. Nevertheless, one disadvantage of SOFCs that make them not well suited for certain applications is the length of time that is required to heat up and cool down the system, resulting in the brittle component used and because of problems associated with thermal expansion mismatches. This restricts the use of SOFCs in applications that require rapid temperature fluctuations, which is particularly true for transport applications, where a rapid start-up and cool down is essential. Moreover, SOFCs operated at high temperatures have the higher cost of energy and components. Thus, there are considerable interests in lowering the operating temperature of smaller SOFCs to reduce the start up and cool down time, and in particular to reduce costs of components such as interconnect, manifolding and sealing materials.

2.1.3 Intermediate Temperature Solid Oxide Fuel Cells (IT–SOFCs)

From the problems mentioned above on the high temperature operation of conventional SOFCs, there has been an effort over the past few years to lower the SOFC operating temperature below 800°C. The SOFC at a reduced operating temperature can overcome some of these problems and bring additional benefits:

- Low cost metallic materials e.g. ferritic stainless steels can be used as interconnect and construction materials. This makes both the stack.
- More rapid start up and shut down procedures.

- Simplifies the design and materials requirements of the balance of plant making the balance of plant cheaper and more robust. (Balance of plant is widely assumed to constitute 50% of the cost of the SOFC system)
- Significantly reduces corrosion rates.

2.2 Materials for Cathodes

The SOFC places severe demands on the materials used as the electrolyte, the anode, the cathode and the interconnect. Each component must meet certain requirements and has more than one function. All components must possess chemical and physical stability in the appropriate chemical environment (oxidizing and/or reducing), be chemically compatible with the other components, have proper conductivity, and have similar thermal expansion coefficients to the other components to avoid cracking or delamination during fabrication and operation. On top of this it is also important that the SOFC components are of low cost and are strong, yet easy to fabricate [Ormerod R.M., 2003].

In this work, the cathode materials have been focused. The important required properties of cathode materials for SOFCs are as follow:

- High electrical conductivity
- High O^{2-} ion conductivity
- High catalytic activity for oxygen reduction
- Compatibility with other cell components
- Stability in an oxidizing atmosphere
- Porous structure

As electrolytes are developed that operate at reduced temperatures, within the intermediate–temperature regime, one of the main limitations to the performance of electrochemical cells is the air electrode. Electrode performance is dictated by the reaction kinetics and transport properties of the electrode materials, and for high temperature devices, materials that use only a triple-phase boundary (TPB) reaction mechanism offer acceptable performance. However, as temperature is reduced, TPB

kinetics becomes a limiting feature of the device. To overcome this problem, a mixed ionic–electronic conductor (MIEC) is required. MIECs function effectively as intermediate temperature electrodes because of the improvement of the kinetics of the oxygen reduction reaction because of the enhancement of the active area from the TPB to a double inter-phase electrode (MIEC)-air as illustrated in Fig. 2.5. In this case, MIEC materials provide not only the electrons for the reduction of oxygen but also the ionic conduction required to ensure the transport of the formed oxygen.
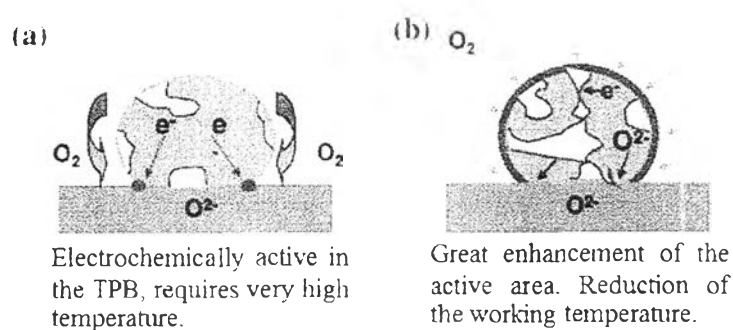

(a)

Electrochemically active in the TPB, requires very high temperature.

(b) O_2

Great enhancement of the active area. Reduction of the working temperature.

Figure 2.5 Active areas for oxygen reduction electrochemical reaction in a (a) pure electronic conductor and (b) mixed ionic-electronic conductor (MIEC) [Aguadero, A. *et al.*, 2012].

