Chapter-1

Introduction and Literature review

CHAPTER 1: Introduction and Literature Review

1.1 Motivation of the work

Since the beginning of the industrial revolution, the primary source of energy for human activity has been fossil fuels[1]. This category of fuels includes coal, oil, and natural gas. There is no question that during the previous two hundred years, they have been a significant factor in advancing human civilization. However, mounting worries over its finite reserves, the resulting environmental degradation, unpredictable prices, and inconsistent supplies have led in a gradual shift toward the growth of alternate energy sources and its energy conversion technologies that are more efficient[2].

In developing countries, the economic growth, particularly China and India, there has been a huge growth in energy use, In current energy markets. a significant increase in energy consumption in today's energy markets. India ranks third in the world in terms of energy consumption as a percentage of the global total, following China and Japan. Figure 1.1 depicts the energy demand and consumption patterns in India through the year 2050. India's planning commission recorded the same amount of energy use in its energy policy report. To counteract the depletion of natural resources and the finite supply of fossil fuels, government agencies and private sector organizations around the world are turning to renewable energy sources.[3]

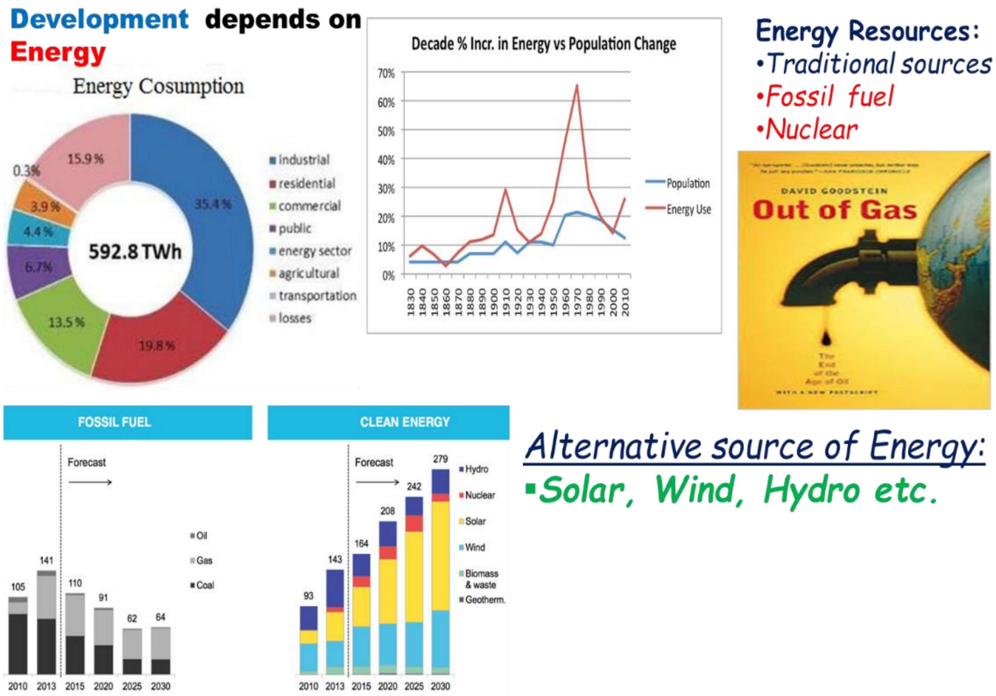

Figure1. 1: Energy demand and its consumption (Ref: www.maritimeexecutive.com)

A solution to the world's future energy needs is found in alternative energy supplies, which are environmentally beneficial and independent of our diminishing natural resources. Small-scale power generation is now being generated using a variety of alternative energy methods. Solar, wind, tidal, hydroelectric, and geothermal energy sources all fall within this category. Images of alternative energy technology such as solar panels and wind farms are all too familiar to most people. On days when it's cloudy or there is no wind, they are reliable providers of electrical energy, but their energy source is unstable. Due to their lack of mobility, their uses are relatively restricted; a windmill will not be of much aid to a diesel vehicle's power plant, a solar panel unable to produce electricity in the night, etc. As a result, large-scale industrial and home applications of these renewable energy resources are still in the early phases of development. As an alternative, nuclear fission and other non-renewable technologies have been offered as potential future energy sources. There are, however, certain safety and environmental concerns. It is possible that large-scale nuclear power plants might benefit from nuclear power. However, high-level radioactive waste is the main worry. Proper development of renewable energy resources is needed to minimize greenhouse gas byproducts and maximize the use of fossil fuels as a limited energy source. A fuel cell is a very reliable new technology for generation of electricity from renewable energy sources. Fuel cells have become increasingly popular as a result of environmental concerns about traditional power sources like internal combustion engines[4]. Removal of pollutants and the release of hazardous gases and substances into the atmosphere, as well as groundwater contamination by leaking fuel tanks with toxic-fuel additives are the primary goals (used to reduce pollutants). The fuel cells can solve all the problems related with the combustion of fossil fuels and hydrocarbon fuel sources. Just extracting the gasoline from the ground is a major cause of pollution. Third-world nations' capacity to compete for limited energy resources will be affected by the availability and ability to employ dependable fuel sources that can be used to manufacture hydrogen for fuel cells. Biomass, methane, methanol, and ethanol are all promising new sources of environmental advantages. Carbon dioxide and other greenhouse gases, toxic pollution from burning fossil fuels, the fall in oil output worldwide and the deregulation of electric power companies will lead to the widespread usage of fuel cells in the next several years.

In 1962, the field of energy research underwent a paradigm shift, "solid electrolyte fuel cells" were demonstrated for the first time by scientists at Westinghouse Electric Corporation (formerly Siemens Westinghouse), which is now part of the Siemens Group [4]. Fuel cells were first reported by Sir William Grove and remained mostly a laboratory curiosity until the advent of space flight. Although nuclear power and the possibility of environmental contamination were considered more perilous, fuel cells were seen as a safer and more reliable source of supplying electricity in outer space. Fuel cell technology is poised to be the next great technological leap forward, thanks to significant advances in the creation of low-cost fuel cells and the rising prices of traditional power production and fuel supplies. Fuel cells in a hydrogen energy economy might be an important feature of a long-term energy supply in the long run. Future international demand for fuel cell systems in transportation, power generation and other energy-related industries is enormous.

1.2 Fuel Cells

A fuel cell is an electrochemical conversion device that utilizes the inherent tendency of oxygen and hydrogen to react to transform chemical energy (such as H_2, butane, methane, or even diesel and gasoline) in the form of electrical energy. Anode, cathode, electrolyte, and connection make up the entirety of the device, which is devoid of moving elements [4].The advantages to the environment are enormous since the fuel is not burned in the process of producing the electricity. The characteristics of fuel cells are

- High Energy Conservation
- Fuel flexibility (Hydrocarbon fuel)
- Highly efficient
- Negligible by-products
- Co-generation (hot air and hot water) capability
- Rapid load response and compact construction.

