

# Chapter-1: Introduction and Literature Review

## 1.1 Overview of the Work

Nowadays energy markets are dominated by a substantial increase in energy demand due to the strong economic growth in the developing countries in all over the world [1]. Energy demand pattern up to the year 2050 and energy consumption pattern in India is shown in Fig. 1.1 [2], [3]. There are many sources of energy like traditional sources of energy, fossil fuels, nuclear sources of energy etc. Traditional energy sources have low efficiency and no longer in use. Limited fossil fuel reserves and continuous ecological degradation compelled governments and industries all around the world to look for renewable energy sources and technologies for power production [4], [5]. Nuclear power is a relatively clean form of energy and may be suitable for large-scale power stations [6]. But, the major concern is its high-level radioactive waste. On the other hand, alternate energy resources are considered a long-term solution to the world's future energy demands, since they are environment-friendly and independent of our declining limited natural resources.

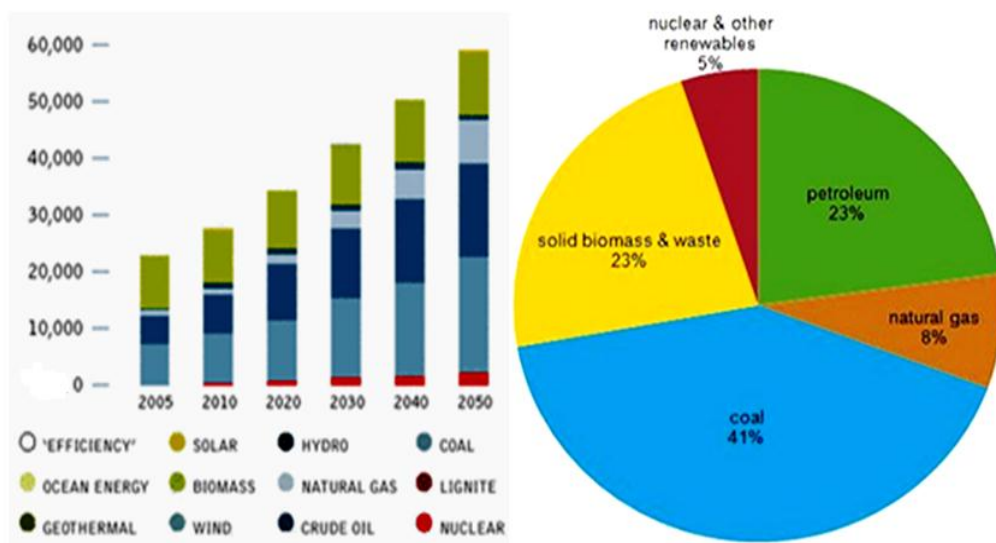


Figure 1.1: Energy demand (in Joule) and its consumption [Source: maritime executive.com]

There are several alternative and renewable energy based technologies are being developed like solar, wind, tidal, biomass, hydroelectric, ocean and geothermal technologies etc. But, these alternate energy technologies have some limitations [7] and difficulties with the stability of their energy as source, for example, on a cloudy or windless day. Their applications are somewhat limited due to lack of portability; a windmill is not much helpful to the power plant of a diesel truck, a solar panel fails to provide power at night, etc. Due to the limitations of these alternative energy sources it is better to look for sufficiently develop renewable energy resources. Among the available renewable energy sources & energy conversion devices, a fuel cell is an emerging technology for efficient and clean power generation [8], [9]. A fuel cell is an electrochemical energy conversion device, which converts chemical energy of the fuels directly into the electricity. However, environmental issues have played a major role and emphasized one of the major strengths of the desire to use fuel cells.

## **1.2 Fuel Cells: an overview**

A fuel cell is an electrochemical device that converts chemical energy (of fuels such as hydrogen, methane, butane or even gasoline and diesel) into electrical energy by exploiting the natural tendency of oxygen and hydrogen to react [9]. It is a simple device, containing no moving parts and only four functional components: anode, cathode, electrolyte, and interconnect. Since the energy is generated without combusting the fuel, the environmental benefits are significant.

In 1962, first time, by scientists at Westinghouse Electric Corporation (now Siemens Westinghouse), a revolution in energy research occurred due to the demonstration of the feasibility of extracting electricity from a device called a “solid electrolyte fuel cell”. Sir William Grove discovered the fuel cell principle and until the

advent of space-travel was mainly a laboratory curiosity. Fuel cells were looked upon as a safer and more reliable method to supply power, than other more potentially dangerous technologies in outer space, i.e., nuclear power, and the fear of environmental contamination in the event of a failed launch or re-entry. Major in-roads in the development of low cost fuel cells, escalating costs of existing power generation and fuel resources have brought fuel cell technology to the forefront, as our next technological revolution. The future international market for fuel cell systems in transportation [4], power generation [10] and all other energy sectors is potentially huge.

### 1.3 Types of Fuel Cell

Fuel cells are classified on the basis of electrolyte they employed. A few of the most promising types of fuel cell and their comparison is described in Table 1.1.

**Table 1.1:** Comparison between different types of fuel cells

| Fuel Cell Systems                    | Electrolytes                                | Operating Temperature | Fuel Supply                        | Application with efficiency             |
|--------------------------------------|---|-----------------------|------------------------------------|---|
| Polymer Electrolyte Membrane (PEMFC) | Immobilized, acidic, polymer                | RT to 200 °C          | Liquid ethanol                     | Small Units, up to automobiles (50-55%) |
| Alkaline Fuel Cell (AFC)             | Circulating liquid or Matrix as KOH         | RT to 200 °C          | Hydrogen or NH <sub>3</sub>        | Small Units and automobiles (50-55%)    |
| Phosphoric Acid Fuel Cell (PAFC)     | Concentrated acid gel                       | 160 to 220 °C         | Hydrogen or Converter              | Power Plants 50 to 200 kW (40-50%)      |
| Molten Carbonate Fuel Cell (MCFC)    | Molten salt as nitrate, sulphate carbonates | 600 to 620 °C         | Hydrogen, CO, Natural gas, propane | Power Plants up to Mega-W (45-50%)      |
| Solid Oxide Fuel Cell (SOFC)         | Doped and Co-doped Ceria and YSZ            | 500 to 1000 °C        | Natural gas or propane             | Small to Large Power Plants (45-60%)    |

The above table reflects the kind of chemical reactions that take place in the cell, the kind of catalysts required, the temperature range in which the cell operates, the fuel required, and other factors. These characteristics, in turn, affect the applications for which these

cells are most suitable. Among the aforementioned types of fuel cells, solid oxide fuel cells have gained much attention during in last few years because use of stable solid electrolyte, robustness and high efficiency in comparison to others [8], [9].