2.2.1 Co–Based Perovskites

Most of the state of the art MIEC materials belong to the perovskite-oxide family (ABO_3-type), mixed metal oxides, in which both A- and B-sites can be partially or fully substituted leading to a wide range of oxygen stoichiometries and transport properties. Among them, the Co-based materials have been intensively investigated because of their suitable electrochemical properties. Extensive research efforts have been focused on the $LaCoO_3$-based materials that have demonstrated an excellent combination of high electronic conductivity with good ionic conductivity [Figueiredo, F.M. *et al.*, 1998]. It is worth noting that doped $LaCoO_3$ materials were first investigated as the cathode material for high-temperature SOFCs, which benefited from their high melting point and outstanding chemical stability in oxidizing environments at high temperature (700–1000 °C) [Petrov, A.N. *et al.*, 2006; Zuev, A.Y. *et al.*, 2007], in combination with the previously stated

electrochemical properties. Although $LaCoO_3$ has attractive electrochemical performance at high temperature, some properties, especially the ionic conductivity, have reduced when the operating temperature decreases to intermediate temperature.

The introduction of an alkali earth metal (smaller valence) to the La–Co–O system leads to the formation of solid solutions La–Me–Co O (Me = Ca, Sr, Ba) in which partial substitution of La^{3+} for Me^{2+} leads to an increase of mean oxidation state of cobalt ions and a significant increase of oxygen deficiency [Petrov, A.N. et al., 2006]. During the A-site substitution procedure in $La_{1-x}Me_xCoO_{3-\delta}$, charge compensation is firstly achieved by the increase of valence of cobalt, oxygen non-stoichiometry increases to maintain the charge neutrality [Nakamura, T. et al., 1983]. It is known that important properties of doped lanthanum cobaltite such as oxide-ion and electrical conductivity in ambient atmosphere are directly related to their defect structure [Zuev, A.Y. et al., 2007]. Among the doped lanthanum cobaltites, Sr doping has received most attention not only in this respect but also because of its excellent catalytic activity for oxygen reduction [Teraoka, Y. et al., 1984; Søgaard, M. et al., 2006; Rudberg, E.A. et al., 2005]. While $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC) phases were suggested as promising candidates for the SOFC cathode, the substitution of a transition metal, such as Cr, Cu, Fe and Ni, for cobalt has been found to lead to an increase of oxygen non-stoichiometry and improve substantially the electrocatalytic activity of the cathodes in comparison with $LaCoO_3$ [Zuev, A.Y. et al., 2007, Kharton, V.V. et al., 1998; Yaremchenko, A.A. et al., 1999]. Petrov et al. (2006) concluded that copper substitution into the cobalt sub–lattice leads to the appearance of negative-charged defects on the Co site and formation of oxygen vacancies. Introducing chromium into the cobalt sub-lattice decreases the electrical conductivity and TEC, but increases the sinterability and mechanical strength. Nickel substitution, however, presents a limited stable solid solution formation range (Ni $\geq$ 0.4,), but in contrast to chromium substitution, the electronic conductivity of the material increases with increasing nickel content. Hrovat et al. (1996) also find an optimum composition for cathode performance when Ni = 0.6, finding the TEC of the ceramics in air to be 11.9×10^{-6} K^{-1}. To overcome these issues, the systems with both A- and B-site substitution have been developed such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$

(LSCF) [Tai, L.-W. *et al.*, 1995]. Although $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) perovskite materials exhibit very good conductivities, they also exhibit the large thermal expansion mismatch with the other cell components, causing thermomechanical failure [Qiu, L. *et al.*, 2003].

2.2.2 Ni–Based Perovskites

Co–based perovskites present very high values of electrical conductivity and oxygen permeation leading to very low values of polarization resistance at intermediate temperatures, and are therefore of interest as electrodes. Despite their attractive performance, Co-based compounds present several difficulties in practical operation, and therefore attention is now directed towards non–Co–containing materials. $LaNiO_{3-\delta}$ is also a potential MIEC cathode material but is only stable at temperatures less than 850°C, which severely limits its technological application. The stabilization of the nickelate perovskite at higher temperatures has been a widely used strategy to obtain a suitable cathode material. Among the different dopants in the $LaNi_{1-x}B_xO_3$ system (B = Al, Cr, Mn, Fe Co and Ga), Chiba *et al.* (1999) found that the $LaNi_{0.6}Fe_{0.4}O_3$ composition displays the highest electrical conductivity (580 S cm^{-1} at 800 °C) and relatively low thermal expansion coefficient (11.4 × 10^{-6} K^{-1}) that matches with that of the SOFC electrolytes. In the $LaNi_{1-x}Fe_xO_3$ (x = 0.2-0.5) system, the thermal expansion and the oxygen permeability was found to increase with the Ni content [Kharton, V.V. *et al.*, 1999]. The x = 0.4 composition was also found to display the highest electrochemical performance along the $LaNi_{1-x}Fe_xO_3$ series with area-specific resistance measured as 5.5 Ω cm^2 at 600°C using a $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ electrolyte, which is unfortunately significantly higher than Co-containing perovskites [Kammer, K. *et al.*, 2006].