1.3 Types of Fuel Cell

Type of electrolyte used in fuel cells determines how fuel cells are classified. Among other things, the cell's initial working temperature range, the types of catalysts used, the amount of fuel required, and other variables are influenced by the occurring chemical reactions [8]. The most promising types of fuel cells include

- PEMFC (Polymer Electrolyte Membrane Fuel Cell)
- AFC (Alkaline Fuel Cell)
- PAFC (Phosphoric Acid Fuel Cell)
- MCFC (Molten Carbonate Fuel Cell)
- SOFC (Solid Oxide Fuel Cell)

Table 1.1: Comparison of various fuel cell

Fuel Cell Systems	**Electrolytes**	**Operating Temperature**	**Fuel Supply**	**Application with efficiency**
Polymer Electrolyte Membrane	Immobilized, acidic, polymer	Room Temp. to 200 °C	Liquid ethanol	Small Units, up to automobiles (50-55%)
Alkaline Fuel Cell	Circulating liquid or Matrix as KOH	Room Temp. to 200 °C	Hydrogen or NH_3	Small Units and automobiles (50-55%)
Phosphoric Acid Fuel Cell	concentrated acid gel	160 to 220 °C	Hydrogen or Converter	Power Plants 50 to 200 kW (40-50%)
Molten Carbonate Fuel Cell	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	Doped and Co-doped Ceria and YSZ	500 to 1000 °C	Natural gas or propane	Small to Large Power Plants (45-60%)

1.4 Solid Oxide Fuel Cell (SOFC)

1.4.1 General Introduction

The SOFC (solid oxide fuel cell) is promising as a potential advance tool to produce electricity at cheaper rate when compared to currently available fossil fuels. This is because there is an increased demand for high quality and reliable energy along with increasing expectations for environmental sensitivity. In this scenario, SOFC is promising as a potential breakthrough tool. It is feasible to establish an electrochemical reaction at the electrodes just by supplying fuel and air, which means that low-cost component materials can be utilized in the cell. This is because the reaction can be achieved without the usage of expensive noble metal catalysts. The structure of a solid oxide fuel cell, also known as a SOFC, resembles that of a sandwich, with a thick electrolyte on one side and porous, permeable electrodes on the other (anode and cathode). They offer a very appealing and diverse method of conducting electrochemical reactions at the electrodes efficiently without the use of costly noble metal catalysts, and they have a significantly less environmental affect than the conventional power production systems like gas turbines. This is because the electrochemical reaction that takes place at the electrodes is carried out through the electrochemical reaction. The following are some of the advantages of SOFC-based electrical power generation systems:

- High-efficiency power generating
- Thermal efficiency is high
- Long term performance stability

- Combined heat and electricity generation for industrial and domestic applications.
- Capability of functioning while fueled by a wide range of different hydrocarbons
- The solid electrolyte of SOFCs avoids the corrosion and liquid management challenges confronting PAFCs and MCFCs.

There has also been a drop of 1or 2 orders of magnitude in the gases based on nitrogen and sulfur that are accountable for acid rain and other health issues that are associated with a degenerative nature. In addition, the internal reforming of natural gas that takes place inside the fuel cell stack can help increase the efficiency of SOFC systems. It is easy to adjust SOFC systems to meet the load that is necessary thanks to modular construction, and if fuel is present, SOFC is able to continue operating in nearly any environment.

1.4.2 Operation of Solid Oxide Fuel Cells

A SOFC's (solid oxide fuel cell's) operational schematic is seen in figure 1.2. The structure of the cell is comprised of two electrodes that are porous, and in between them is an electrolyte. A current of air passes through the cathode (which is also known as "air electrode").

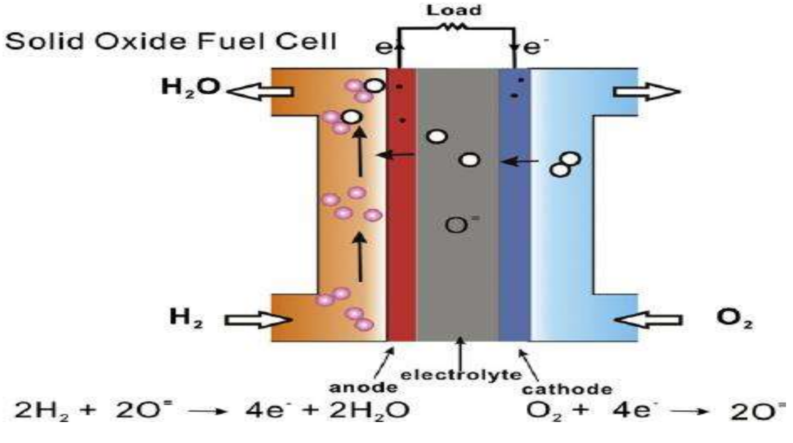

Figure1. 2: Operation principle of a SOFC (Ref: researchgate.net)

The following reactions takes place during the working of solid oxide fuel cells.

$$\text{Cathode:} \quad O_2 + 4e^- \rightarrow 2O^{2-} \qquad (1.1)$$

$$\text{Anode:} \quad H_2 + O^{2-} \rightarrow H_2O + 2e^- \qquad (1.2)$$

$$\text{Cell:} \quad 2H_2 + O_2 \rightarrow 2H_2O \qquad (1.3)$$

$$(2CO + O_2 \rightarrow 2CO_2) \qquad (1.4)$$

Depending on the gas pressures, the cell voltage is typically 1.1-1.2 V (open circuit) with hydrogen gas at the anode and pure oxygen at the cathode. However, with current densities ranging from 250 to 500 $mAcm^{-2}$, the cell voltage drops to 0.8 -0.6 V per cell under load circumstances. For large voltages, several cells are linked in series or parallel. Interconnect materials connect individual cells to produce stacks or modules. Different designs and sizes of stack are currently available, depending upon the required power output of the module or stack. Several SOFC designs are available including the tubular (as shown in Fig.1.3), monolithic and planar (shown in Fig.1.4) types. Of the three designs, the tubular design, also known as the Westinghouse design, has the lowest power density (150 - 200 kW/m^3) and requires expensive fabrication methods in its construction.

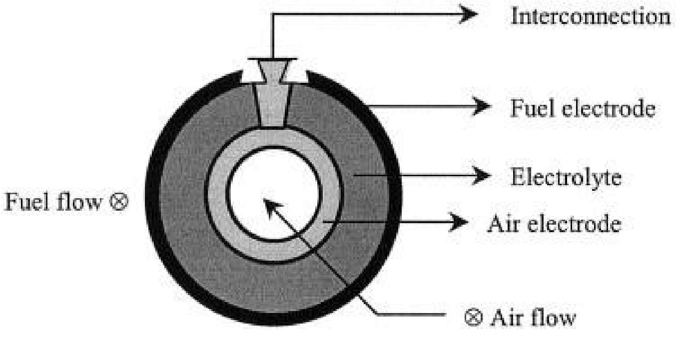

Figure1. 3: Typical tubular SOFC configuration (end view) (Ref: researchgate.net)

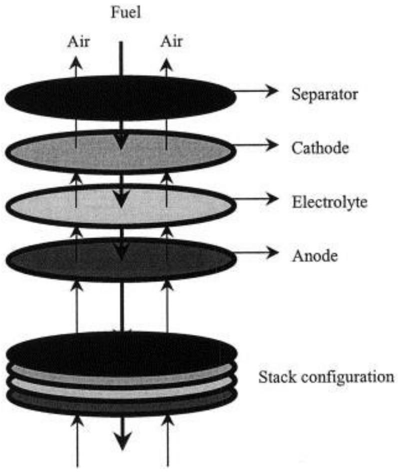

Figure1. 4: Configuration for a planar design SOFC (Ref: researchgate.net)

The monolithic SOFC offers the maximum power density (1.5 - 3 MW/m^3) depending on the gas flow configuration, but it also necessitates costly fabrication procedures. Planar SOFCs have the most cost-effective design, with potentially reduced manufacturing costs and a power density of roughly 1 MW/m^3, making them the favored cell design for many SOFC developers worldwide.