## **1.4 Solid Oxide Fuel Cell (SOFC)**

### **1.4.1 General Introduction**

The solid oxide fuel cell (SOFC) is promising and potential breakthrough tool for the low cost production of electricity in comparison with currently available fossil fuels because of increased demand for high quality and reliable energy with increasing expectations for environmental sensitivity [9]. In SOFCs, it is possible to achieve an electrochemical reaction at the electrodes simply by supplying fuel and air without using expensive noble metal catalysts. Solid oxide fuel cells (SOFCs) are comprised of a layered structure of a dense electrolyte sandwiched between porous and permeable electrodes (anode and cathode) [9]. Electrical power generation systems based on SOFC have the following advantages:

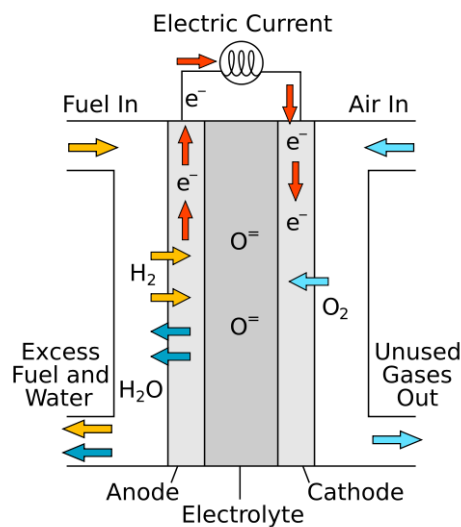
- High power generation efficiency
- High thermal efficiency
- Long term performance and stability
- Combined heat and electricity generation for industrial and domestic applications.
- Capable of operating on a wide variety of hydrocarbon fuels
- SOFC has a solid electrolyte, which eliminates the corrosion and liquid management problems of the PAFC and MCFC

Furthermore, SOFC system efficiencies can be improved by the internal reforming of natural gas within the fuel cell stack [11]. With modular construction, it is possible to

adapt SOFC systems to suit the load required and, as long as fuel is present, the SOFC is able to continually operate in almost any environment.

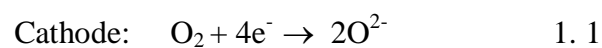
### 1.4.2 Operation of Solid Oxide Fuel Cells

Figure 1.2 shows schematically how a solid oxide fuel cell works. The cell is assembled with an electrolyte sandwiched between two porous electrodes. Air flows along the cathode (which is therefore also called the "air electrode").



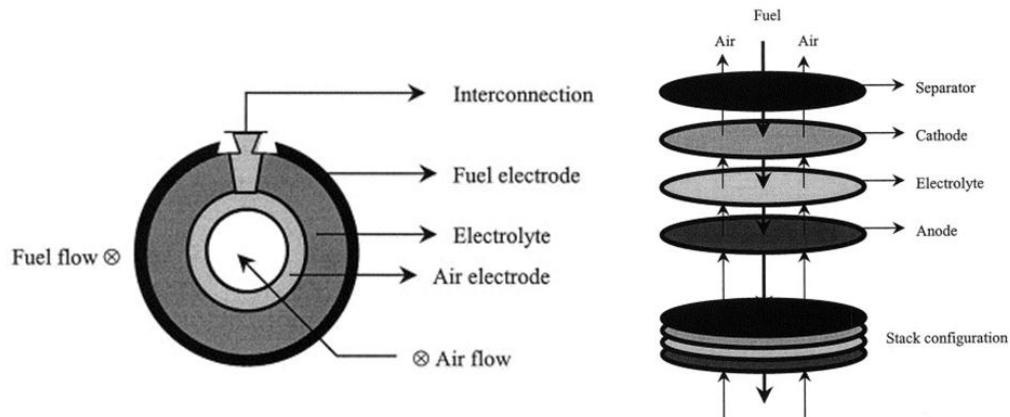
**Figure 1.2:** Working principle of SOFC [Ref: researchgate.net]

The following electrochemical reactions occur within the cell.



The open circuit cell voltage is approximately 1.1-1.2 V with hydrogen gas at the anode and pure oxygen at the cathode depending upon the pressure of each gas. However, under load conditions the cell voltage reduces to ~0.8-0.6 V per cell for current densities ranging between 250 to 500 mAcm<sup>-2</sup>. Therefore, for substantial voltages, a number of

cells are connected in series or parallel. Several SOFC designs are available, including the tubular and planar (Fig. 1.3).



**Figure 1.3:** Tubular SOFC configuration (end view) and planar design SOFC [source: researchgate.net]

Out of these designs, the planar SOFC has the most economical design, with potentially lower fabrication cost and a power density of around  $1 \text{ MW/m}^3$  that makes it the preferred cell design for many SOFC developers around the world.

## 1.5 Materials Selection for the Component of SOFC

The material selection requirements for SOFC are quite challenging, stubborn and well established [12], [13]. On the basis of the characteristics of cell as oxygen-ion conductor, electronic conductivity, stability in both oxidizing and reducing conditions, density and fuel flexibility there are following essential components:

### 1.5.1 Electrodes (Cathode and Anode)

The main two electrodes are anode and cathode by which electrolyte was sandwiched in the cells. Cathode acts in oxygen atmosphere where oxygen molecules dissociated into oxygen ions to reach the electrode/electrolyte interface. In some designs (e.g. tubular) the cathode contributes over 90% of the cell's weight and therefore provides structural support for the cell [14]. Due to the strong oxidizing atmosphere, at high temperature, it's not easy to choose lower cost metals. Any reduction in operating

temperature lowers the operating costs and expands the materials selection, creating an opportunity for additional cost savings. The challenge is to sinter the cathode adequately, often by co-sintering with the other components while maintaining sufficient interconnected porosity.

