

CHAPTER I

INTRODUCTION

1.1 Background

Energy is one of the most fundamental parts of our universe. People use energy to do work. Nowadays, major of energy comes form crude oil. Nevertheless, the amount of petroleum fuel in the world is limited and its price is increasing everyday. Hence, most researchers have tried to find new energy resources such as fuel cell. While the technology for these electrochemical power plants has existed since 1839, fuel cells have recently gained popular recognition and come under serious consideration as an economically and technically viable power source. Furthermore, fuel cells are considered as a prime candidate for 'green' energy production: clean, quiet, and efficient. Despite their relatively new arrival on the popular scene, fuel cells have already found their way into early commercial testing in stationary (building) applications and prototype testing in mobile and portable applications.

1.2 Fuel Cell

A fuel cell is a device that converts the chemical energy of a fuel (hydrogen, natural gas, methanol, gasoline, etc.) and an oxidant (air or oxygen) into electricity. In principle, a fuel cell operates like a battery. Unlike a battery however, a fuel cell does not run down or require recharging. It will produce electricity and heat as long as fuel and an oxidizer are supplied.

Both batteries and fuel cells are electrochemical devices. As such, both have a positively charged anode, a negatively charged cathode and an ion-conducting material called an electrolyte. Fuel cells are classified by their electrolyte material. Electrochemical devices generate electricity without combustion of the fuel and oxidizer, as opposed to what occurs with traditional methods of electricity generation.

Fuel cell construction generally consists of a fuel electrode (anode) and an oxidant electrode (cathode) separated by an ion-conducting membrane. Oxygen passes over one electrode and hydrogen over the other, generating electricity, water and heat. Fuel cells chemically combine the molecules of a fuel and oxidizer without burning or having to dispense with the inefficiencies and pollution of traditional combustion.

Fuel cell types are generally characterized by electrolyte material. The electrolyte is the substance between the positive and negative terminals, serving as the bridge for the ion exchange that generates electrical current. There are several kinds of fuel cells which are shown in Table 1.1

Table 1.1 Types of fuel cells

Fuel Cell Name	Electrolyte	Operating Temperature (°C)	fuel
Alkaline fuel cell (AFC)	Potassium hydroxide (KOH)	50-200	Pure hydrogen or hydrazine
Direct methanol fuel cell (DMFC)	Polymer	60-200	Liquid methanol
Phosphoric acid fuel cell (PAFC)	Phosphoric acid	160-210	Hydrogen from hydrocarbons and alcohol
Sulphuric acid fuel cell (SAFC)	Sulphuric acid	80-90	Alcohol or impure hydrogen
Proton-exchange membrane fuel cell (PEMFC)	Polymer, proton exchange membrane	50-80	Less pure hydrogen from hydrocarbons or methanol
Molten carbonate fuel cell (MCFC)	Molten salt such as nitrate, sulphate, carbonates	630-650	Hydrogen, carbon monoxide, natural gas, propane, marine diesel
Solid oxide fuel cell (SOFC)	Stabilised zirconia and doped perovskite	600-1000	Natural gas or propane
Solid polymer fuel cell (SPFC)	Solid sulphonated polystyrene	90	Hydrogen

Every fuel cell has two electrodes, one positive and one negative, called the cathode and anode, respectively. The reactions that produce electricity take place at the electrodes.

1.3 Solid Oxide Fuel Cells (SOFCs)

Solid oxide fuel cells (SOFCs) are a promising clean power source for a variety of stationary and mobile applications. One of the advantages of SOFCs over polymer electrolyte membrane (PEM) based fuel cells is their fuel flexibility, which includes tolerance to impurities in the fuel as well as operation with fuels other than hydrogen. As a result of this fuel flexibility, SOFCs are being developed for automotive auxiliary power units (APUs) which can operate using reformed diesel fuel, and thus can be implemented before establishment of a hydrogen infrastructure. The primary reason for the improved fuel flexibility of SOFCs is their high operating temperature, which accelerates the electrode reaction rates. However, this high operating temperature also increases the rates of undesired reactions and creates thermal stresses during cycling, so a major objective in SOFC development is to decrease the operating temperature. As the operating temperature decreases, reduced electrode reaction rates can lead to decreased conversion efficiencies of certain fuels and/or increased inhibition by impurities, both of which can limit fuel flexibility [1].

High temperature cells

In the late nineteenth century, conduction was not yet understood. Later, Nernst observed at the University of Göttingen, that stabilized zirconia (ZrO_2 doped with Ca, Mg, Y) was an insulator at room temperature, an ionic conductor from 600–1000 °C and a mixed conductor (both electronic and ionic) at around 1500 °C. The main part of the solid oxide fuel cell was therefore discovered. The fuel cell concept was demonstrated by Baur and Preis in the 1930's using zirconium oxide, but many improvements were necessary to make a competitive device. In the 1950's, simple, straightforward design made cheaper manufacturing processes possible: the flat plate fuel cell.