2.2.3 Ruddlesden–Popper Types

Ruddlesden–Popper type materials (A_2BO_4) which is comprised of alternating perovskite blocks with a rock-salt intergrowth have recently attracted significant attention as alternatives to conventional perovskites for use as promising cathode materials for the next generation of intermediate-temperature SOFCs (IT–SOFCs) [Takahashi, S. *et al.*, 2010; Amow, G. *et al.*, 2006]. These materials,

particularly the nickelate series ($La_{n+1}Ni_nO_{3n+1}$), consists of n consecutive $LaNiO_3$ perovskite layers, alternating with LaO rock-salt layers, stacking along the crystallographic c–axis as shown in Fig. 2.6. Such layered MIECs display diverse defect chemistry, allowing non-stoichiometric defect structures (hypo- and hyper-stoichiometry) because of their oxygen content through tailoring A- and B-site compositions. This feature makes these oxides very attractive of their good electrical and electrochemical properties [Amow, G. et al., 2006; Greenblatt, M., 1997; Zhang, Z. et al., 1995]. Moreover, materials in this group also exhibit coefficient of thermal expansion (CTE) values close to those common SOFC electrolyte materials [Chiba, R. et al., 1999]. The low electronic conductivity of La_2NiO_4, however, needs to be improved [Kharton, V.V. et al., 2004].
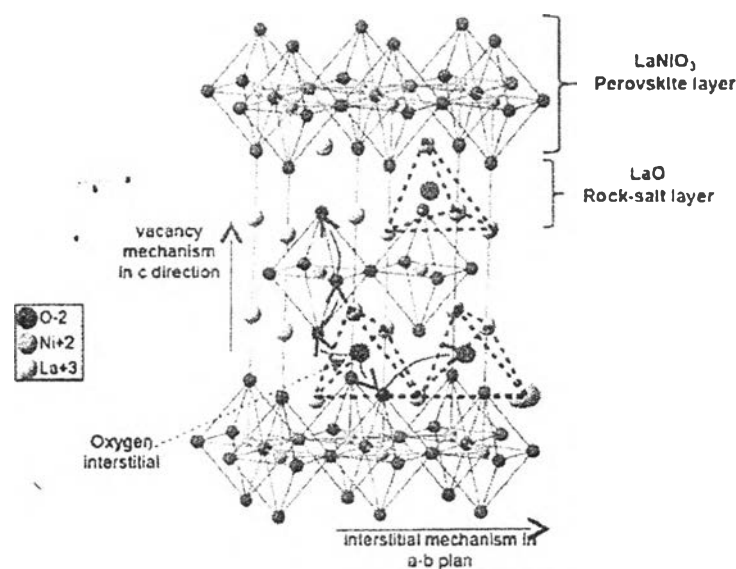

Figure 2.6 Schematic diagram of the La_2NiO_4 structure showing the vacancy and interstitialcy ionic transport directions and $LaNiO_3$ perovskite and LaO rock-salt layers are indicated [Aguadero. A. et al., 2012].

2.2.4 Double Perovskites

Because of almost all elements in the periodic table can be accommodated on the A and/or B sites. perovskite structures with the general formula ABO_3 are highly useful structures [Ormerod, R.M., 2003; Fuertes, V.C. et al., 2011]. If two atoms, B and B', are placed on two crystallographic different B-

sites, a layered perovskite is formed with the general formula $A_2BB'O_6$. B and B' can be completely or partially ordered depending on the size and charge differences between the B ions and the degree of order also strongly affected on the properties of these materials. Besides, the double perovskite materials can be written with formula as $A_3B_2B'O_9$ [Fuertes, V.C. *et al.*, 2011]. Because ordering can be in a rock salt pattern, with different cations occupying alternating BO_6 octahedra, the B–site ordered perovskites should be similar to the relatively open structural framework as Ruddlesden-Popper structure which allows for the accommodation of hyperstoichiometric oxide-ions in the rock-salt layer resulting improvement of ion conductivity. Because of its wide range of properties, the double perovskites is interesting to be the new candidate of IT-SOFC cathode [Fuertes, V.C. *et al.*, 2011; Nowick, A.S. *et al.*, 1999].