1.4.3 High and Intermediate Temperature Solid Oxide Fuel Cells

1.4.3.1 High Temperature Solid Oxide Fuel Cells (HT-SOFCs)

The high operating temperature of SOFC (which approaches 1000 °C) demonstrates its superior efficiency over conventional energy conversion devices. When this occurs, the energy contained in the high-temperature exhaust gases can be recovered using gas or steam turbines, increasing the SOFC system's overall efficiency to roughly 70%. 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)

1.4.3.2 Demerits of HT SOFC

Although the output is high, HT-SOFC suffers some serious demerits. The cost of materials is expensive, especially for connecting and construction materials. Interconnects are used to transport electrical current between distinct cells in the stack and to separate the fuel and oxidant supply. For HT-SOFC, a ceramic such as lanthanum chromite is used as interconnect, or a sophisticated refractory alloy based on mechanically alloyed Y/Cr if the temperature is confined to 1000 °C. In either scenario, interconnect accounts for a significant amount of the stack's cost. The materials used to build the stack, as well as the rest of the plant, must be refractory enough to retain and handle the high-temperature gas streams. As a result of the volatility of chromium-containing ceramics and alloys, stack components may become contaminated if they are utilized. This is especially important for future material and component demand from used stacks when the presence of a dangerous substance like Cr^{6+} would necessitate special disposal methods.

1.4.3.3 Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs)

Operation of the SOFC between the temperature 500-600 °C, termed as IT-SOFC can overcome some of the problems of HT-SOFCs. The new generation of electrolytes like Gd-doped ceria (CGO), Sr and Mg doped Lanthanum Gallate (LSGM) which possess much higher oxide ions conductivity at temperature below 600 °C w.r.t. YSZ electrolyte are considered as promising electrolytes.

1.4.3.4 Merits of Intermediate Temperature Solid Oxide Fuel Cells

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

- Because cost-effective metallic materials such as ferritic stainless steels or even metal-alloys can be employed as interconnect and building materials at temperatures below 600°C, they can be utilized as interconnect and construction materials. This reduces the cost and improves the reliability of the plant's stack and balancing.
- Lower temperature operating allows for faster start-up and shut-down procedures.
- The design and material requirements of the balance of plant are simplified when the operating temperature is reduced.
- Low operating temperature reduces considerably corrosion rates.

The modifications in cell and stack design, cell materials, design, and operation, as well as operating circumstances, that are necessary for operation at low temperatures.

1.5 Application Areas

The main areas of application for fuel cells include stable energy sources, space applications, and transportation. Homes, commercial buildings, industrial locations, ports, and military stations would all use stationary energy sources as their major power supply. They're ideal for small-power-grid applications at colleges and military locations, for example. The possibility of stationary SOFC power generation is no longer a pipe dream. Siemens Westinghouse was able to conduct thorough evaluations of many models' tubular systems.

SOFCs are employed in trucks and automobiles in the transportation sector. Auxiliary power units will most likely be used in diesel trucks to power electrical systems such as air conditioning and on-board electronics. Such units eliminate the need for diesel trucks to be left running during halt stops, saving money on diesel fuel and significantly reducing diesel pollution and truck noise.

Figure1.5: Application of SOFC (Ref: lyte.energy)

1.6 Different Components of SOFCs

1.6.1 Electrodes (Cathode and Anode)

Anode and cathode are the principal two electrodes that are used in cells, and they are used to sandwich electrolyte between them. Cathode reactions take place in oxygen-rich environments, leading to the dissociation of oxygen molecules into oxygen ions when they approach the electrode/electrolyte contact. According to Park et al. [5], some designs, such as tubular, have the cathode contributing more than 90 percent of the cell's total weight. As a result, the cathode acts as a structural support for the cell. When the temperature is high, the presence of a strong oxidizing environment makes it difficult to select metals with a lower cost. Any decrease in the temperature at which operations are carried out results in a decrease in operating expenses, as well as an expansion of the materials choices, which creates a potential for additional cost savings. The difficulty lies in properly sintering the cathode, which is often accomplished by co-sintering with the other components while preserving an acceptable amount of linked porosity.

In order to make equivalent performance of anode and cathode, anode must be able to function in a low-pressure environment and have porosity, electrical conductivity and compatibility with thermal expansion. The presence of a reducing environment, in conjunction with the criteria for electrical conductivity, makes the system an interesting candidate material. Addition of pore formers like starch, carbon, or thermosetting resins is done so that the porosity of the material can be preserved. During the firing process, they burn away, leaving pores in their wake. Nickel has been the primary focus of development due to the relative ease and availability with which it can be obtained. The following characteristics must be present in the SOFC electrodes for them to function properly [6]:

- High electronic and less ionic conductivity
- Optimized porous structure for mass transfer of gas species
- Suitable with every cell component in terms of thermal expansion
- Chemically inert
- Resilience against 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 (≤ 0.2 ohm/cm^2)
- Moderate materials and fabrication cost

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

Eminent cathode materials: Doped lanthanum cobaltite & manganite (LSC & LSM), (LSM-YSZ) composite, Lanthanum-Barium cobaltite (LBC), $Pr_{0.6}Sr_{0.4}MnO_{3\pm\delta}$ (PSM) etc.

Eminent anode materials: Porous Ni, NiO/YSZ, NiO/SDC, La doped Strontium titanate (LST), Ni-Cu-YSZ, $Ba_{0.5}La_{0.5}Ti_{0.3}Mn_{0.7}O_3$, etc.

1.6.2 Electrolyte

The oxygen molecule has been transformed into oxygen ions in the cell, which must travel to the fuel side via the electrolyte. It's an important part of SOFCs. For the migration of oxygen ions, electrolyte must be satisfied:

- Electrolyte should be temperature independent
- The electrolyte should have a strong ionic conductivity but no electrical conductivity.
- Fully dense to prevent a short circuit of reacting gases within it.
- It must be thin also to minimize resistive loss in the SOFC.
- Electrolyte must be chemically, thermally, and structurally stable over a broad temperature range with respect to the other materials.

Eminent electrolyte materials: Yttria stabilized zirconia (YSZ), Gd/Sm doped ceria (GDC/SDC), 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.

1.6.3 Interconnect

Similarly, to how a gasoline-powered internal combustion engine requires multiple cylinders to generate enough power, fuel cells must be used in conjunction to provide sufficient voltage and current. As a result, interconnects are needed to connect the cells and provide a way to collect the electrical current generated by the cells. The connector serves as the cathode's electrical connection while shielding it from the anode's reducing environment. Because of the high working temperature of the cells, as well as the harsh surroundings, interconnects must meet the most stringent standards of all cell components:

- Hundred percent electronic conductivity and zero porosity (to avoid mixing of fuel and oxygen).
- It must be compatible with other fuel cell components in terms of thermal expansion and inertness.
- It will be subjected to both the anode's reducing and the cathode's oxidizing environments at the same time.
- 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 (Solid Oxide Fuel Cell) which works at about 1000 °C, $LaCrO_3$ doped with an alkaline earth element (Sa, Mg, Ca, etc.) is used as interconnect to enhance its conductivity. Ca-doped yttrium chromite has taken too because it has good thermal expansion compatibility, particularly in reduced atmospheres [7]. Recently, "Ferritic stainless steel (FSS)" with the doping of Nb and Ti elements has been tested at 800 °C in air for 70 cycles.