The anode must meet most of the same requirements of the cathode for electrical conductivity, thermal expansion compatibility, porosity, and has to function in a reducing atmosphere. The reducing atmosphere combined with electrical conductivity requirements makes the system as attractive candidate materials. In order to maintain porosity, pore formers such as starch, carbon, or thermosetting resins are added. These burn out during firing and leave pores behind. Mostly development has been focused on nickel due to its abundance and affordability. The main requirements of the SOFCs electrodes are [9], [13], [15] High electronic and less ionic conductivity

- Porous structure optimized for the mass transport of the gas species
- Thermal expansion compatible with those of the other cell components
- Chemically inert
- Resistance to thermal cycling
- High catalytic activity and good mechanical strength
- Good adherence to the other cell components and porosity
- Minimum inter-diffusion and Low volatility
- A superficial resistivity ( $\leq 0.2 \text{ ohm/cm}^2$ )
- Moderate materials and fabrication cost

The polarization loss occurs at electrodes due to voltage drop as low operating temperature.

**Major cathode materials:** Doped lanthanum cobaltite & manganite (LSC & LSM), (LSM-YSZ) composite, Lanthanum-Barium cobaltite (LBC),  $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_{3\pm\delta}$  (PSM) etc.

**Major anode materials:** Porous Ni, NiO/YSZ, NiO/SDC, La doped Strontium titanate (LST), Ni-Cu-YSZ,  $\text{Ba}_{0.5}\text{La}_{0.5}\text{Ti}_{0.3}\text{Mn}_{0.7}\text{O}_3$ , etc.

### 1.5.2 Interconnect

Just as an internal combustion engine depends on several cylinders to provide enough power to be used alike fuel cells in combination in order to generate enough voltage and current. This means that the cells need to connect together and a mechanism for collection of electrical current needs to be provided, hence the need for interconnects. The interconnect functions as the electrical contact to the cathode while protecting it from the reducing atmosphere of the anode. The high operating temperature of the cells combined with the severe environments means that interconnects must meet the most stringent requirements of all the cell components [15]:

- 100% electronic conductivity, no porosity (to avoid mixing of fuel and oxygen).
- Thermal expansion compatibility and inert with respect to the other fuel cell components.
- It will be exposed simultaneously to the reducing environment of the anode and the oxidizing atmosphere of the cathode.
- Absence of mass transport effects in the presence of chemical gradients that may lead to the formation of voids or high contact resistances
- No time dependent phase change
- Low material and fabrication cost

For YSZ based SOFC operating at about 1000 °C,  $\text{LaCrO}_3$  doped with an alkaline earth element (Ca, Mg, Sr, etc.) is used as interconnect to improve its conductivity. Ca-doped yttrium chromite has considered also because it has better thermal expansion compatibility, especially in reducing atmospheres. Recently, Ferritic stainless steel (FSS)



with minor additions of Nb and Ti elements has been carried out at 800 °C in an air for 70 cycles.

### 1.5.3 Electrolyte

The main component in the SOFC is the solid electrolyte. The function of the electrolyte is to transport the oxygen ion without significant losses from the cathode to the anode. The transport of oxygen ions in the electrolyte occurs through the oxygen vacancies in the oxygen sub-lattice. The concentration of vacancies and their mobility determines the electrolyte conductivity. Among the number of suitable oxide ion conductors, high oxygen diffusivity has been observed in oxides which exhibit large tolerance for atomic disorder.

In the cell, oxygen molecule has been converted into oxygen ions that must migrate through the electrolyte to the fuel side. For the migration of oxygen ions, electrolyte must satisfy the following criteria [8], [13], [15]:

- The electrolyte must possess a high ionic conductivity and no electrical conductivity.
- It must be fully dense to prevent short-circuiting of reacting gases throughout it.
- It should be thin also to minimize resistive losses in the cell.
- As with the other materials, it must be chemically, thermally, and structurally stable over a wide range of temperature.

**Major electrolyte materials:** Ytria stabilized Zirconia (YSZ), Sm/Gd doped ceria (SDC/GDC), Sr & Mg doped Lanthanum gallate (LSGM), Li doped CGO (Li-CGO), tri-doped ceria  $Ce_{1-x}(Pr_{1/3}Sm_{1/3}Gd_{1/3})_xO_{2-\delta}$  etc.

The main difficulty, which limits the operation of these components, is their high operating temperature range from 800 °C to 1000 °C [16]. This high temperature decreases the cell life time and increases the cost of materials. It is also necessary to

identify new electrode-electrolyte materials in order to be able to decrease the operating temperature of the SOFC so that inexpensive manifolding materials can be used and the cost of the initial thermal energy required to heat the cells can be lowered. Lowering the temperature can significantly improve the thermal expansion incompatibilities. However, by lowering the operating temperature of the fuel cell, the ionic conductivity of the electrolyte is significantly decreased. Therefore, for the fuel cell output at intermediate-temperatures are favorable than the output observed at higher temperature.

## **1.6 High and Intermediate Temperature Solid Oxide Fuel Cell**

### **1. 6.1 High Temperature Solid Oxide Fuel Cells (HT-SOFC)**

The enhanced efficiency of SOFC in comparison with other energy conversion systems is borne out by its high operating temperature exceeds 800 °C. The components for HT-SOFCs are the following:

- Electrolyte: 8-mol % yttria stabilized zirconia (YSZ)
- Anode: Ni-YSZ cermet
- Cathode: Sr doped lanthanum manganite (LSM)
- Interconnect: Doped lanthanum chromate (LCR)

### **1.6.2 Demerits of High Temperature Solid Oxide Fuel Cells**

Although the power output is high, HT-SOFC suffers with some serious demerits. Material costs are high, particularly for interconnect and construction materials. For high temperature SOFC, a ceramic such as lanthanum chromite is used as interconnect, or, if the temperature is limited to <1000 °C, a sophisticated refractory alloys e.g. based on mechanically alloyed Y/Cr can also be utilized for interconnect. In either case interconnect represents a major proportion of the cost of the stack. A potential drawback to the use of chromium containing ceramics and alloys is the volatility of the material,

which can result in contamination of the stack components. This has an increased significance for future reclamation of materials and components from using stacks where the presence of a toxic material such as  $\text{Cr}^{6+}$  would require special disposal procedures.