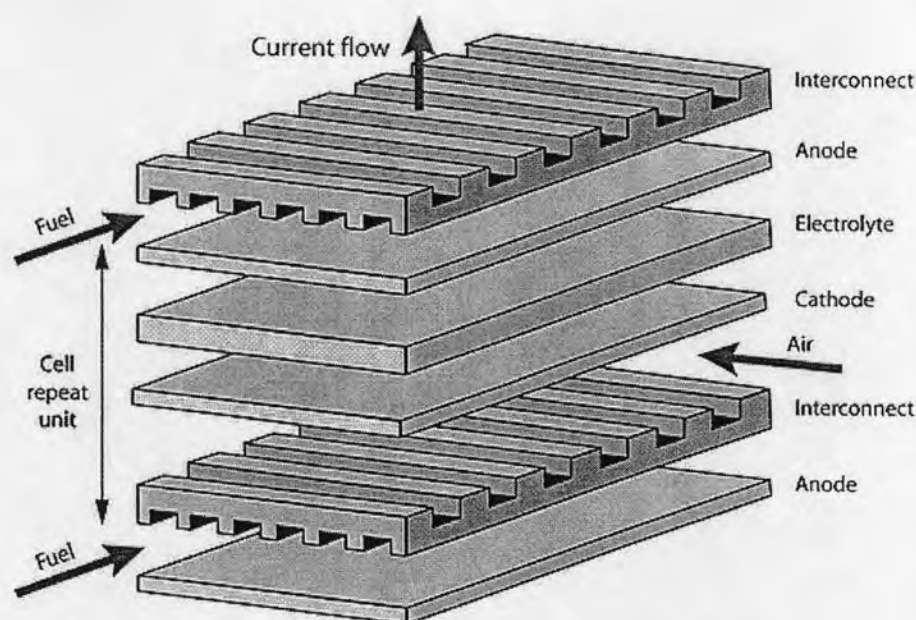


Figure 1.1 Flat plate solid oxide fuel cell

There are a few problems with the flat plate design when used for larger devices: sealing, around the edges, thermal expansion mismatch and cracking (intrinsically brittle ceramics are used). Tubular designs have been developed to solve these problems.

SOFCs are the most efficient devices yet invented, that can convert chemical energy into electrical energy. Both electrodes (cathode and anode) and the electrolyte are made of ceramic materials, since the high operating temperature prevent the use of cheaper metals. The big advantage of the SOFC over the MCFC is that the electrolyte is solid and there are no pumps required to circulate the hot electrolyte. The anode contains nickel, for better electron conduction and catalysis. The operating temperature is between 600 and 1000°C, depending on the generation of the fuel cell (first, second and third, with decreasing operating temperature). However, thermal cycling can cause cracking of the brittle ceramic components. Both hydrogen and carbon monoxide serve as fuels. Common hydrocarbon fuels can be used in SOFC (diesel, natural gas, gasoline, alcohol etc).

1.3.1 Cathode

The electrochemical performance of SOFCs is controlled to a great extent by electrode processes. It is therefore important for the cathode to find materials with a high electrochemical activity for the oxygen reduction reaction. To prevent limitations due to supply of oxygen to the electrolyte, it is necessary to tailor the microstructure of the electrodes in terms of thickness and porosity with respect to their electrical and electrochemical properties. State of the art zirconia based SOFC systems employ $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) as cathode material [2, 3]. This material is an electronic conductor and is chemically compatible with zirconia electrolytes. It has a high activity for the dissociative adsorption of oxygen on the surface, however it possesses only very limited oxygen ionic conductivity.

1.3.2 Electrolyte

The electrolyte is the dense, gas-tight layer of each cell that acts as a membrane separating the air on the cathode side from the fuel on the anode side. There are many ceramic materials that are being studied for use as an electrolyte, but the most common are zirconium oxide based. Besides being air-tight, the electrolyte must also be electrically insulating so that the electrons resulting from the oxidation reaction on the anode side are forced to travel through an external circuit before reaching the cathode side. The most important requirement of the electrolyte, however is that it must be able to conduct oxygen ions from the cathode to the anode. For this reason, the suitability of an electrolyte material is typically measured in ionic conductivity.

1.3.3 Anode

SOFC anodes should exhibit a good electrical conductivity and a high activity for the oxidation of the fuel gas. For state of the art SOFC systems a Ni-cermet, i.e. a mixture of metallic nickel and a ceramic component are used. The ceramic component normally is yttria-doped zirconia [2, 4]. The ceramic compound is added to the cermet to adjust the thermal expansion coefficient of the anode to the electrolyte and to prevent the nickel particles in the porous structure from coalescence. Since nickel is a

metallic conductor and zirconia is an oxygen ionic conductor, this anode can also be regarded as a mixed ionic electronic conductor.

1.3.4 Interconnect

Interconnect can be either a metallic or ceramic layer that sits between each individual cell. Its purpose is to connect each cell in series, so that the electricity each cell generates can be combined. Because interconnect is exposed to both the oxidizing and reducing side of the cell at high temperatures, it must be extremely stable. For this reason, ceramics have been more successful in the long term than metals as interconnect materials. However, these ceramic interconnect materials are extremely expensive. Fortunately, inexpensive metallic materials are becoming more promising as lower temperature (600-800°C) SOFCs are developed.

1.3.5 Compatibility of the materials system

In today's SOFCs the electrolyte is the supporting and load bearing structural element in the single cell with a thickness of 150 to 250 μm . It supports the thin (10 to 30 μm) electrodes. The interconnector used for stacking the single cells is also a thick, stiff structure with a thickness of about 2 to 5 mm. The compatibility requirements for the materials system can be summarized as follows:

- The thermal expansions of the single components of the cell have to match. This is after all important for the thermal expansion of the load bearing structural elements. Except the thermal expansion of the porous thin electrodes might be somewhat different from the electrolyte without causing problems.
- Chemical compatibility is necessary. No intermediate phases should be formed at the interfaces during manufacturing and operation.
- The electrode performance should allow intermediate temperature operation.
- High ionic conductivity of the electrolyte is necessary. The electrode performance alone is not sufficient for good performance of the whole system.