1.7 Materials Selection for SOFCs

It is challenging to choose materials for SOFCs, stubborn and well established [8]–[10]. There must be no electronic conductivity in the electrolyte; it must be dense and rigid during cell operation. The electrodes (anode and cathode) must be porous, gas-permeable, and have more electronic conductivity and charge transfer kinetics. Chemically, mechanically, and architecturally, the anode and cathode materials must be compatible with the electrolytes and connection materials in their respective gas environments. As an electronic conductor, the interconnect (bi-polar separator plate) material which links the cathodes of two cells must be dense and impermeable while also being stable under reducing as well as oxidizing conditions. In addition to this, it needs to be compatible with the anodes and cathodes it connects on a chemical, mechanical, and structural level. The high working temperature range of these SOFCs, which ranges from 900 to 1100 °C, is another significant challenge that hinders their functionality. This temperature increase shortens the lifetime of the cell and rise in the cost of the materials necessary to manufacture the fuel cell, as it necessitates the use of costlier high-temperature alloys to house the cell and costlier ceramics to connect the individual fuel cells. To reduce the operating temperature of the SOFC, novel electrode-electrolyte materials must be discovered. This will not only make it possible to use materials that are inexpensive, but it will also make it possible to minimize the cost of the construction thermal energy that is necessary to heat the cells, which will result in a cost savings.

1.7.1 Factors influencing ionic conduction of the electrolyte

The ionic conductivity of the electrolyte materials is more relevant. There are a lot of different parameters that might affect how electrolytes behave in terms of their ionic conductivity. There is tremendous effort for the improvement of ionic conductivity of the electrolyte. Composition, microstructure, and treatment are all linked in terms of how they affect the electrical properties of a material. A relation between these factors and electrical conductivity are shown in fig 1.6.

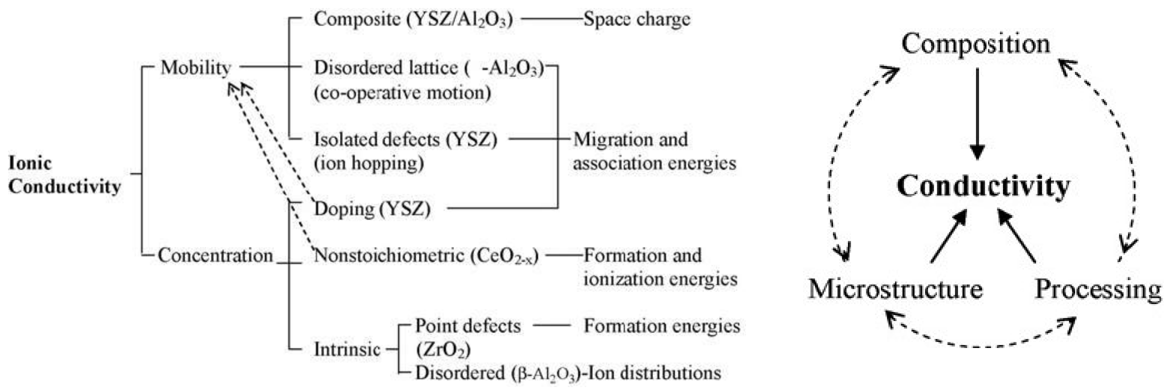

Figure1.6: (a) The main sources of ionic carriers in oxides, as well as their various mobilities, have been collated from the literature. (b) The relationship between polycrystalline materials' composition, microstructure, processing, and electrical conductivity at a particular temperature and in each environment. [11]

By choosing an aliovalent dopant and adjusting its concentration, the ionic conductivity of electrolytes can be made as high as possible[12]–[16].

The following factors can enhance the conductivity of electrolyte

- Doping and multiple doping can improve the ionic conductivity.
- When an additional phase is added to an electrolyte in order to generate a composite electrolyte, the grain boundary shifts, which in turn causes a change in the electrical conductivity of the electrolytes.
- Ionic conductivity is influenced by grain boundary properties such as impurity segregation and space charge.
- The final ionic conductivity is additionally influenced by processing factors such as density, impurity content, heating history, and microdomain development.

1.8 Present Scenario of electrolyte for Solid Oxide Fuel Cells

In between last 10 years from 2010-22*, there are nearly 2 Lakhs publication on electrolyte for SOFCs. Also, number of publications increases every year on electrolyte this indicates the work on solid electrolytes increased. In 2010 it was 17,619 which is very low in comparison to ~45,554 in 2021. The most popular electrolytes are YSZ, LSGM, ceria-based, Bismuth based and apatite-based electrolyte. Among all of these electrolyte's numbers of publication is high for Bismuth based electrolyte. Work on Apatite based is very less than bismuth based due to its demerit of low ionic conductivity. Publication on YSZ is relatively lower than CeO_2 and greater than that of $LaGaO_3$. YSZ has also a demerit to achieve high operating temperature whereas $LaGaO_3$ has problem of leakage current and expensiveness. In apatite there is no leakage current, also it is not expensive as compared to other electrolyte and its operating temperature is low. Number of publications in journal on Lanthanum Based apatite in 2021 is 30.

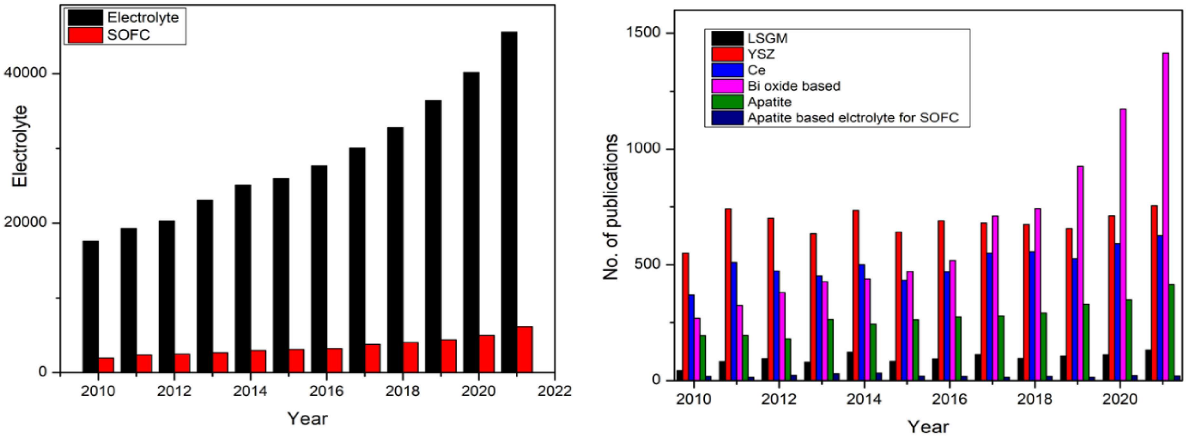

Figure1.7: Present Scenario of electrolyte: a comparative study

1.9 Apatite-type Materials

The fluorite or perovskite crystal structures, such as YSZ and substituted-CeO_2, the perovskite crystal structure, such as LSGM, are generally used as the electrolytes for SOFCs. But materials have various (usually non-cubic) structural types may be able to compete with more "traditional" materials in terms of electrical transport qualities (low electronic and high ionic conductivities), making them candidates for use as SOFC electrolytes. For comparison, few of these were shown in the below figure.