2.3 Preparation Routes

The physical and electrical properties of cathodes depend not only on their composition, but also on their microstructure. Adequate porosity in the cathode with high triple phase boundary sites is necessary to yield a high performance cathode. Cathode's microstructure is mostly related to the preparation route, both the powder preparation and the forming process. Sol-gel process is considered to be the most practical method for the powder preparation for various applications where fine porous ceramics are needed, such as membranes, sensors and solid oxide fuel cell.

2.3.1 Sol–Gel Process

Sol-gel processing has been extensively used to prepare amorphous and crystalline materials. The handling of precursor by heat treatment is the factor needed to be considered. In general, the sol-gel process is the synthesis of an organic network at low temperatures by a chemical reaction in solution. This technique involves the transition characterized by a relatively rapid change from a liquid (solution or colloidal solution) into a solid (gel–like state).

Sol-gel technology can be divided into two types. The first type is colloidal method. This method involves the suspension of solid particles in a liquid

to form a sol [Schmidt, H., 1994]. The second type is polymeric method. This method involves the polymerization of organometallic compounds, such as alkoxides that provide a convenient source for "inorganic" monomers to form a gel with three-dimensional network structure. The metal alkoxides, $M(OR)_n$, generally consist of metal atom, M, bonded through oxygen to one or more alkyl groups, where n is the valence of the cation. In my work, metal alkoxides are chosen. to powder preparation.

Generally, the precursor is dissolved in a suitable organic solvent in order to form a solution. The solvent must be carefully selected so that a solution with high concentration of the required component is obtained [Yi, G. *et al.*, 1991].

Sol–gel processing involves the following steps:

- precursor formation
- hydrolysis to form solution (sol)
- polycondensation
- film and gel formation
- organic pyrolysis by heat treatment
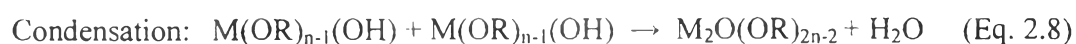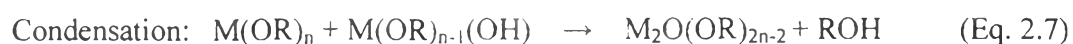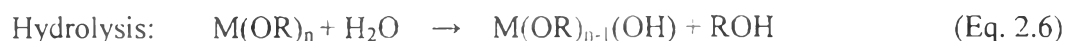- densification and crystallization by annealing process

In the first step, starting materials (metal alkoxides) are mixed in the selected solvent system to form a solution. In the gelation process, the transition from a solution into solid involves the simultaneous hydrolysis and polycondensation of metal alkoxide precursor. The following step, pyrolysis, involves in the removal of all organic compounds.

At present, metal alkoxides are used as the precursors for polymeric gel in sol-gel processing. These precursors are readily used with a suitable organic solvent, which is usually alcohol, to get a solution. The metal alkoxide bond is, in general, extremely susceptible to hydrolytic reaction leading to metal hydroxides or hydrated oxides. The choice of an alkoxide can be considered by many factors including metal content, reactivity, availability, cost, and sensitivity to moisture and decomposition temperature.

A compound with less organic content and high metal content is a proper precursor. Less organic solvent content causes in less volumetric shrinkage

during drying and annealing. Therefore, film has less a tendency to crack. However, a compound with high metal content is usually much more reactive, it may be difficult to prepare a stable solution. For alkoxides with different alkyl groups, the reactivity usually increases in the order of methyl > ethyl > propyl > butyl > higher order alkyl groups [Kwok et al., 1993].