### **1.6.3 Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFC)**

Operation of the SOFC between the temperatures range 500-600 °C, termed as Intermediate Temperature Solid Oxide Fuel Cell (IT-SOFC) and can overcome some of the problems of High Temperature Solid Oxide Fuel Cell. The new generation of electrolytes such as Gd-doped ceria (CGO), Sr and Mg doped lanthanum gallate (LSGM) which possess much higher oxide ions conductivity at temperature below 600 °C with respect to YSZ electrolyte is considered as promising electrolytes.

### **1.6.4 Merits of Intermediate Temperature Solid Oxide Fuel Cells**

Due to low Operating temperature below 600 °C, IT-SOFC offers several benefits. Some of the salient features are pointed below:

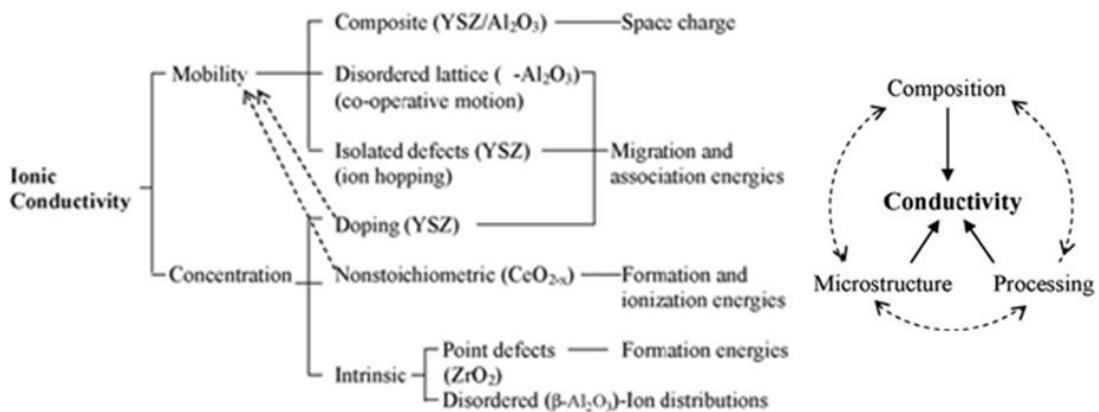
- Operation at less than 600 °C means that low cost metallic materials, e.g. ferritic stainless steels or even metal-alloys can be used as interconnect and construction materials. This makes both the stack and balance of plant cheaper and more robust.
- Lower temperature operation offers the potential for more rapid start up and shut down procedures.
- Reducing the operating temperature simplifies the design and materials requirements of the balance of plant.
- Low operating temperature significantly reduces corrosion rates.

In order to operate at reduced temperatures, several changes need to be made to cell and stack design, cell materials, reformer design and operation, and operating conditions.

The present work has been focused on electrolyte material of SOFC at intermediate temperature range. Since electrolyte must possess a high ionic conductivity, discussed earlier, therefore it is necessary to discuss the factors that affect the ionic conduction through the material.

### 1.7 Factors Influencing Ionic Conduction of The Electrolyte

In the electrolyte materials, optimizing the ionic conductivity is of more importance. The ionic conductivity of electrolytes can be influenced by many parameters. There has been made an enormous effort for the improvement of ionic conductivity of the electrolyte. Composition, microstructure and processing are fully related to each other in the electrical properties [17], [18]. A relation between these factors and ionic conductivity of the oxide electrolyte is shown below in Fig. 1.4.



**Figure 1.4:** (a) The major sources of ionic carriers in oxides and their respective mobilities compiled from literatures (b) The correlation of composition, microstructure, processing and electrical conductivity in polycrystalline materials under given temperature and surrounding atmosphere [Hui, et al., 2007]

Hence, the following factors can enhance the conductivity of electrolyte

- Doping and multiple doping can improve the ionic conductivity. The ionic conductivity of electrolytes can be maximized through composition modification by selecting an alio-valent and iso-valent dopant with suitable ionic radii and its concentration [19]–[21].

- Introducing a second phase to form a composite electrolyte may change grain boundary and therefore vary the electrical conductivity of the electrolytes [22], [23].
- Properties of grain boundaries such as impurity segregation and space charge play an important role in the ionic conductivity [23], [24].
- Processing conditions also influence the final ionic conductivity depending on density, the level of impurities, thermal history and formation of microdomain [23].

Out of these factors, there are some other parameters which directly or indirectly affect the ionic conductivity.

Since, ionic motion is the action of ions hopping, under the influence of an electric field, through the lattice via defects. The rate of ion conduction is described by very common equation (1.5) [26], [27].

$$\sigma = nq\mu \quad 1.5$$

$\sigma$  is the ionic conductivity ( $S.cm^{-1}$ ),  $n$  is the number of mobile ions in a given volume of lattice ( $cm^{-3}$ ),  $q$  is the magnitude of the charge for the oxygen ion (coulombs) and  $\mu$  is the mobility of the ions ( $cm^2 sec^{-1} V^{-1}$ ). In the case of oxygen-ion conductors, conduction occurs via anion vacancies, so that

$$\sigma_v = C_v q_v \mu_v \quad 1.6$$

where the subscript v means vacancy and  $C_v$  is the number of anion vacancies per unit volume ( $cm^{-3}$ ) According to the Nernst-Einstein relation, the mobility is related to diffusion constant [27],  $D$  by the equation:

$$\mu = qB = qD/kT \quad 1.7$$

where,  $B$  is the absolute mobility.  $D$  is given by

$$D = a^2 v_0 \exp(\Delta S_m/k) \exp(-\Delta H_m/kT) \quad 1.8$$

where, 'a' is the jump distance of vacancy (cm),  $v_0$  is an appropriate lattice vibration frequency ( $\text{sec}^{-1}$ ) and  $\Delta S_m$ , and  $\Delta H_m$ , are the activation entropy ( $\text{eV K}^{-1}$ ) and activation enthalpy (eV) of diffusion respectively. Since  $C_v$ , is represented as:

$$C_v = [V_{0\cdot\cdot}]\{1-[V_{0\cdot\cdot}]\}N_o \quad 1.9$$

where,  $N_o$  is the number of oxygen sites per unit volume, the following equations can be obtained using (1.5), (1.7), (1.8) and (1.9).