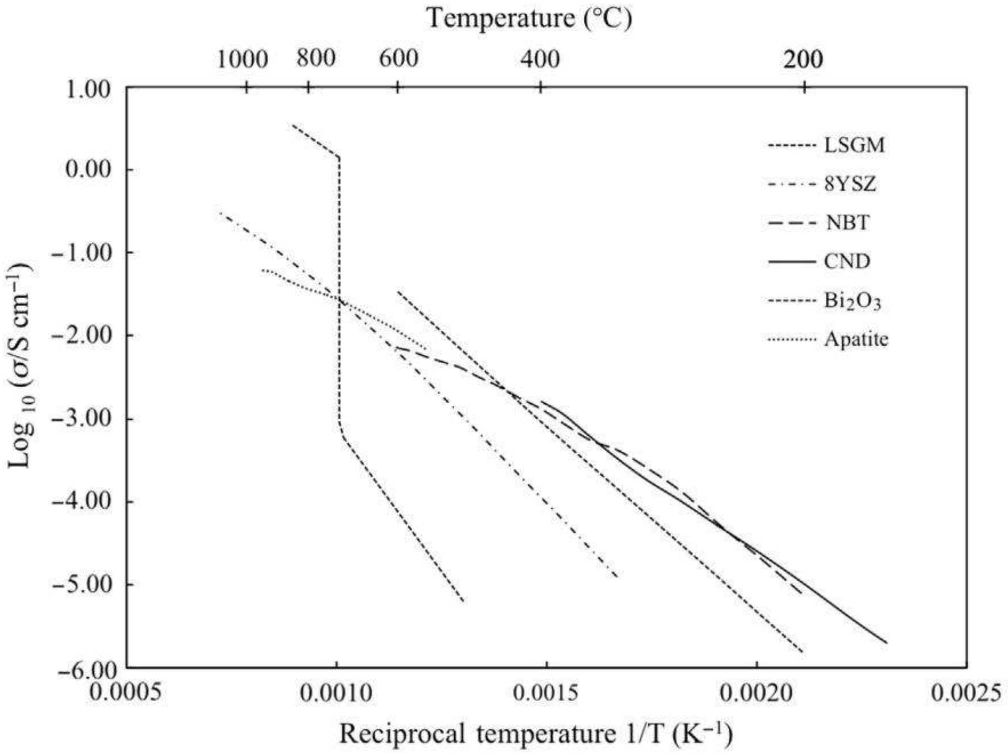

Figure 1.8: Conductivity of oxygen ion conductor including candidate SOFC electrolytes. $La_{0.8}Sr_{0.2}Ga_{0.9}Mg_{0.1}O_{3-\delta}(LSGM), Zr_{0.84}Y_{0.16}O_{1.92}(8YSZ), Na_{0.5}Bi_{0.49}Ti_{0.98}Mg_{0.02}O_3(NBT)$ $, Ce_{0.9}Nd_{0.1}O_{1.95}(CND), Bi_2O_3$ *and* $La_{10}Si_{5.8}Mg_{0.3}O_{26.8}(Apatite)$

These materials are appealing for two reasons. First, since the more traditional electrolytes have been investigated extensively, their performance may be near to optimal. A significant improvement in the level of attainable ionic conductivity may result from the identification of novel structures that exhibit oxide ion conductivity. The second factor is that, from a scientific standpoint, these materials frequently exhibit unique transport characteristics that are intriguing from a fundamental point of view (for example, anisotropic interstitial conduction in apatite silicates).

The layered Aurivillius-type $Bi_2Me_xV_{1-x}O_{5.5-\frac{3x}{2}-\delta}$ (“BIMEVOX”, where Me is a metal cation such as Cu, Ni, Co or Mg) Materials had sparked a lot of curiosity in the past. However, because to worries regarding Bi volatilization at intermediate temperatures and in recent years, there has been a decrease in their thermodynamic instability in the reducing atmospheres they are exposed to during SOFC operation.

With an emphasis on its usefulness in SOFCs, this section offers an overview of one of the more often studied apatite material families, specifically the lanthanum apatite silicates. For a more detailed examination of the materials chemistry underpinning these possible electrolytes, the reader is directed to recent reviews [17]. There has been a lot of interest in employing apatite-type oxides as SOFC electrolyte materials since the finding of high oxide ion conductivity for $(Nd/La)_{10}Si_6O_{27}$ in 1995. The possibility of using these oxides in solid oxide fuel cells has sparked interest in them. It has been brought to people's attention that these oxides exhibit high ion conductivities [18], which was followed by reports of similar very well oxide ion conductivity for germanium-containing counterparts [19]. To achieve the ideal stoichiometry for apatite oxide, the ideal composition is $A_{10}(MO_4)_6O_2$, where A = Rare earth or alkaline earth metals and M = Si, Ge, P, V, and their configuration is an $A_4(MO_4)_6$ framework (Fig. 1.9. (a)) with the residual A_6O_2 units filling the paths inside the frame - work (Fig. 1.9 (b))[20].

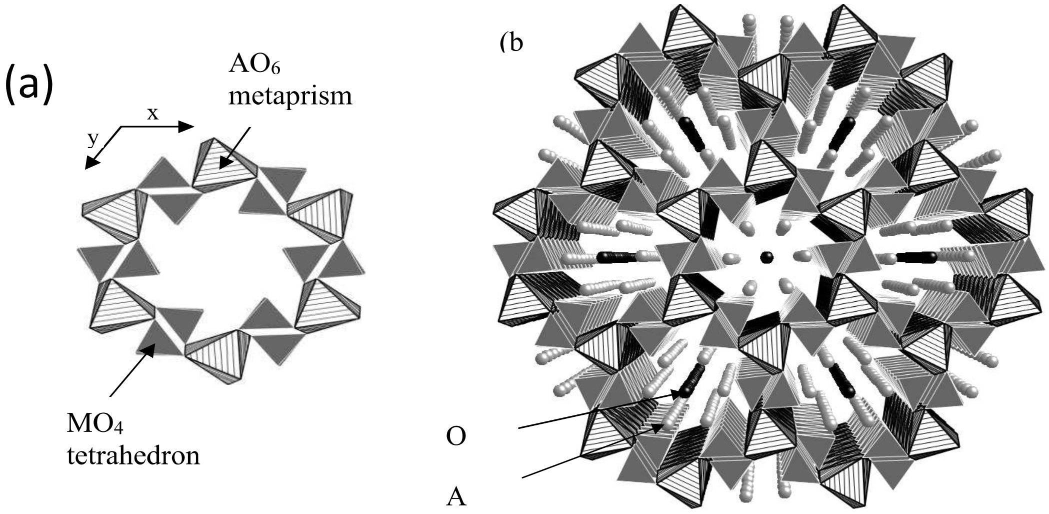

Figure 1.9:(a) $A_4(MO_4)_6$ frame-work (AO_6 trigonal metaprisms associated to MO_4 tetrahedra) (b) Entire construction, with the A_6O_2 units completing the framework's channels

1.9.1 Conductivity Optimization

Amid the many diverse rare-earth apatite systems that have been synthesized, the lanthanum silicates and germanates stand out and has the maximum conductivities[21]–[23]. Such apatite systems have the potential to support a large range of different dopant species. (e.g. B, Ga, Mg, Ca, Sr, and Ba) [24]–[27]. When compared to germanate apatite's, silicate apatite have a lower activation energy, which gives better conductivity at lower temperatures (Fig. 1.10). Silicates have generated a lot of interest as potential candidates for use as SOFC electrolytes due to the cost effective of the raw materials required to produce them.