1.3.6 Operation of SOFC

The operation of the solid oxide fuel cell is straightforward: oxygen atoms are reduced on the porous cathode surface by electrons. The oxide ions diffuse through the electrolyte to the fuel rich and porous anode, where they react with the fuel (hydrogen) and give off electrons to an external circuit. A large amount of heat is produced by the electrochemical reaction, which can be used by an integrated heat management system. Since it takes a long time to reach its operating temperature, the best applications for SOFCs are ones that use both the heat and electricity generated: stationary power plants, auxiliary power supplies. Start-up time problems could be solved by using supercapacitor batteries for the first few minutes of operation in mobile applications. [5]

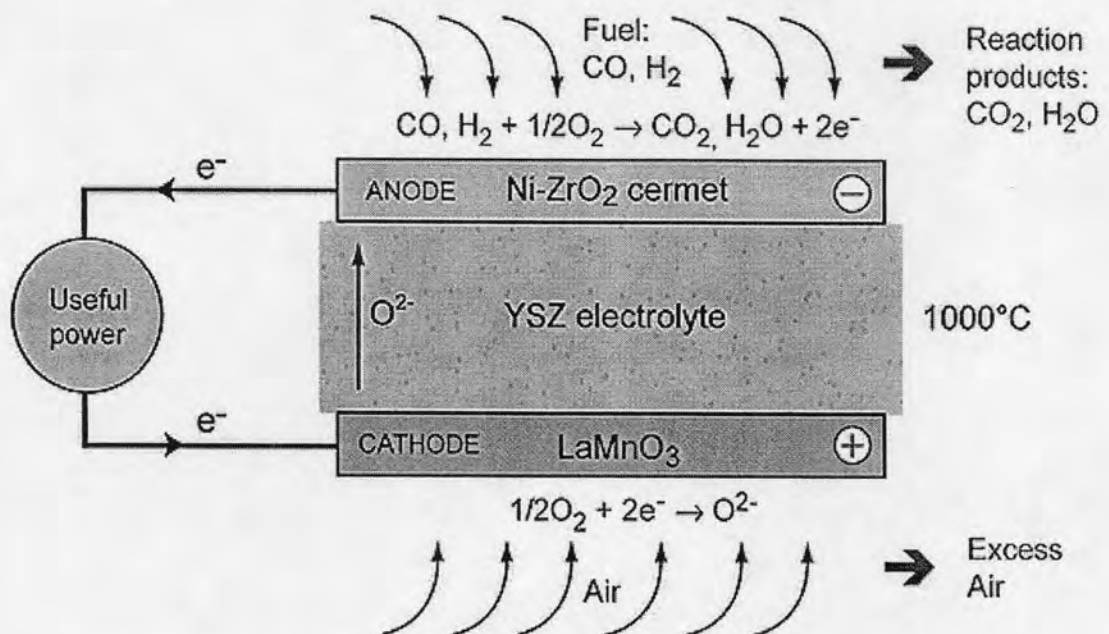


Figure 1.2 Operation of a SOFC

1.4 Perovskite[*]

Perovskite (calcium titanium oxide, CaTiO₃) is a relatively rare mineral on the Earth's crust. This oxide crystallizes in the orthorhombic (pseudocubic) crystal system. It is found in contact metamorphic rocks and associated mafic intrusives, nepheline syenites, and rare carbonatites. Perovskite was discovered in the Ural

mountains of Russia by Gustav Rose in 1839 and named for Russian mineralogist, L. A. Perovski (1792-1856).

Perovskite is also the name of a more general group of crystals which take the same structure. The basic chemical formula follows the pattern ABO_3 , where A and B are cations of different sizes (for example, $LaMnO_3$). Formed under the high pressure conditions of the Earth's mantle, the pyroxene enstatite ($MgSiO_3$) is a perovskite-structured polymorph which may be the most common mineral in the Earth. Perovskite is used as catalyst in certain types of fuel cells.

1.4.1 Structure

The perovskite structure is adopted by many oxides that have the chemical formula ABO_3 . The structure is very versatile having many useful technological applications such as ferroelectrics, catalysts, sensors, and superconductors. The general crystal structure is a primitive cube, with the B-cation in the middle of the cube, the A-cation in the corner and the anion, commonly oxygen, in the centre of the face edges. The structure is stabilized by the 6 coordination of the B-cation (octahedron) and 12 of the A cation. The packing of the ions can be thought of the A and O ions together form a cubic close packed array, where the B ions occupy a quarter of the octahedral holes.

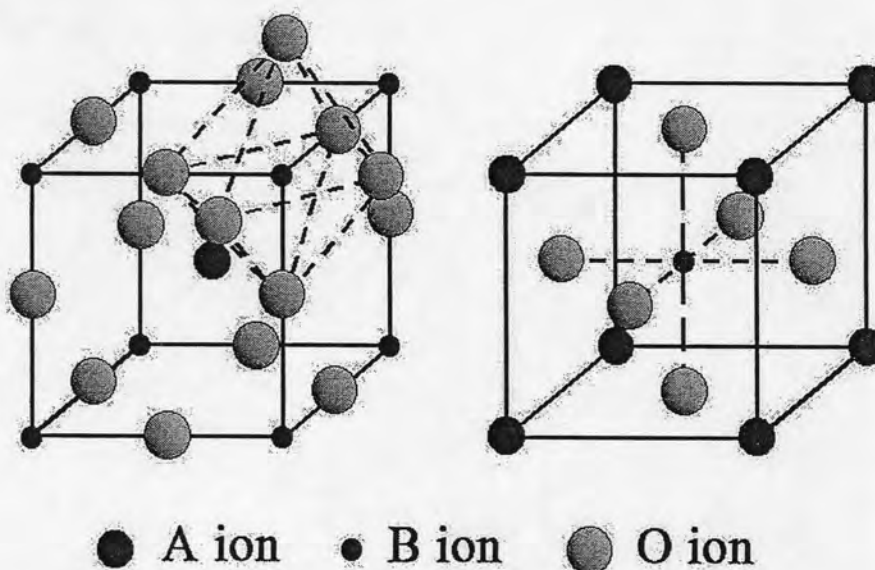


Figure 1.3 ABO_3 ideal perovskite structure showing oxygen octahedron containing the B ion linked through corners to form a three-dimensional cubic lattice.