$$\sigma T = A' [V_{0\cdot\cdot}]\{1-[V_{0\cdot\cdot}]\}\exp(-\Delta H_m/kT) \quad 1.10$$

$$A' = (4e^2/k) a^2 v_0 N_o \exp(\Delta S_m/k) \quad 1.11$$

For small values of  $[V_{0\cdot\cdot}]$  Eq. (1.10) can be approximated as:

$$\sigma T = A' [V_{0\cdot\cdot}] \exp(-\Delta H_m/kT) \quad 1.12$$

The enthalpy term can be replaced by a general activation energy term,  $E_a$  as

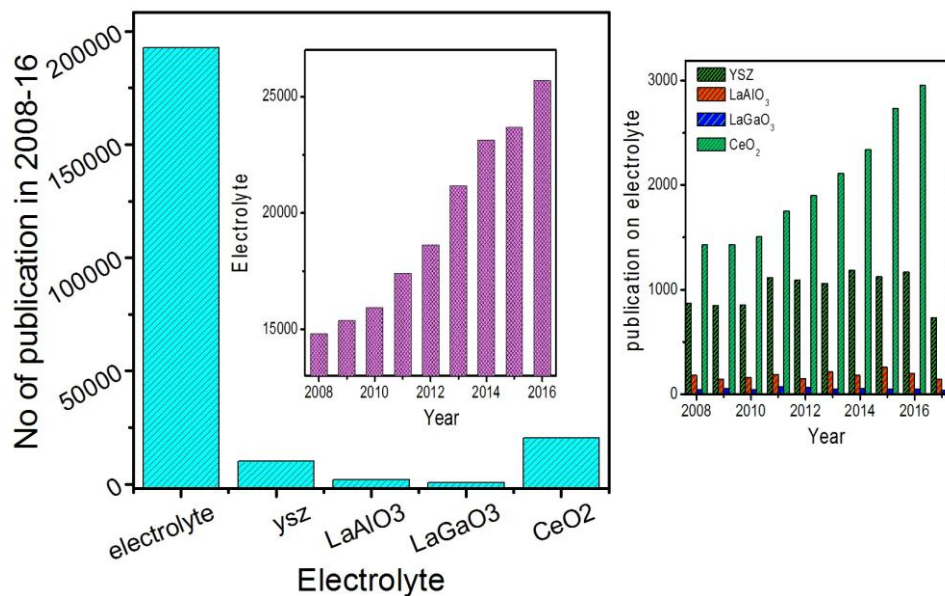
$$\sigma T = \sigma_o \exp(-E_a/kT) \quad 1.13$$

where,  $\sigma_o$  is a pre-exponential constant, T (K) is the absolute temperature and  $E_a$  ( $\text{Scm}^{-1}$  K) is the activation energy for oxygen diffusion. In this way temperature directly affects the ionic conductivity ( $\sigma$ ).

## 1.8 Present Scenario of Electrolyte For Solid Oxide Fuel Cell

Keeping into the mind all above mentioned requirements for ionic conduction for electrolytes, it is necessary to investigate the different types of electrolytes which have possible oxide ions for ionic conduction for SOFC. For this, it has been collecting information about the publication on different electrolytes. During the last ten years, from 2008-17, there are nearly two lacs publications on electrolytes for SOFC. Also, the number of publications on electrolytes keeps on increasing every day; this indicates the work on solid electrolytes highly demanded day by day. The no of publications on electrolytes, in 2008 was 14,828, which are very low in comparison to ~25,699 in 2016. The most popular electrolytes are Yattia Stablize Zirconia YSZ),  $\text{LaAlO}_3$ , Lanthanum

Galatte ( $\text{LaGaO}_3$ ), and ceria based electrolyte like CSO and CGO. Among all of these electrolyte, the no. of publication is high for ceria based electrolytes. The work reported on  $\text{LaGaO}_3$  is very less because of its lower ionic conductivity. The no. of publications based on YSZ is relatively lower than that of  $\text{CeO}_2$  and higher than that of  $\text{LaGaO}_3$ . YSZ has also a demerit because it works on high operating temperature, whereas  $\text{LaGaO}_3$  has the problem of leakage current and expensiveness. On the other hand, In  $\text{LaAlO}_3$ , there is no leakage current, not much expensive and also operating temperature is low. These properties made  $\text{LaAlO}_3$  as a cost-effective substitute of LSGM, YSZ and ceria based electrolytes. A comparative report of publications since last ten years on various electrolytes is shown in Fig. 1.5. A very few report on  $\text{LaAlO}_3$  shows that there is much attention required for this material.

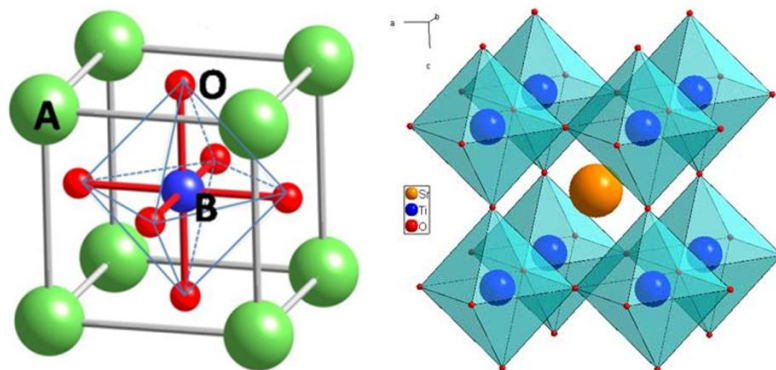


**Figure 1.5:** Present scenario of electrolytes

Since,  $\text{LaAlO}_3$  has a perovskite structure. So, it is necessary to discuss briefly about the perovskite structure and its properties.