There are two important reactions in polymeric gel formation. These reactions are partial hydrolysis, followed by condensation polymerization. Polymerization steps via hydrolysis and condensation reaction are followed:

Hydrolysis: $M(OR)_n + H_2O \rightarrow M(OR)_{n-1}(OH) + ROH$ (Eq. 2.6)

Condensation: $M(OR)_n + M(OR)_{n-1}(OH) \rightarrow M_2O(OR)_{2n-2} + ROH$ (Eq. 2.7)

Condensation: $M(OR)_{n-1}(OH) + M(OR)_{n-1}(OH) \rightarrow M_2O(OR)_{2n-2} + H_2O$ (Eq. 2.8)

The M–O–M network product is formed by polycondensation reactions, as shown in Eq. 2.7-2.8 which alcohol and water are produced as the by–product. These reactions lead to a different degree of gelation regarding to the appropriate amount of water. Other critical parameters needed to be considered are viscosity of the solutions. Therefore, many applications of controlled hydrolysis to obtain a desired molecular structure and appropriate viscosity of the solution are employed to improve spin ability and coating ability [Yi, G. et al., 1991].

2.3.2 Sol–Gel Preparation of SOFC Cathode

Screen printing is typically used to apply the electrode material on electrolytes. The screen-printed electrode is often fired above 1100°C to assure strong contact with the electrolyte, but it reduces the surface area of the electrode, thus reducing its catalytic activity. Due to the desired in high surface area powder, sol–gel powder processing has been proposed to improve the contact between the electrode and electrolyte, while retaining its porous microstructure. This process offers several advantages:

- The microstructure and composition of electrode materials can be controlled with relative ease.
- Low-temperature processing is possible.
- The electrode and electrolyte adherence is strong.

- The highly porous structure and high surface area can be produced.

Currently, there are some reports related to the sol-gel processing of $La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_3$ cathode [Liu, J. *et al.*, 2006]. They found that the LSCF that obtained from sol-gel process with particle size 20-40 nm in diameter. This will result in a high specific surface area and a high triple phase boundary (TPB) length.

2.4 Literature Review

While the traditional $La_xSr_{1-x}MnO_3$ (LSM) cathode performs adequately at 800-1000°C, its poor oxygen ionic conductivity results in high electrode resistance at lower temperatures. Researchers have tried to solve the mixed conductivity in the cathodes using two approaches:

(1) Mixing an ionically conducting material with an electrically conducting material to create a two-phase cathode e.g. LSM-YSZ [Kim, J.W. *et al.*, 1999].

(2) Replacing the present materials with perovskites displaying high mixed conductivity [Kharton, V.V. *et al.*, 1998].

The first approach can improve only the contact area between electronically and ionically conductive phases, while the second approach can extend the size of the active region and improve the kinetics at temperatures below 800°C [Adler, S.B., 2004]. Thus, my work is focused on the second approach.

One of the potential candidate as a cathode for IT-SOFCs is $La_xSr_{1-x}CoO_3$ (LSC). LSC was found to exhibit a mixed ionic conduction characteristic, exhibiting relatively higher ionic conductivities than LSM due to a greater concentration of oxygen vacancies [Maguire, E. *et al.*, 2000; Dusastre, V. *et al.*, 1999; Steele, B.C.H. *et al.*, 2001]. Ullmann *et al.* (2000) have shown that the electrical conductivity of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ is about 1300 S/cm and the ionic conductivity is about 0.093 S/cm at 800°C. However, the present limiting factor of this compound is its thermal expansion coefficient (TEC) mismatch with the electrolyte candidates, such as yttria stabilized zirconia (YSZ) or Gd doped ceria (GDC), having the values in the range of 20×10^{-6} K^{-1}. This high value of TEC could produce stress at the interface during thermal cycling [Tu, H.Y. *el al.*, 1999]. This is in agreement with Lui *et al.* (2003)