Although the primitive cube is the idealized structure, differences in radius between the A and B cations can alter the structure to a number of different so-called distortions, of which tilting is the most common one. With perovskite tilt the BO_6 octahedron twists along one or more axes to accommodate the difference. Complex perovskite structures contain two different B-site cations. This results in ordered and disordered variants.

The perovskite structure shares the property of ferroelectricity with garnet and olivine. Many superconducting ceramic materials have perovskite-like structures. [6]

1.4.2 Properties of perovskite

- Oxygen Adsorption Property

Oxygen desorption properties from perovskite oxides have been studied as a function of the nature and concentration of dopant atoms introduced into both the A- and B-sites. Previous work examining oxygen desorption using TPD from perovskite oxides has shown that two types of oxygen can become desorbed [7]. Oxygen desorbed at lower temperatures, termed α oxygen, corresponds to adsorbed surface oxygen, and that desorbed at higher temperatures, designated β oxygen, is desorbed from lattice sites within the perovskite.

- Electrical Properties

Solids may be classified in terms of their resistivity or conductivity as conductors, insulators, or semiconductors. Closer examination of the microscopic conditions for Ohm's law involves free electron density in solids. These classifications of solid materials can be visualized in terms of the band theory of solids and are strongly correlated with the interatomic spacing in the solid. The electron energy levels in a solid are often expressed in relation to the Fermi energy. The conducting electron density in a metal can be calculated from the Fermi energy. The electrical

conductivity of semiconductors can be enhanced by doping to produce n-type or p-type semiconductors. A current-carrying conductor placed in a magnetic field will exhibit a transverse voltage from the magnetic force exerted on the moving charges. Called the Hall effect, this voltage is proportional to the magnetic field strength and is used in Hall probes for the measurement of magnetic fields.

The electrical conductivity of perovskites also shows wide variations. Several compounds have been used for their dielectric properties, while others show metallic conductivity, although most are semiconductors. As for other compounds, the electrical behavior in perovskites depends on the outermost electrons, which may be localized at specific atomic sites or may be collective. Since localized electrons may carry a spontaneous moment, there is a strong correlation between the electrical and magnetic properties of perovskites. Rare-earth perovskites containing transition ions show widely differing electrical properties. Electrical conductivity is a measure of how well a material accommodates the movement of an electric charge. It is the ratio of the current density to the electric field strength. Its SI derived unit is the Siemens per meter, but conductivity values are often reported as percent IACS. IACS is an acronym for International Annealed Copper Standard or the material that was used to make traditional copper-wire. The conductivity of the annealed copper ($5.8108 \times 10^7 \text{ S/m}$) is defined to be 100% IACS at 20 °C. All other conductivity values are related back to this conductivity of annealed copper. Therefore, iron with a conductivity value of $1.044 \times 10^7 \text{ S/m}$, has a conductivity of approximately 18% of that of annealed copper and this is reported as 18% IACS. An interesting side note is that commercially pure copper products now often have IACS conductivity values greater than 100% because processing techniques have improved since the adoption of the standard in 1913 and more impurities can now be removed from the metal.

Conductivity values in Siemens/meter can be converted to % IACS by multiplying the conductivity value by 1.7241×10^{-6} . When conductivity values are reported in microSiemens/centimeter, the conductivity value is multiplied by 172.41 to convert to the % IACS value.

- Mixed ionic-electronic conductors

Perovskite oxide exhibits both ionic and electronic conductivity. It may show both high oxygen ion conductivity due to the high oxygen vacancy concentration, and a high electronic conductivity due to the mixed-valence state [8]. The B ions can take a mixed-valence state, charge neutrality is maintained by both the formations of oxygen vacancies and a change in the valence state of the B ions. The B-site ion substitution can increase the concentration of oxygen vacancies, such as Cu and Ni ions, which naturally take the divalent oxidation state [9]. If the valence state of the B ions is fixed, neutrality is maintained only by the formation of oxygen vacancies. The oxides may be predominantly ionic conductors, in this case.

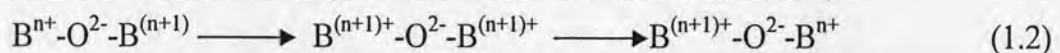
In order to characterize the materials, it is more often to measure their electronic and ionic conductivity instead of concentrations of electrons (holes) and mobile ions (vacancies). The calculated ionic and electronic conductivity, which were separately, measured by using 4-probe ionic direct current and ordinary 4-probe direct current techniques, respectively.

In all materials that there are in principle nonzero electronic and ionic conductivity, the overall electrical conductivity σ_{tot} is the sum of electronic conductivity σ_e and ionic conductivity σ_i , as Equation (1.1),

$$\sigma_{\text{tot}} = \sum \sigma_{ij} + \sigma_e \quad (1.1)$$

where σ_{ij} is the partial conductivity (in $\Omega^{-1}\text{cm}^{-1}$) of the j th-type ionic charge carriers presenting in the solid. . Ionic charge carriers can be either atomic in nature or normally defects of either the anionic or cationic sublattice. Ionic conductivity occurs normally via interstitial sites or by hopping into a vacant site (vacancy motion) or a more complex combination based on interstitial and vacant sites. Electronic (electron/hole) conductivity occurs via delocalized states in the conduction-valence band or via localized states by a thermally assisted hopping mechanism. The presence of electronic conduction in perovskites proceeds via B.

Lattice cations through overlapping B-O-B bonds via a mechanism known as the Zerner double exchange process is shown in Equation (1.2) [14]:



This process is facilitated by strong overlap of the B site cation and O_2^- orbital which is maximized for B-O-B angles at 180° , i.e., cubic structure. In the orthorhombic structure, the tilting of BO_6 give rise to a decrease in the B-O-B overlap and thus would be expected to provide a larger barrier to electronic conduction. In the above double exchange mechanism, electronic conduction requires the presence of B site cations with multiple valences.