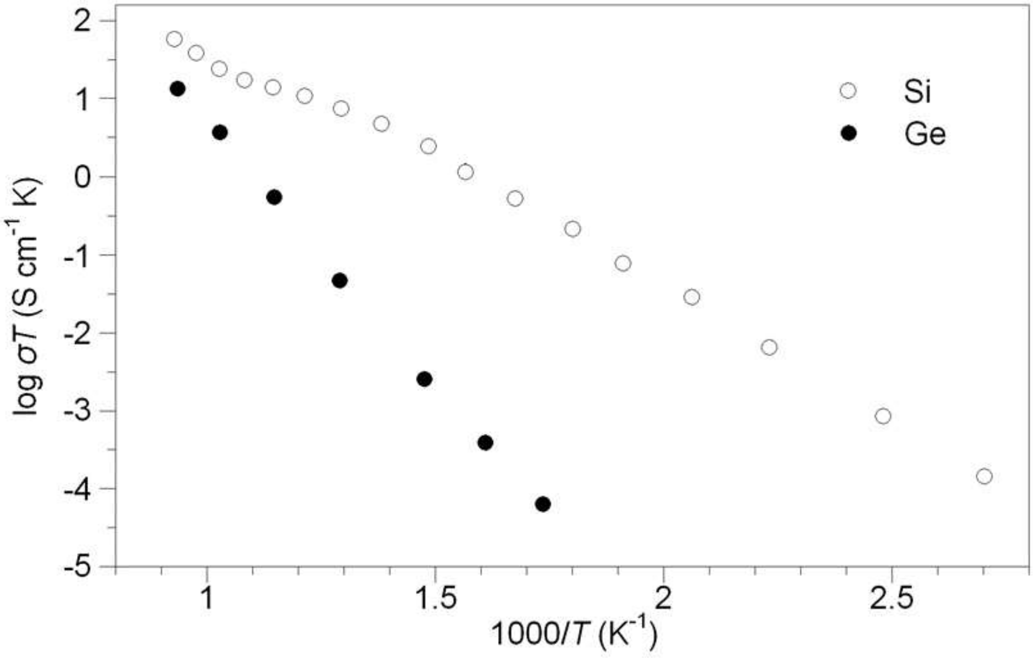

Figure 1.10: Samples of $La_{10}Si_5GaO_{26.5}$ and $La_{10}Ge_5GaO_{26.5}$ with bulk conductivity maps. Two phases have the same conductivity at higher temperatures; however, the later phase has a higher activation energy, which results in a significantly less conductivity at low temperatures. This difference in activation energy between the 2 apatite-type materials is demonstrated by the significant difference in conductivity at lower temperatures. The information is gathered using the approach outlined in [28]

A selection of conductivity data for silicates of the apatite type. $A_{9.33}Si_6O_{26}$ where A = La, Pr, Nd, Sm and Gd single crystals have shown the conductivities of the order of 10^{-2} mS/cm with the activation energy of 0.71 eV. Further, $A_{9.67}Si_6O_{26.5}$ have shown the conductivity of 1 mS/cm with the activation energy of 0.66 eV. Moreover, with the Ba and Sr substitution, conductivity is of the order of 0.1 mS/cm. However, with the c-axis orientation the conductivity has increased to 10 mS/cm in Sm based compounds with the activation energy of 0.45eV [29]–[33]. This shows that oxygen surplus samples have much higher conductivity than oxygen stoichiometric samples, with extremely low conductivity values for completely stoichiometric samples. These results can be seen by comparing the conductivity of oxygen stoichiometric samples to the conductivity of oxygen excess samples (i.e., both cation and oxygen stoichiometry). These results suggested that the conduction mechanism relies heavily on interstitial oxide ions. It is possible for these interstitial oxide ions to be accommodated in the structure by oxygen non-stoichiometry or Frenkel defect creation. Earlier study suggested that the presence of cation vacancies was assumed to favor this type of defect generation (investigations using neutron diffraction on cation-depleted materials demonstrated a considerable movement of some channel oxide ions in the opposite direction of the optimum location.[34].

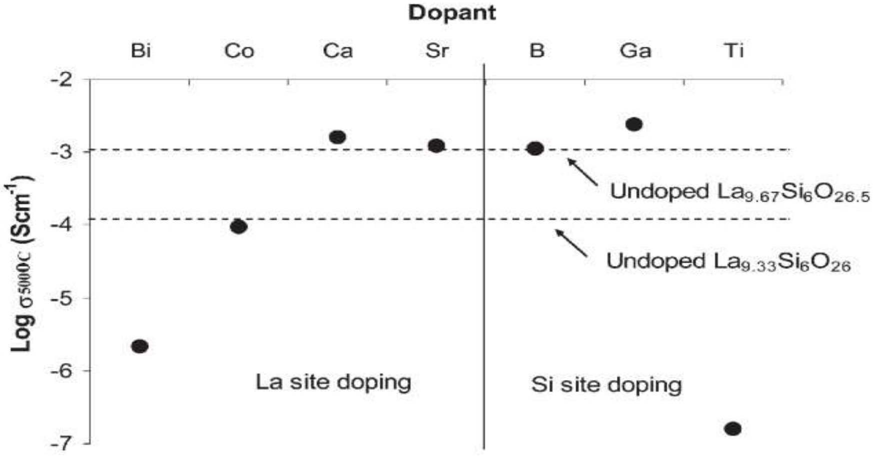

Figure 1.11: A study of the conductivity of oxygen stoichiometric samples with the equal amount of A cation shows that doping the samples with lower valent dopants has a favourable effect on the La site but a deleterious effect on the Si site. (Compositions:$La_{9.67}MSi_6MO_{26.5}$ $(M = Ga, B)$, $La_{9.67}Si_{5.5}Mg_{0.5}O_{26}$, $La_{8.67}MSi_6O_{26}$ $(M = Sr, Ba, Mg, Ca)$) [35].

In the study of the doping, in oxygen stoichiometric samples with cation vacancies, it was shown that doping studies with fewer valent dopants on both the La and Si sites resulted in a decrease in conductivity for the La site but an increase for the Si site. This was discovered as a result of the findings of the investigations. (Fig. 1.11) [35]; this study revealed that the conductivity decreased for La site doping but increased for Si site doping.[35]. In particular, very extensive modelling studies indicated that By substituting small lower-valent cations (like Mg) on the La site, the coordination environment of La changed from nine to six. This caused a change in the channel structure, which may interrupt the movement of interstitial oxide ions. On the other hand, having lower-valent ions on the Si sites led to local cooperative relaxation of the silicate structure, which made it easier for interstitial oxide ions to move[36].

Also, measurements of the conductivity of single crystals (above table) showed that the conductivity parallel to the c-axis is significant higher than the conductivity perpendicular to the c-axis. This demonstrates anisotropic conduction in these systems. The activation energies for both conduction orientations were shockingly close to being the same, which is a discovery that has not yet been completely explained by researchers.

1.9.2 Conduction mechanism in Apatite germinate:

In contrast to apatite-type silicates, which will be discussed in the following section, there is widespread consensus among researchers about the location of the interstitial site and the conduction mechanism in apatite-type germinates [29]–[38]. Based on a possibilities of atomic modelling and neutron diffraction studies for high oxygen excess compounds, $La_8Y_2Ge_6O_{27}$ and $La_{10}Ge_6O_{27}$, the placement of interstitial oxide ions has been found as being connected with the GeO_4 tetrahedra leading to 5 coordinated Ge [39], [40]. The conduction mechanism was hypothesized with the following major points[41] based on computer modelling studies:

i. The interstitial oxide ions supplied by the channel oxide ion, which acts as a "reservoir."

ii. The interstitial oxide ion combines with an adjacent GeO_4 unit to generate a GeO_5

unit.

iii. As a result of the rotation of the GeO_5 unit, a GeO_4 unit that is nearby will transform into a Ge_2O_9 unit.

iv. It is broken down into GeO_5 and GeO_4 units after disassembling the Ge_2O_9 unit, and as a direct consequence of this, the interstitial oxide ion is transferred into the place immediately adjacent to it, producing a "fan-like" trajectory.

It is also possible to conduct perpendicular to the c-axis thanks to the interaction with the GeO_4 tetrahedra, and modeling, according to research, Ion conduction in oxides is better isotropic than in apatite silicates. However, you will need to conduct measurements on single crystals in order to verify this. Modeling studies reveal that channel oxide ion migration through a vacancy mechanism (E_a = 1.05 eV) also plays a role, in addition to the interstitial process that was explained before. However, because there aren't enough channel vacancies in compositions with too much oxygen and a lot of interstitial oxide ions, cooperative conduction through GeO_4 tetrahedra (activation energy (E_a) = 0.79 eV) is thought to be more essential [41].