who also indicated that the mixed ionic-electronic conductor (MIEC) materials such as lanthanum cobalite perovskites exhibit very good conductivities, but exhibit large thermal expansion mismatch with the other cell components, causing thermomechanical failure. Thus, the materials with the Ruddlesden-Popper structure (A_2BO_4) such as La_2NiO_4 have been identified as potential cathode materials for the lower operating temperature SOFCs due to its high oxygen vacancy concentration. The $La_2NiO_{4+\delta}$ structure is made up of sheets of (NiO_6) corner sharing octahedra, interleaved with La_2O_2 layers in which the additional oxygen could be localized. The compound is therefore able to accept oxygen overstoichiometry that leads to potentially high oxygen diffusivity compared to that of the common cathode materials [Boehm, E. et al., 2003; Greenblatt, M., 1997; Darcovich, K., et al., 2005]. Amow et al. (2006) studied $La_2NiO_{4+\delta}$ which was shown to be a superior oxide–ion conductor than conventional solid–oxide fuel cell cathode perovskite materials. They have shown that the electrical conductivity of $La_2NiO_{4+\delta}$ is about 70 S/cm at 800°C. Moreover, materials in this group also exhibit coefficient of thermal expansion (CTE) values in the range of $12.4–13.6 \times 10^{-6}$ K^{-1}, close to the common SOFC electrolyte materials such as the ceria-based electrolytes (13.2×10^{-6} K^{-1}) [Ullmann, H. et al., 2000]. Although Chiba et al. (1999) who also found that the materials in this group also exhibit coefficient of thermal expansion (CTE) values close to those common SOFC electrolyte materials, the electronic conductivity of $La_2NiO_{4+\delta}$ is still not enough for IT-SOFCs cathode. This is also confirmed by Kharton et al. (2004) that the electrical conductivity of $La_2NiO_{4+\delta}$ needs to be improved. So, $La_2NiO_{4+\delta}$, was attempted to improve such properties which have been conducted through substitution of the A-site with alkaline earth ions. Ca and Sr are the most popular dopants due to their compatible ionic radii. However, Ca has been found to have little effect on electrical conductivity, while the replacement of La by Sr leads to a much larger improvement [Hui, Z. et al., 2011; Tang, J.P. et al., 2000; Aguadero, A. et al., 20060]. Ishikawa et al. (1987) synthesized $LaSrNiO_4$ via solid state using a 1:1 ratio of Sr:La and found that the electron density was almost an order of magnitude larger than that of La_2NiO_4. Most efforts on $La_{2-x}Sr_xNiO_4$ (LSNO) have been devoted to understanding structural stability, electrical and thermal behavior of

$La_{2-x}Sr_xNiO_{4+\delta}$ compounds with only a few investigations of the transport of conducting species in the system [Vashook, V.V. et al., 1999; Gopalakrishnan, J. et al., 1977; Takada, Y. et al., 1990]. Zhao et al. (2008) studied the lanthanum deficient compound, $La_{2-x}NiO_{4+\delta}$ (x = 0, 0.05). They found that the D* and k* values for $La_{1.95}NiO_{4.13}$ were higher than that of the stoichiometric compound. Kharton et al. (2001) studied factors affecting ionic transport in oxygen-hyperstoichiometric phases of A_2BO_4 structures such as the lanthanum nickelates and cuprates. They found that decreasing radii of the rare-earth cations in the A-sublattice of both cuprates and nickelates led to a dramatic decrease in ionic transport, similar to that observed with perovskite oxides. Skinner et al. (2000) also studied oxygen transport of $La_{2-x}Sr_xNiO_{4+\delta}$ (x = 0, 0.1) and found that oxygen diffusivity of $La_{1.9}Sr_{0.1}NiO_{4+\delta}$ was higher than that of $La_xSr_{1-x}Co_yFe_{1-y}O_{3-\delta}$, particularly at lower temperatures, but lower than that of $LaCoO_3$. However, $La_{1.9}Sr_{0.1}NiO_{4+\delta}$ appears to be more stable than either of these two materials in terms of thermal expansion behavior at high temperatures. There are still very few reports on the ionic transport in Sr substituted $La_2NiO_{4+\delta}$, particularly with higher Sr substitution content. Moreover, the several works on the Sr substitution on the A-site in La_2NiO_4-based system have followed by Aguadero et al. (2007), Makhnach et al. (2008) and Skinner et al. (2000), but it has been reported by Amow et al. (2006), Fontaine et al. (2006) and Bevilacqua et al. (2003) that processing route and conditions could strongly affect the properties of the material. They found that La_2NiO_4 powder is generally synthesized via the solid state method using oxides, carbonates, or nitrates. Necessarily high firing temperatures result in a low surface area and yield fuel cells with low power because of limited exchange current density. More recently, polymeric methods such as sol–gel synthesis have been explored by Makhnach et al. (2008), Skinner et al. (2000), Fontaine et al. (2006) and Bilger et al. (1992) with their many advantages over other methods, such as homogeneity, low temperature processing, strong adherence between electrode and electrolyte, etc.