Furthermore, the electronic conduction can be n-type or p-type, depending on the material properties and ambient oxygen partial pressure. The energy level shifts from the center of the energy gap toward the empty zone for an n-type semiconductor or the filled band for a p-type semiconductor. An n-type conductor is an electron conductor while a p-type conductor is an electron hole conductor [15].

- Dielectric Properties

Due to the chemical composition, crystal structure and anisotropic properties of high critical temperature superconductors (HTSCs), substrates play a vital role in film properties and hence device characteristics. Since the discovery of HTSCs, there has been a search for dielectric materials that are appropriate for use in a HTSC thin film device technology. The ideal material is chemically compatible and has both a good structural and thermal expansion match to the HTSC. For microwave devices, the material should also have either a relatively high or low dielectric constant and be low loss and isotropic with respect to microwave radiation. High dielectric constants are useful for delay lines while low dielectric constants are needed for the vast majority of microwave devices. Since microwave devices place additional requirements upon the substrate, a single suitable low dielectric constant microwave compatible substrate satisfies the requirements for the majority of all HTSC thin film devices. The dielectric constant of oxides can be predicted using the Clausius-Mossotti relationship which can be rearranged to have the form:

$$\epsilon = \frac{3V_m + 8\pi\alpha_T}{3V_m - 4\pi\alpha_T}$$

Where ϵ is the dielectric constant and α_T (Å^3) is the total polarizability of the substance in molar volume V_m (Å^3). While the relationship is strictly applicable only to cubic materials, it also works as a good approximation to many noncubic materials so long as the electronic conductivity, piezoelectricity and permanent dipole moments are well behaved [10].

- Magnetic properties

In the ideal cubic perovskite structure, each atom of oxygen is shared by two B^{3+} ions, forming a B-O-B angle of 180° . Such a configuration is favorable for super exchange interactions between magnetic B^{3+} cations. This exchange usually results in anti-parallel coupling of nearest-neighbor magnetic moments. When the B^{3+} ions are in two sub lattices ($A_2BB'O_6$) the other spin arrangements are possible. If B' is a diamagnetic ion, the B^{3+} ions are aligned anti-ferromagnetic, and the most important exchange mechanism is believed to be a longer range super exchange interaction through two oxygens of the type B-O-B'-O-B. The B-B separation is now considerably longer than the 0.4 nm separation found in the ideal perovskite. The LnFeO_3 (Ln = lanthanide) perovskites are those that have attracted the most attention because of their possible applications as technological magnetic materials [11]. These compounds show a weak spontaneous magnetic moment, which is attributed to a slight canting of the iron moments, which are otherwise anti-ferromagnetic aligned. Similarly, LnMnO_3 shows very interesting magnetic properties. These manganites containing mostly Mn^{3+} or Mn^{4+} ions show anti-ferromagnetic behavior. However, ferromagnetic behavior is observed in the range from 25 to 35% Mn^{4+} . A weak magnetic interaction was found between Mn^{3+} ions, together with a negative interaction between Mn^{4+} ions and a strong positive interaction between Mn^{3+} and Mn^{4+} . A similar kind of behavior was found for the combination of Co^{3+} and Co^{4+} , but the Cr and Fe compounds were found to be anti-ferromagnetic.

1.4.3 Perovskite synthesis

Preparation of perovskite type membranes consists of three consecutive steps: powder synthesis, shaping and sintering. Firstly, powder synthesis which plays an important role in determining the particle size of the powder, and consequently has an influence on the microstructure of the membrane. There are several methods to synthesize powders, such as a conventional solid-state reaction method and a wet chemical process including thermal decomposition of cyanide, metal-EDTA, chemical co-precipitation and the sol-gel process.

- Powder synthesis

Solid-state reaction

The most common procedure for perovskite oxides synthesis via solid state reactions is the calcination of a homogenous mixture of the corresponding metal-carbonates, hydroxides, and oxides. This is also known as ball milling and calcinations method. This method is very convenient but the impurities are introduced from raw materials, milling media, and the calcination container. Because of the high temperature required for the complete reaction. The problems such as multiphase have to be minimized in order to generate homogeneous high performance perovskite. For example, LSCF represents a typical case. Raw materials La_2O_3 , SrCO_3 , CoO_3 , and Fe_2O_3 were mixed and ball-milled. After drying, then the mixed powders were calcined at $1,000^\circ\text{C}$ to remove impurities and to achieve single-phase perovskite powder. The high temperature was required to complete reaction.

Solution reaction

Solution preparation of perovskite materials generally involves the use of metalloorganic compounds that are dissolved in a common solvent. General ways of making perovskite materials usually adopt mixing the constituent oxides, hydroxides and carbonates. These materials generally have a large particle size. The selection strategy of this approach frequently requires repeated mixing and extended heating at

high temperature to generate a homogeneous and single-phase material. In order to overcome the disadvantages of low surface area and limited control of the microstructure inherent in the high temperature process, precursors generated by sol-gel preparations or co precipitation of metal ions by precipitating agents such as hydroxide, cyanide, oxalate, carbonate, citrate ions etc., have been used.

These gel or coprecipitated precursors can offer molecular or near molecular mixing and provide a reactive environment during the course of subsequent heating and decomposition. Because of the improved solid-state diffusion resulting from the improved mixing, they need a relatively lower temperature to produce similar materials compared to the traditional methods. These methods frequently offer additional advantages, such as atomic/molecular level homogenous mixing of constituent metal ions, better reactivity at lower reaction temperatures, high purity, and good control of stoichiometry and high sinter ability.