## 1.9 Perovskite Oxide System

The perovskite oxides (with general formula,  $ABO_3$ ) e.g.,  $LaAlO_3$ ,  $LaGaO_3$ ,  $CaTiO_3$  etc. are very important material for SOFC, as it has generally stable crystal structure, large free lattice volume and substitution liberty [28], [29]. Perovskite oxides are of great interest of research for their wide applicability in human life as dielectric thermistors, barrier layer capacitors, dielectric amplifier, oxygen sensor, humidity sensor and anode or cathode or electrolyte or interconnect for solid oxide fuel cells etc. An ideal perovskite has a cubic structure. The ideal cubic structure of  $ABO_3$  shows the  $BO_6$  octahedra form a corner-shared network, with remaining voids filled by the cation A (Fig. 1.6). The cubic structure often distorts to tetragonal, rhombohedral or orthorhombic symmetry due to tilting of  $BO_6$  octahedral.



**Figure 1.6:** Perovskite structure  $ABO_3$  and octahedron  $BO_6$  [Ref: sfscientific.com]

## 1.10 Types of Perovskite Oxides

On the basis of cation valencies ( $A^{m+}$  and  $B^{n+}$ ), perovskite oxides can be divided into five categories. The basic criteria of classification of is that sum of the valencies of cations ( $A+B$ ) must be equal to anions (oxygen) valencies to maintain the electro neutrality. The five categories are briefly described one by one below:



### 1.10.1 $A^{1+}B^{5+}O_3$ Type Structure

In this category, A-site is occupied by monovalent cation and B-site by a pentavalent cation. For example,  $LiNbO_3$ ,  $NaNbO_3$ ,  $KTaO_3$ ,  $KNbO_3$  and  $AgNbO_3$  etc. Generally, they have ferroelectric and antiferro-electric materials.  $KTaO_3$  and  $KNbO_3$  are used used in acousto-optic and electro-optic devices while rest are used in electro-optic devices, microwave surface acoustic devices and holographic memory.

### 1.10.2 $A^{2+}B^{4+}O_3$ Type Structure

In this type of perovskite oxides, A-site of is occupied by divalent cations and B-site is occupied by tetravalent cations. In electro-ceramics, a number of perovskite oxides are studied by the general formula  $A^{2+}B^{4+}O_3$  where A cations are alkaline earth metal (A= Sr, Ba, Co, and Pb etc.) and B cations transition elements (B=Ti, Sn, Zr, Hf, Mo, Th etc.). Some important examples of  $A^{2+}B^{4+}O_3$  series are  $CaTiO_3$ ,  $BaTiO_3$ , and  $PbTiO_3$  and  $PbTiO_3$  are used as piezoelectric and ferroelectric materials. They are utilized as a piezoelectric transducer, phonograph pickups, air transducers, instrument transducers and ultrasonic devices.

### 1.10.3 $A^{3+}B^{3+}O_3$ Type Structure

In such type of perovskite oxides, both A and B cation sites are occupied by trivalent cations. Where  $A^{3+}$  cation is rare earth metal ions while  $B^{3+}$  cation is a transition metal ions, respectively. Some of the well known examples of  $A^{3+}B^{3+}O_3$  type structure are  $BiMnO_3$ ,  $LnCoO_3$ ,  $LaNiO_3$ ,  $GdCoO_3$ ,  $LaCoO_3$ ,  $LaFeO_3$ ,  $LaMnO_3$ ,  $LaFeO_3$  and  $LaCrO_3$  etc.. This type of perovskite materials is extensively studied due to their fascinating structural, electrical and magnetic properties. These are more preferred potential candidates for the cathode and interconnect in a solid oxide fuel cell.

### 1.10.4 $A^{4+}B^{2+}O_3$ Type Structure and $A^{5+}B^{1+}O_3$ Type Structure

These categories of perovskite are not easily available in previous reported literatures. Several investigations have been focused on the conductivity of perovskite oxide structure due to their relatively open structure. Ionic conductivity of perovskite oxides is discussed in terms of structurally related parameters, such as tolerance factor, specific free volume and oxygen deficiency. The Goldschmidt tolerance factor is given by the formula

$$t_{GS} = (r_A + r_O) / \sqrt{2}(r_B + r_O) \quad 1.14$$

where,  $r_i$  (with  $i = A, B$  or  $O$ ) is ionic radii of cations and anion in  $ABO_3$  perovskite. The tolerance factor and the specific free volume were both a function of ionic radius and the tolerance factor decreased with increasing the specific free volume. The optimum tolerance factor was found to be around 0.96 due to the balance between the specific free volume and the tolerance factor in order to obtain the maximum conductivity for  $A^{3+}B^{3+}O_3$  type perovskite. The optimum oxygen deficiency in order to obtain the maximum electrical conductivity was around 0.2. The effect of ionic size of dopant ions in A and B site can change electrical conductivity. Electrical conductivity of perovskite oxides is oxygen ion conductors. Perovskite-type oxides have been considered to be a potential material for solid electrolytes of SOFCs and have been widely studied as reviewed by Kendall et al. [28].

There are following conditions to obtain high ionic conductivity of perovskite oxides:

- The  $A^{3+}B^{3+}O_3$  type perovskite is preferred for high oxygen ion conductivity whereas  $A^{2+}B^{4+}O_3$  type perovskite is not good for the oxygen ion conductor.
- The optimum tolerance factor is near unity from the viewpoint of lattice stability and equivalence in oxygen site. The larger specific free volume is desirable in the

view of the mobility of oxygen ion. The specific free volume linearly increases with the decrease of the tolerance factor for each series with fixed A-site cation.

- The change of the tolerance factor due to doping should be as small as possible.

The optimum oxygen deficiency  $\delta$  to obtain the maximum electrical conductivity is around 0.2. When  $\delta$  is considerably larger than 0.2, the electrical conductivity decreases probably due to short range interaction among vacancies. Doped perovskite has better conductivity than that of undoped.