It does not only pay attention to A-site substituted materials. B-site substituted materials have also proposed to improve the appropriate property for IT–SOFCs cathode. Ruddlesden-Popper structure is comprised of alternating

perovskite blocks with a rock–salt, the new family materials as called double perovskites also have been recently more attention. Because of almost all elements in the periodic table can be accommodated on the A and/or B sites, perovskite structures with the general formula ABO_3 are highly useful structures [Fuertes, V.C. *et al.*, 2011]. If two atoms, B′ and B″, are placed on the two crystallographic different B-sites, a layered perovskite is formed with the general formula $A_2BB'O_6$. B and B′ can be completely or partially ordered depending on the size and charge differences between the B ions and the degree of ordering also strongly affected on the properties of these materials. One variation of pervoskite structure is a double perovskite with the general formulation $A_3B_2B'O_9$ when the B:B′ ratio is 2:1. Such structure could have the ordering in a rock–salt pattern with different cations occupying alternating BO_6 octahedra. The B–site ordered perovskites should be similar to the relatively open structural framework as Ruddlesden-Popper structure which allows for the accommodation of hyper-stoichiometric oxide–ions in the rock–salt layer resulting improvement of ion conductivity. Because of its wide range of properties, the double perovskites is interesting to be the new candidate of IT-SOFC cathode [Nowick, A.S. *et al.*, 2000; Nowick, A.S. *et al.*, 1999].

Recently, Kim *et al.* (2009) studied a family of double perovskite oxides, $NdBa_{1-x}Sr_xCo_2O_{5+\delta}$ (x = 0 and 0.6), to be used as IT-SOFC cathodes. They also found that the substitution of Co by Ni in $GdBaCo_{2-x}Ni_xO_{5+\delta}$ leads to slightly improved performance in SOFC with an important advantage of lower TEC because the TEC value decreases with increasing Ni content and reaches 16.7×10^{-6} K^{-1} for the x = 0.6, which is ~13% lower than the TEC of the x = 0 sample. Moreover, Hu *et al.* (2013) successfully synthesized $GdBaCo_{2-x}Ni_xO_{5+\delta}$ (x = 0-0.8) synthesized by a citrate–gel modified chemical route, by which we have achieved a high level of substitution up to x = 0.8 and resulted that the TEC value was also reduced. Although the electrical conductivity decreases with increasing Ni content, all Ni compositions still show conductivity more than 300 S/cm up to 900°C, which is adequate for employing them as cathodes in SOFC. Not only the electrical conductivity which is significant property of SOFC cathode, but the ionic conductivity is also concerned. Tao *et al.* (2002) reported that in perovskites with the formulation $A_3B_2B'O_{9-\delta}$, when B′ was the

valance +5 elements such as Nb and Ta, could exhibit high proton and oxygen ion conductivity. So, the improvement of ionic conductivity should be found in the B-site ordered perovskites. However, there are still very few reports on the electrical conductivity in the double perovskites with the formulation $A_3B_2B'O_{9-\delta}$, particularly with B-site as Nb and Ta substitution on Ni, while the ionic transport property seems to never study before.

In the present work, the improvement of cathode materials for IT-SOFCs was investigated into 2 approaches including the substitution of dopants on A- and B-sites of perovskite based structures, Ruddlesden-Popper and double perovskite. The high amount of Sr substitution on $La_{2-x}Sr_xNiO_{4\pm\delta}$ ($x \leq 0.8$) and the new family of $La_3Ni_2MO_9$ (M = Nb or Ta) double perovskite were synthesized via a simpler and environmentally friendly sol-gel route. The effect of the Sr substitution on the A-site on the phase formation, physical, electrical properties and ionic transport property of $La_{2-x}Sr_xNiO_{4\pm\delta}$ was also studied. Data for the samples of the same materials prepared via the solid state reaction route is also presented for comparison. While, the new double perovskites family, $La_3Ni_2MO_9$ with M = Nb or Ta was also studied including synthesis and characterization. These new compounds have been synthesized simply by both solid-state reaction and sol-gel process. The effects of synthesis routes and B-site dopants (Nb and Ta) on phase, morphology and electrical conductivity were investigated as the primary results.