In 2004 Kuan-Zong Fung, et al. [12] synthesized the sol-gel method using polyacrylic acid (PAA) as chelating agent, LSCo and LSCu electrocatalyst nanoparticles were synthesized in a nanoscale range of 25–50 nm. The electrical conductivities of the sintered $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ and $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{3-\delta}$ decreased with the increasing temperature from room temperature to 95°C. Both LSCo and LSCu systems exhibit excellent electrical conductivities of more than 1200 S/cm when the strontium addition was more than 25%. The electrical conductivities of strontium doped lanthanum cobaltite and cuprate are rationalized by the formation of electron holes due to the strontium addition.

-Wet chemical synthesis of perovskite

Because of the perovskite synthesis via solid-state reaction has found that the impurities occurred. For this reason, the improvement of the perovskite synthesis has been interested continuously. A series of chemical methods, especially solution reaction or wet chemical synthesis or liquid phase synthesis, have been developed from solid-state synthesis. Solution reactions have been developed from solid-state synthesis to produce the required properties of raw perovskite powders, such as spray-pyrolysis, freeze drying, precipitation, sol-gel and liquid mix process, etc.

It is widely known that the synthesis of ceramic powders by using the conventional solid-state synthesis promotes the crystal growth and resulting in a hard agglomeration. The good sintered ability may be obtained when the preparation procedure is weak agglomerates are formed. Therefore, the properties of the raw material powder are largely determined by the properties of the raw material powders, which several requirements are imposed, fine particles ($< 1 \mu\text{m}$), narrow size range, no aggregation, controlled particle shape, uniformity in chemical and phase compositions, and high purity [13].

Liquid mix process is a generic name for various processes that start with a homogeneous solution containing the desired cations, which use additives and evaporation to convert the homogeneous liquid to rigid cross-linked polymer, and which utilize heat to convert the polymer into a homogeneous oxide powder.

Solubility is one of the most important considerations in solution techniques. Metal oxalates, sulphates, nitrates, chlorides, and acetates were avoided. Because of the low solubility of these compounds could lead to the phase separation in the final product. Not only it is desirable that solubility being high in order to minimize the amount of solvent which must be removed, but also the particular components must be compatible, e.g., iron sulfates could not be combined with barium chloride. Because of barium sulfate would precipitate in the reaction.

The perovskite powders made by wet chemical methods are very fine, and can be not agglomerate, which facilitates the densification process. The powders made from wet chemical methods using sintering temperature which can be lower than those made from conventional solid-state synthesis methods. By means of these wet chemical methods, it is possible to obtain monophasic, pure, fully reacted powders with submicronic and even nanometric sizes, homogeneous and narrow size distribution, and very reactive characteristic. When comparing several techniques in wet chemical methods, liquid mix process is distinguished in the case of less energy consumption, simplest technology, and potential to get fine particles and a singlephase powder. Both adding several acids such as citric, malic acid, or etc. and adjusting the pH of aqueous solution are used to provide the fine homogeneous perovskite with the high surface area.

- Powder Sizing

Uniaxial pressing is accomplished by placing the powder in to a rigid die and applying pressure along a single axial direction through a rigid plunger, or piston to achieve compacting. Pressing results in the direct contact of particles, reduces the average distance between particles, and changes the shape of particles. The apparent density of a compact was controlled by mixing of the proper various particles size fractions.

To enhance the compacting, before pressing, the powder should be disaggregated by mixing the powder with solvent such as isopropanol in the ultrasonic bath or added a couple drops of acetone to reduce the surface tension.

- Sintering

Sintering is the process whereby powder compacts are heated so that adjacent particles fuse together. The fusing of particles results in an increase in the density of the part and hence the process is sometimes called densification. There are some processes such as hot isostatic pressing which combine the compaction and sintering processes into a single step.

The density of the component can also change during sintering, depending on the materials and the sintering temperature. These dimensional changes can be controlled by an understanding and control of the pressing and sintering parameters, and components can be produced with dimensions that need little or no rectification to meet the dimensional tolerances. The driving force for sintering is the decrease in surface free energy that occurs as the surface area of the polycrystalline aggregate is reduced. This process can be achieved by solid-state reaction or alternatively in the presence of a liquid phase. When a powdered aggregate is sintered, pore size is reduced, and the grain growth can be much enhanced. The growth of the neck is due to the transport of matter or of the counter-flow of vacancies between the particles and the pores. In crystalline powder, its transport occurs by diffusion (bulk, surface, or grain boundary diffusion), whereas in amorphous materials, it occurs by viscous flow. Kuczynski has defined the neck growth as in Equation 1.3.

$$X^n/r^m = kt \quad (1.3)$$

Where X and r are defined in Equation 1.1, t is the time, k is the temperature dependent constant, n and m are constants dependent on the mechanisms of growth, viscous or bulk diffusion, surface diffusion, or evaporation and condensation.

Three stages of sintering can be distinguished. The early stage or initial stages during which the necks form at points of particle contact and the particles usually center approach each other. At this stage the individual particles are still distinguishable. The intermediate stage during that the necks become large, resulting in the formation of an interconnected pore structure. The third or the final stages during, the pores become isolated. Elimination of the interconnectivity of pores eliminates surface and vapor transport.

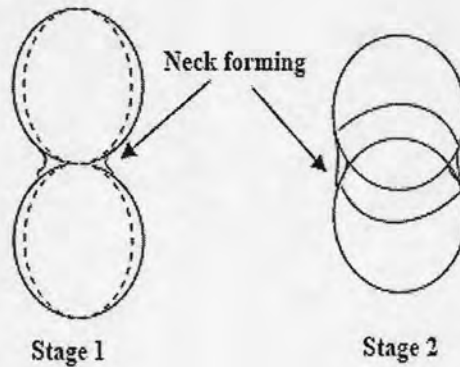


Figure 1.4 Mechanism of sintering.