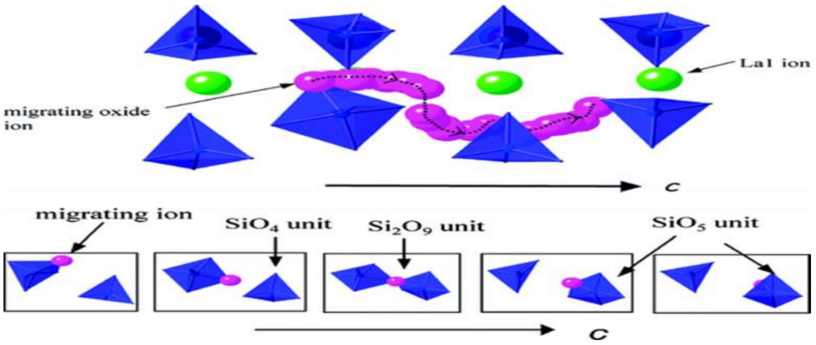

Figure 1.12:(a) The atomistic simulation investigations revealed an interstitial oxide-ion migration pathway through the channel in $La_{9.67}Si_6O_{26.5}$, as well as a probable mechanism for such a sinusoidal pattern. (b) View from a wider angle that shows how Si polyhedra relax and turn.[42]

In contrast to apatite-type germanates, apatite-type silicates have been the subject of a plethora of hypotheses on the conduction pathway of the interstitial oxide ion; however, there is not yet a consensus regarding this topic among all researchers.

The location of the interstitial oxide ion is at the channel perimeter, according to Kendrick et al., and co-operative movements of such silicate substructure facilitate the migration of the interstitial oxide ion., resulting in a complicated sinusoidal pattern down the c-axis. (Fig.1.13 a)[43] by using a mixture of powder diffraction techniques, (^{29}Si NMR), and computational modeling of $La_{9.33}Si_6O_{26.5}$. Additionally, it was hypothesized that the conduction that runs perpendicular to the c-axis, known as inter-channel conduction, may be explained by a chain of two cooperative 'SN2' ("bimolecular nucleophilic substitution") type methodology that involve concomitant rotation of the tetrahedra.

In other research, Masubuchi and his colleagues [44] suggested the channel oxide ion migration along the c-axis. They did this by looking at structural studies that compared oxygen stoichiometric samples with and without cation vacancies. These studies were based on the comparison of oxygen stoichiometric samples with and without vacancies for cations. In view of the growing anisotropic displacement of channel oxide ions all along c-axis in a sample with cation vacancies, they hypothesized that channel oxide ions migrate cooperatively. They hypothesized that a tiny silicate rotation caused by a cation vacancy facilitates channel oxygen cooperative migration [44].

Ali et al. advised that channel oxide ion conduction along the c-axis happening by a vacancy mechanism and a non-linear migration pathway, via route: "a silicate oxide ion near the channel − interstitial oxide ion − channel oxide ion − interstitial oxide ion − silicate oxide ion pathway". However, the people indicated that this non-linear migration was discontinuous through entire unit cells [44] .

Béchade et al. postulated a non-linear cooperative migration of the interstitial oxide ion more recently [45], with their findings pointing to an interstitial oxide ion position towards the channel centre. A local structural relaxation must be made possible for the interstitial oxide ion to drive the neighbouring channel oxide ion to the next interstitial site and take its place. In order for this to happen, a local structural relaxation is required (Fig. 1.13b). The oxide ion that was displaced from the channel centre and is now located at an interstitial site pushes the following channel oxide ion to an interstitial position to create a defect complex. This complex can be represented using the Kroger-Vink notation, $2O_o \rightarrow V_o^{\bullet\bullet} + (2O_i'' + V_o^{\bullet\bullet})$ The 'push-pull' process of migration of oxide ion along the c-axis is mediated by this defect complex $(2O_i'' + V_o^{\bullet\bullet})$. [45].

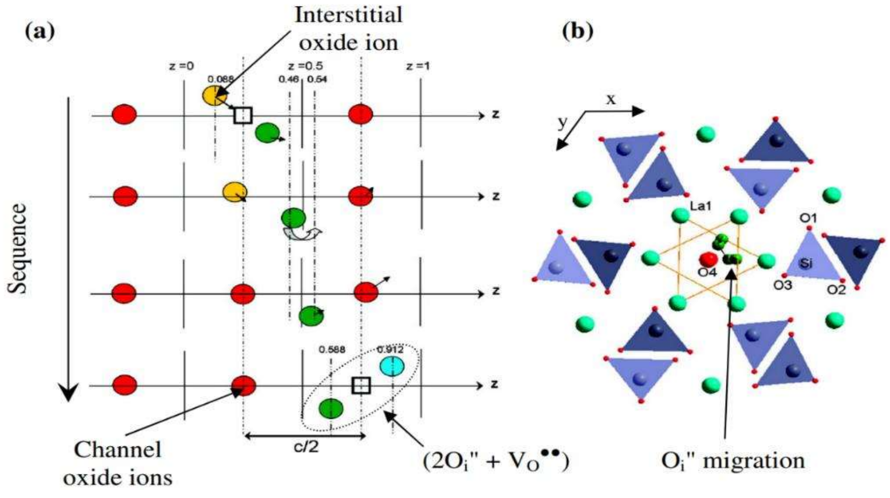

Figure 1.13: (a) Diagrammatic sequence depicting the production and migration of the $(2O_i'' + V_o^{\bullet\bullet})$ defect complex, which is accomplished by a "push-pull" process down the c-axis and in the direction of the electron cloud. (b)Non-linear Oi'' migration on the ab plane as a result (top view). [45].

Different ideas have been put forward about how the oxide ions move through these apatite silicates, but they all point to the interstitial oxide ion and where it is in the structure as being important. In contrast to apatite-type germanates, where the location of the interstitial site and the conduction mechanism are universally agreed upon, there is still disagreement over the place of the interstitial site as indicated above: the difficulties in precisely pinpointing this interstitial position can be attributed to the low interstitial site occupancy (upper bound close to 0.5 O per formula unit) [41] and the considerable displacement displayed by both interstitial sites.

1.9.3 AO_6 Metaprism Twist Angle in Apatite-type Materials

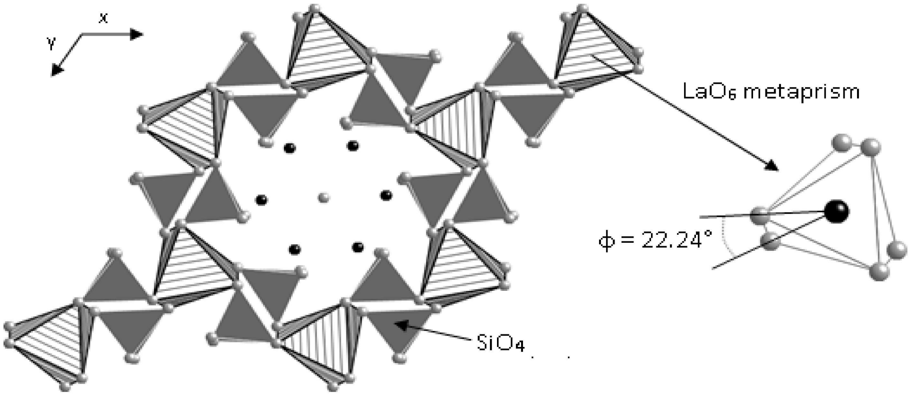

Figure 1.14: The LaO_6 metaprism twist angle is 22.24° in this polyhedral model of $La_{9.67}Si_6O_{26.5}$.