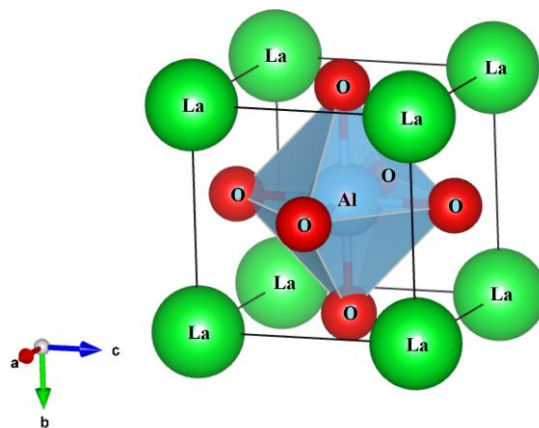
According to Kilner and Brook, in doped perovskite oxide maximum ionic conductivity is achieved when there is minimum elastic strain present in the lattice [26]. Kim (1989), studied the effect of ionic radius and valence of the dopant cation on the lattice parameter of oxide perovskite and a critical ionic radius,  $r_c$ , was defined as the ionic radius of the dopant that neither causes expansion nor contraction of the host perovskite lattice [26]. Yahiro et al. and Eguchi et al. studied the electrical conductivity of the electrolyte as a function of the ionic radius of the dopant. A distinct maximum of the electrical conductivity was found for the dopant with the ionic radius greater than host ion and a maximum appears for divalent and trivalent dopant ions [19]. The ions giving the most significant rise in the conductivity cause the smallest change in the lattice parameters, as compared with the undoped system. This behavior arises from the formation of the associated point defects when the concentration of a dopant exceeds a certain value. As a consequence, the mobility of oxygen vacancies decreases. There is a minimum in the activation energy for the concentration of Sr, which is accompanied by a maximum in the conductivity of the electrolyte.

On the basis of above report, it has been concluded that perovskite structure is suitable for electrolyte material for SOFC. It is reported above that, electrolyte materials having the perovskite structure, e.g.,  $\text{LaAlO}_3$ ,  $\text{LaGaO}_3$ ,  $\text{LaInO}_3$  etc. are very important for

SOFC. In  $\text{LaAlO}_3$ , there is no leakage current, not much expensive and also its operating temperature is low. These properties made  $\text{LaAlO}_3$  as a cost-effective substitute over LSGM, YSZ and ceria based electrolytes.

## 1.11 Lanthanum Aluminate ( $\text{LaAlO}_3$ )

Among various perovskite oxides, lanthanum aluminate ( $\text{LaAlO}_3$ ) (abbreviated LAO) and its derivatives have find application in the field of high frequency capacitors, magneto hydrodynamic generators, substrate for super conducting, ferroelectric thin films and colossal magneto resistance [30] and electrolyte for solid oxide fuel cells [31]. LAO shows high chemical and mechanical stability this leads suitable use of LAO over  $\text{LaGaO}_3$  and ceria based electrolyte. Due to lower operating temperature of LAO has given dominant nature over YSZ. Also, mechanical strength of LAO is higher than that of  $\text{CeO}_2$  and its derivatives. Nguyen and Dokiya reported a strengthening effect of mixing LAO and the chemical stability of LAO was also confirmed [32]. Pure Lanthanum aluminate is a rhombohedral structure with space group R-3c at room temperature and transform to cubic at  $\sim 500^\circ\text{C}$ . In addition, this material have low cost, moderate thermal expansion and higher stability with respect to reduction and volatilization [33]. The ideal perovskite structure of LAO is shown in Fig. 1.7.



**Figure 1.7:** Ideal perovskite structure of LAO with  $\text{AlO}_6$  octahedron

There is some confusion about the structure of LAO at different temperature. Different authors reported different structure regarding its structure at different temperatures which is illustrated below in Table 1.2.

**Table 1.2:** Rhombohedral and cubic modifications of  $\text{LaAlO}_3$  at different temperatures

| Authors                   | Structure | Temperature | Lattice parameters (Å) |
|---------------------------|-----------|-------------|------------------------|
| Chakoumakos et al. (1998) | R-3c      | 296K        | a=5.36462, c=13.1096   |
| Chakoumakos et al. (1998) | Pm-3m     | 1223K       | a=3.82842              |
| Howard et al. (2000)      | R-3c      | 15K         | a=5.3598, c=13.0859    |
| Howard et al. (2000)      | R-3c      | 295K        | a=5.3647, c=13.1114    |
| Howard et al. (2000)      | R-3c      | 812K        | a=5.3895, c=13.1919    |
| Lehnert et al. (2000)     | R-3c      | 300K        | a=5.36382, c=13.1091   |
| Lehnert et al. (2000)     | R-3c      | 800K        | a=5.3862, c=13.1923    |
| Lehnert et al. (2000)     | Pm-3m     | 973K        | a=3.81593              |
| Zhao et al. (2004)        | R-3c      | RT          | a=5.3660, c=13.1090    |
| Vasylechko et al. (2005)  | R-3c      | 12K         | a=5.3594, c=13.0840    |
| Nakatsuka et al. (2005)   | Pm-3m     | RT          | a=3.7913               |

This transition of phase is due to  $\text{BO}_6$  octahedral tilting. This tilting in perovskites can be understood at one level due to a single driving mechanism, namely a Zone boundary soft mode, involving the motions of more or less rigid octahedral [34]. This Zone Boundary Transition (ZBT) occurs due to collapse of the  $R_{25}$  phonon mode [35], [36]. A details discussion about tilting and ZBT is given in chapter 5. Pure LAO has increased conductivity with increasing temperature. Its advantage is that it has a good ionic conductivity at low partial pressure and operates effectively at much lower temperatures [37] (below 800 °C). It is a good ionic conductor with a transference number ( $T_f$ ) nearly equal to 0.99. All about the ion conducting behavior of LAO is mentioned in chapter 3.