Closed pores isolated from grain boundaries shrink very slowly because grain boundary diffusion is far away from the pores. The growth of grains, therefore, hinders the attainment of theoretical density, since the pore's growth is also enhanced. It is essential, therefore, to retard grain growth so that densification of the compact can continue to the theoretical limit. This is particularly important with the present trend of using ultrafine particles as starting materials for the fabrication of technical ceramics. Surface diffusion becomes important in the case of very fine particles. Grain boundary diffusion and volume diffusion are the main mechanisms causing shrinkage of the neck, whereas surface diffusion does not contribute to any shrinkage. The most important diffusion paths during the sintering of two spheres with a grain boundary are surface diffusion, grain boundary diffusion, volume diffusion from the

grain boundary to the neck surface, and volume diffusion from the sphere surface to the neck surface. The sintering rate also affected by the crystallization and growth processes, which occur concurrently. The sintering rate is reduced when there is intensive grain growth because when diffusion forms the pores occurs toward the boundaries of individual grains, the distance over which diffusion occurs with a reduction in pores is determined by the size of the crystals.

1.5 Literature review

In 2001 D.P. Fagg, *et al.* [16] have studied the stability and mixed conductivity in La and Fe doped SrTiO₃ in the search for potential SOFC anode materials. Both physical properties and the level of mixed conduction obtained in La and Fe doped SrTiO₃ are widely influenced by composition. In contrast to La free compositions, La containing compositions show high stability against reaction with yttria stabilized zirconia (YSZ) and a closely matching thermal expansion coefficient ($\sim 1 \times 10^{-5} \text{ K}^{-1}$). Faradaic efficiency measurements for Sr_{0.97}Ti_{0.6}Fe_{0.4}O_{3- δ} and La_{0.4}Sr_{0.5}Ti_{0.6}Fe_{0.4}O_{3- δ} show ionic transference numbers in air between 5×10^{-3} to 4×10^{-2} and 2×10^{-4} to 6×10^{-4} respectively, decreasing with decreasing temperature. The substitution of La for Sr is observed to deplete the level of both ionic and total conductivity obtained in air.

Kuan-Zong Fung, *et al.* [12] synthesized LSCo and LSCu electrocatalyst particles in a nanoscale range of 25–50 nm. The electrical conductivities of the sintered La_{1-x}Sr_xCoO_{3- δ} and La_{1-x}Sr_xCuO_{3- δ} decreased with the increasing temperature from room temperature to 95°C. Both LSCo and LSCu systems exhibit excellent electrical conductivities of more than 1200 S/cm when the strontium addition was more than 25%. The electrical conductivities of strontium doped lanthanum cobaltite and cuprate are rationalized by the formation of electron holes due to the strontium addition.

In 2005 Meilin Liu, *et al.* [17] studied electrical properties and sulfur tolerance of La_{0.75}Sr_{0.25}Cr_{1-x}Mn_xO₃ under anodic conditions. Complex metal oxides with composition of La_{0.75}Sr_{0.25}Cr_{1-x}Mn_xO₃ (x= 0.4, 0.5, 0.6) (LSCM) have been synthesized and examined as anode materials for solid oxide fuel cells (SOFCs).

LSCM compositions show excellent tolerance to both reduction and oxidation but the crystal structure transforms from hexagonal in air to orthorhombic in H₂. The volume change associated with this phase transformation is only about 1%, thus having little effect on other properties. The total electrical conductivity increases with the content of Mn, whereas the resistance to sulfur poisoning increases with the content of Cr. Fuel cells using LSCM as the anode show very good performance when pure hydrogen is used as the fuel. However, they do not appear to be stable in fuels containing 10% of H₂S.

J.R. Frade, *et al.* [18] developed intermediate-temperature solid oxide fuel cells (IT SOFCs) which required novel anode materials with high electrochemical activity at 800–1070 K. In order to assess the role of oxide components of Ni- and Cu-containing cermets, a series of electrodes containing 8% yttria stabilized zirconia (Y8SZ), Ce_{0.8}Gd_{0.2}O_{2-δ}(CGO) and TbZrO_{4-δ} with fluorite-related structure, zircon-type Ce_{0.8}Ca_{0.2}VO_{4+δ}, pyrochlore Gd_{1.86}Ca_{0.14}Ti₂O_{7-δ}(GCTO) and La_{0.9}Sr_{0.1}Al_{0.65}Mg_{0.15}Fe_{0.20}O_{3-δ} perovskite, were studied in contact with (La_{0.9}Sr_{0.1})_{0.98}Ga_{0.8}Mg_{0.2}O_{3-δ} (LSGM) electrolyte. The best performance was found for anodes comprising a stable ion-conducting component, such as Y8SZ or GCTO, and one Ce-containing phase, such as CGO or cerium vanadate. Anode performance is less dependent on the ionic conductivity of oxide components than on redox stability or interaction between different cell materials. Surface modification with ceria substantially reduces overpotentials of all cermet anodes. For Ni–CGO and Cu–CGO, such activation yields about 100–115mV at 1073K and 200 mA/cm² in 10% H₂–90% N₂ for both anodes.

In 2006 Tatsumi Ishihara, *et al.* [19] have revealed the effects of additives to Ni anode. When Mn or Ag was added, the estimated activation energy for anodic reaction increased. Therefore, the activity of reaction site in Ni anode may decrease by the addition of Ag or Mn. In contrast, the addition of Fe greatly decreased the apparent activation energy of Ni anode and so, the activity of reaction site on Ni seems to improve by addition of Fe. The power generating property of the SOFC single cell using SSC (Sm_{0.5}Sr_{0.5}CoO₃) as cathode LSGM/SDC (La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃ / Sm doped CeO₂) as electrolyte and Ni–Fe–SDC

(NiO(Fe₃O₄)–Sm doped CeO₂) as anode reached the values of 3270, 1951, 612 and 80 mW/cm² at 973, 873, 773 and 673 K, respectively. Successful demonstration of thin film SOFC single cell at such low temperature may open new SOFC application field, for example, mobile power source.