The metaprism twist angle (φ), in addition to the bond lengths and angles determined from the atomic locations received from the data of powder diffraction, can provide additional structural knowledge for apatite-type materials. As was mentioned previously, Apatite structure can be conceptualized as consisting of an $A_4(MO_4)_6$ framework (an AO_6 metaprism connected to MO_4 tetrahedra), with the residual A_6O_2 units (or A_6X_2 for halide-containing apatites) filling the channels inside the framework. Crystallochemical variation appears to have a significant impact on the twist angles of the

AO_6 metaprism, according to the findings of structural research conducted by White et al. on a diverse collection of apatite-type materials. (i.e. substitution/insertion on A, M and X sites) [46]:

- Because bigger cations are more likely to be accommodated at the channel A site first, the twist angle change follows a parabolic pattern as a function of doping concentration in systems that have been substituted with larger divalent A cation
- When it comes to systems that have halides as a replacement, the twist angle will decrease when the formula unit's average ionic radius increases (unless there is a substantial degree of divergence from P63/m symmetry or cation ordering)[46].

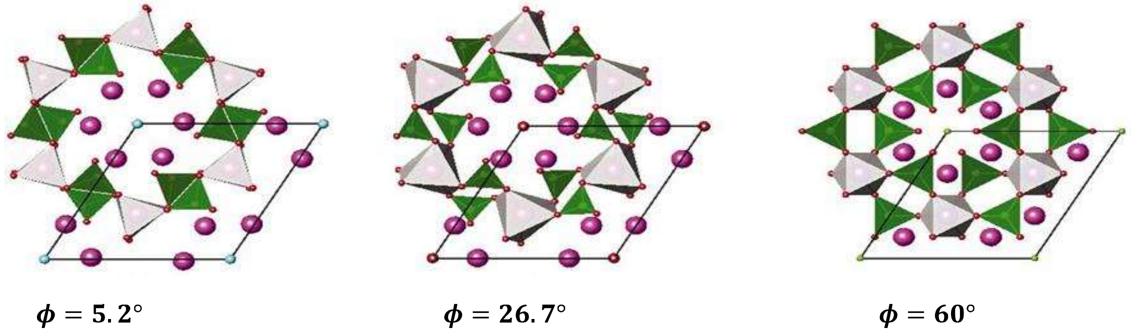

Figure 1.15: Examples of apatites have different metaprism twist angle ϕ.

As shown in Figure 1.15, the channel size is proportional to the "metaprism twist angle(φ): Small twist angles offer more area in the channel, but large twist angles move the oxide ions from the tetrahedra closer to the channel centre, reducing the available free space[47]. Furthermore, as per theoretical conduction mechanisms in apatite type germanates/silicates, the migration of interstitial oxide ions along the c direction is necessary, may be aided by dynamic changes in the metaprism twist angle.

$Ca_4Pb_6(AsO_4)Cl_2, Pd_{10}(PO_4)_6(OH)_2, and$ a model structure having twist angle φ equal to 60° are three examples of apatites that have different metaprism twist angles. These examples (form left) show that the channel space decreases as the metaprism twist angle increases.[47]

1.10 Objective of Present Investigation

The apatite based FOICs (discovered by Nakayama in 1995) showed high ionic conductivity like perovskite based FOICs in low temperature regime (LTR) [48]–[54]. Among these FOICs, due to its anisotropic ion conduction ($\sigma_c^{\parallel}/\sigma_c^{\perp} > 10$), lanthanum silicate oxyapatite i.e., $La_{10-\alpha}^{3+}(SiO_4)_6^{4-}O_{2+\delta}^{2-}$ (LSO) is most interesting and attracted the researcher [48]–[56]. Various experiments and theoretical studies predict that O_{int} (interstitial Oxygen) promotes cooperative movements between the O4 ion and excess oxygen is introduced as interstitial charge carriers to maintain electrical neutrality with La ions. There are 4 channels proposed for the conduction. Channels no. 1 and 2 are formed by the oxygen vacancies in between La(4f)-O4, channel no. 3 is nearest to the Si vacancy site and channel no. 4 is linked to the formation of oxygen Frenkel defects. Thus, there is scope of conductivity enhancement in polycrystalline LSO. In polycrystalline sample, grain alignment and doping are the two common methods to get the desired properties in the sample, the same has been employed by various research groups in the last few years. Grain alignment and c-axis alignment is done by various methods such as sol-gel and arc melting, respectively. Various doping such as Al, Mg at B-site and Alkaline earth and Rare earth substitutions at A-site have been done in order to get conductivities in the range of 1 S/cm but unfortunately, conductivity is achieved in the range of 10-50 mS/cm. Though the two kind of conduction mechanism, namely, pushpull and interstitial are well described for the oxyapatite but its dynamics is still scarce at large. Thus, in the present thesis, we are investigating the alteration in the structural and dynamics disorder with Ca-substitution in the LSO.

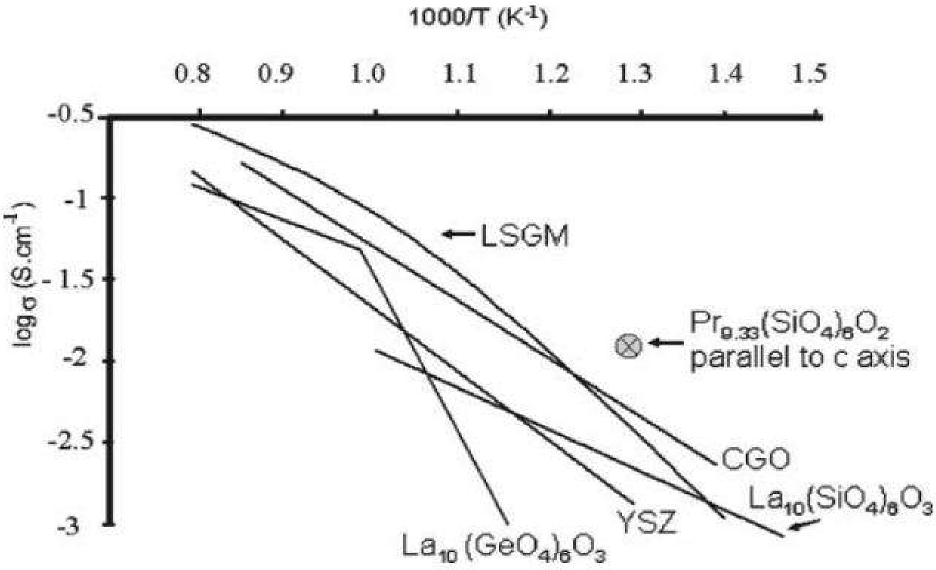

Figure 1.16: Comparison of conductivity data for selected oxide-ion conductors [37-43].

The primary goal of this research is to investigate Lanthanum silicate-based electrolyte materials for SOFCs in order to improve conductivity. It is proposed:

(i) To synthesize $La_{9.67}Si_6O_{26.5}$, $La_{9.67-x}Sr_xSi_6O_{26.5}$ (x=0.05, 0.10 and 0.15), $La_{9.67-x}Ca_xSi_6O_{26.5}$ (x=0.05, 0.1 and 0.15), and $La_{9.67-x}Ba_xSi_6O_{26.5}$ (x=0.05, 0.1 and 0.15) by Solid state route.

(ii) To investigate the material's powder using DTA(differential-thermal analysis) and TGA (thermo-gravimetric analysis).

(iii) To study the crystal structure of single-phase compositions using powder X-ray diffraction technique.

(iv) To study the microstructure employing scanning electron microscope (SEM).

(v) To study temperature dependence of conductivity employing impedance analyzer.

(vi) To correlate the structure with the conduction behavior.