The limitation of this electrolyte is that it is susceptible to reduction on the anode (fuel) side. At low operating temperatures (500-700 °C) grain boundary resistance is a significant barrier to ionic conductivity. Efforts are underway to develop compositions

which address these problems. However, the conductivity of LAO based electrolyte has lower conductivity than that of YSZ [38]. In order to enhance the conductivity of LAO different workers perform different experiments. For reducing the operating temperature and to obtain better ionic conductivity many attempts have been made. Lanthanum aluminate based perovskite may be a likely candidate for a cost effective solid electrolyte. In order to enhance the oxygen conduction addition of divalent cations in LAO is expected. The conductivity of doped Lanthanum aluminate is higher than that of undoped LAO [23], [29], [39]. A system based on LAO, by adding suitable dopants can probably become a good conductor. Recently, it was found that simultaneous substitution of Sr ion on the La-site and Mg ion on Al-site of LAO can enhance the conducting value which is slightly higher than that of Yttrium-stabilized Zirconia (YSZ) [40], [41]. Fung et al. Study of comparison of dissolution behavior and ionic conduction between Sr and/or Mg doped  $\text{LaGaO}_3$  and  $\text{LaAlO}_3$  [39]. Park and Choi described electrical conductivity of Sr and Mg doped  $\text{LaAlO}_3$  [42]. Lybye et al. Investigated the conductivity of A- and B- site doped  $\text{LaAlO}_3$ ,  $\text{LaGaO}_3$ ,  $\text{LaScO}_3$ , and  $\text{LaInO}_3$  [29]. It was found that Aluminium (Al) gives the highest conductivity in case of doped LAO at La-site than that of Scandium (Sc) and Indium (In) doped. Hayashi et al. Changed the tolerance by doping and suggest that the optimum dopant on A-site for  $\text{La}^{3+}$  is  $\text{Sr}^{2+}$  and on the B-site for  $\text{Al}^{3+}$  is  $\text{Mg}^{2+}$  [43].

For further enhancement of conductivity of LAO, many attempts have been made and it has been found that double substitution with larger cations such as Ca/Sr/Ba ions on the La-site can increase the ionic conductivity. A certain rise in the conductivity can be achieved if an iso-valent together with La ions [44] or a greater number of the dopants are introduced concurrently into the LAO lattice. The ionic conductivity can be raised by aliovalent substitution(s), which in turn increases the concentration of ionic defects. The perovskite oxides with general formula,  $\text{ABO}_3$  e.g.,  $\text{LaAlO}_3$ ,  $\text{LaGaO}_3$ , etc. are very

important materials for SOFC, as they generally have stable crystal structure, large free lattice volume and high substitution liberty. The conductivity in the electrolyte system depends on the ionic size and concentration of substituent. On various electrolytes e.g., CeO<sub>2</sub> double substitution has been applied to optimize effective ionic radius for better conductivity. Generally, it is believed that in case of perovskite, only B-site substitution can control the electrical properties of perovskite material. However, A-site substitution, many times alter the bonding strength between B-site cation and O-site anion. It competes with B-site cation to form A-O bond. Alio-valency of A- site cation even alters the bandwidth, varies overlap integral and hence the radial extension. The overlap integral can be measured in terms of tolerance factor. With the substitution, the effective ionic radii can be modified hence the size of the critical triangle (AAB or BBA triangle) [19]. Therefore, the oxide ion migration depends upon the size of the critical triangle or in the other words A-site substitution. A detail discussion is given in chapter 4 and chapter 5.

The conductivity in the electrolyte materials is basically due to the conduction of excess oxide ions through interstitial sites, i.e. availability of easy oxide ion conduction pathways through interstices, excess or vacancies of oxide ions and their conduction mechanism [45]. It was reported that in LAO, continuous conduction pathways available for conduction [46]. There were numerous attempts done to understand the conduction mechanism of oxide ions in the electrolyte or electrode/electrolyte interface using Ag/Pt and reveals that it is very complex to predict the conduction mechanism using Ag or Pt as electrodes. There are various mechanisms to explain the oxide ion conduction some of them are often referred as gas phase or pore diffusion [47] gas boundary layer diffusion [48], oxygen adsorption on zirconia or Pt [49], dissociation of the oxygen molecule [24], [50], [51], surface diffusion of adsorbed oxygen on Pt [51]–[53], the charge transfer

step [24], [54], [55], electronic conductivity [56]–[58], bulk diffusion of oxygen through Pt [56], [59] or electrolyte [60], and vacancy diffusion [61].

## 1.12 Objective of Present Investigation

The main objective of the present investigation is to develop cost effective novel electrolyte material for SOFC with high ionic conductivity at intermediate temperature range. For this purpose lanthanum aluminate based electrolyte material has been chosen. It has been also purposed to study the structural and electrical properties and tried to establish a correlation between them. In order to meet the above objectives it has been planned to:

- [1] Synthesize lanthanum aluminate ( $\text{LaAlO}_3$ ) and study its temperature and frequency dependent electrical properties, followed by structural properties using various characterization techniques and its conduction mechanism.
- [2] Enhance the electrical conductivity by simultaneous doping techniques on lanthanum aluminate with 1% Sr and 1% Mg on La and Al-site, respectively, i.e.,  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Al}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$  (LSAM).
- [3] Develop double substitution on above investigated electrolyte system with barium (Ba) having larger ionic radii (alio-valent) than that of La ion, i.e., the electrolyte system  $\text{La}_{0.9-x}\text{Sr}_{0.1}\text{Ba}_x\text{Al}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$  and study its structural-conductivity correlation.
- [4] Prepare a non aqueous tape of one of the above chosen system, i.e.,  $\text{La}_{0.89}\text{Sr}_{0.1}\text{Ba}_{0.01}\text{Al}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$  in accordance with the conditional requirements of the thin electrolyte system for a better electrolyte material for solid oxide fuel cell.
- [5] Develop double substitution on above investigated electrolyte system with samarium (Sm) having smaller ionic radii (iso-valent) than that of La ion, i.e.,



$\text{La}_{0.9-x}\text{Sr}_{0.1}\text{Sm}_x\text{Al}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$  and establish a correlation between structure and conductivity.

- [6] Investigate the effect of electrode paste on oxygen ions path at the electrode/electrolyte interface using different electrode paste like silver (Ag) and platinum (Pt) on the above studied system.

Details of all the synthesis & measurement techniques for investigating system have been given in the next chapter. The results of the present investigate are described in the subsequent chapters of the thesis.