John T.S. Irvine, *et al.* [20] investigated electronic conductivity of the potential SOFC anode material La_{1-x}Sr_xCr_{0.5}Mn_{0.5}O_{3±δ} in the range 0.2 < x < 0.3. XAS has indicated defects controlling electronic transport in La_{1-x}Sr_xCr_{0.5}Mn_{0.5}O_{3±δ} associated with the Mn cation only. This material shows thermally activated conduction behaviour consistent with polaronic transport. At 900°C, conductivity in air increases with Sr²⁺ via an increase in [B_B] holes (B—transition metal).

In 2006 Shaorong Wang, *et al.* [21] developed a multilayer tape casting and co-sintering process to fabricate large area anode-supported electrolyte film, which is critical for planar type reduced temperature solid oxide fuel cells (SOFCs). Nickel/yttria-stabilized zirconia (Ni/YSZ), nickel/scandia-stabilized zirconia (Ni/ScSZ) cermet, ScSZ, Ce_{0.8}Gd_{0.2}O_{1.9} (CGO), and La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF)–CGO were used as materials of anode substrate, anode functional layer, electrolyte, interlayer and cathode, respectively. The area-specific resistance (ASR) of the obtained single cell was found to be ~0.99 Ωcm² at 850°C with H₂/O₂ as the operating gases, and the maximum power density achieved ~0.63 Wcm⁻². The thickness of the (Zr,Ce)O₂-based solid solution formed at the ScSZ/CGO interface during high temperature sintering was investigated. The results illustrate that fabrication of anode-supported electrolyte film for planar SOFCs with a CGO interlayer is possible by multilayer tape casting procedure, which is both cost-effective and feasible.

In 2007 Weitao Bao, *et al.* [22] synthesized new anode material for intermediate temperature solid oxide fuel cells (IT-SOFCs) with a composite of La_{0.7}Sr_{0.3}Cr_{1-x}Ni_xO₃ (LSCN), CeO₂ and Ni. EDX analysis showed that 1.19 at% Ni was doped into the perovskite-type La_{0.7}Sr_{0.3}CrO₃ and Ce could not be detected in the perovskite phases. Results showed that the fine CeO₂ and Ni were highly dispersed on the La_{0.7}Sr_{0.3}Cr_{1-x}Ni_xO₃ substrates after calcining at 1450°C and reducing at 900°C. The thermal expansion coefficient (TEC) of the as-prepared anode material is 11.8x10⁻⁶ K⁻¹ in the range of 30–800°C. At 800°C, the electrical conductivity of the as-prepared anode material calcined at 1450°C for 5 h is 1.84 S cm⁻¹ in air and 5.03 S

cm^{-1} in an $\text{H}_2 + 3\% \text{H}_2\text{O}$ atmosphere. A single cell with yttria-stabilized zirconia (YSZ, 8 mol% Y_2O_3) electrolyte and the new materials as anodes and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM)/YSZ as cathodes was assembled and tested. At 800°C , the peak power densities of the single cell was 135 mWcm^{-2} in an $\text{H}_2 + 3\% \text{H}_2\text{O}$ atmosphere.

Bo Huang, *et al.* [23] synthesized $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ powders were prepared using a simple combustion process. The results showed that the decomposition of the precursors occurs in a two-step reaction and temperatures higher than 1100°C are required for these decomposition reactions. The performance of the conventional electrolyte-supported cell LSCM/LSGM/PCM while operating on humidified hydrogen was modest with a maximum power density of 165, 99 and 62 mWcm^{-2} at 850, 800 and 750°C , respectively, the corresponding values for the cell while operating on ethanol stream was 160, 101 and 58 mWcm^{-2} , respectively.

X.J. Chen, *et al.* [24] developed and applied novel $(\text{La,Sr})(\text{Cr,Mn})\text{O}_3/(\text{Gd,Ce})\text{O}_{2-\delta}$ (LSCM/GDC) composite electrode as solid oxide fuel cell (SOFC) anode for direct oxidation of methane. The optimum composition of the LSCM–GDC composite anode is 33 wt. % LSCM and 67 wt. % GDC. At an output current density of 0.5 Acm^{-2} , the overpotential of the composite anode in wet H_2 and wet CH_4 at 850°C is 0.073 and 0.248 V (i.e., an anodic resistance of 0.146 and $0.496 \Omega\text{cm}^2$), respectively. This shows that the LSCM/GDC composite anode is a promising anode for the oxidation of H_2 and CH_4 . Electrochemical impedance spectroscopy is measured as a function of operating temperature and dc bias to understand the oxidation pathway of CH_4 on the LSCM/GDC composite anode. The results indicate that the developed LSCM/GDC composite anode can effectively suppress carbon deposition when using weakly humidified CH_4 and possesses an electrochemical performance that is comparable with a Ni cermet.

1.6 The objectives of the thesis

The objectives of this study are as follows:

1. To synthesize perovskite powders of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{Ni}_x\text{O}_3$ ($x= 0.1, 0.2, 0.3$), $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{Cu}_x\text{O}_3$ ($x= 0.1, 0.2$), $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{Al}_x\text{O}_3$ ($x= 0.1, 0.2, 0.3, 0.4$) and $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{Mn}_x\text{O}_3$ ($x= 0.1, 0.2$)
2. Study the properties of synthesized perovskite oxides for application in SOFC anode.