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Chapter I

Introduction

1.1. General Introduction

During the 20th century, energy consumption increased dramatically and an unbalanced energy management exists. As the main resources of world’s energy supply, the current hydrocarbon fuels such as oil, coal and natural gas has been created two major problems along with the utilization. The first problem is that the resources are limited and the second is that they have been accused of causing global warming due to the NOx, SOx and COx gas emissions [1]. Energy consumption/production is created by using the combustion of fossil fuels, which is having severe impact on world economics and ecology [1-3]. It increased the interest to develop an alternative energy source, which should be cost effective, more sustainable and environmental friendly. Electrochemical energy sources including batteries, fuel cells, and supercapacitors are the most suitable energy storage and conversion devices [3]. Of the above, Fuel cells, particularly solid oxide fuel cell (sofc) provide more advantages than the traditional energy conversion devices, due to their high efficiency, fuel adaptability, reliability, modularity and low levels of NOx and SOx emissions [3,4].

In the last 10 years, the exponential rapid growth for the development in solid oxide fuel cells (SOFCs) has been made to construct and operate SOFC stacks and to confirm their technological feasibility as an energy converter [5, 6]. Now days, the SOFC have been focused for several applications such as stationary power generation, residential use and transportation [7-9]. The required properties of the materials like thermal & chemical stability, suitable electrical conducting properties, minimal
reactivity in different cell components, etc. are included for the development of the SOFC [1]. Hence, the current designs of the higher operation temperature SOFC required the use of expensive materials and it leads the problems with the seals and interconnects. The development of intermediate temperature SOFCs could extend the cell life times, it make possible to use the inexpensive metal components as interconnects and reduce the fabrication cost. For the intermediate temperature solid oxide fuel cell applications, the oxygen ion conductors as solid electrolytes should have higher conductivity at intermediate temperature. Hence, in the present work, oxygen ion conductors as solid electrolyte have developed for solid oxide fuel cell applications.

Generally, solid electrolytes should satisfy numerous requirements, including fast ionic transport, negligible electronic conduction, thermodynamic stability over a wide range of temperature, oxygen partial pressure, etc. In addition, they must have thermal expansion compatibility with that of electrodes and other construction materials, negligible volatilization of components, suitable mechanical properties and negligible interaction with electrode materials during the operation. The nanocrystalline metal oxide compounds have the small grain size, which lead to the increase of ionic conductivity and also the stabilization of high-temperature crystal structure.

Present chapter starts with the introduction and classification of fuel cell and also provides a brief description on the materials aspects of solid oxide fuel cell with special emphasize towards the oxygen ion conductors. Finally, the aims of the present investigation are presented.
1.2. Fuel cell

A fuel cell is the energy conversion device that generates the electrical energy by conversion of chemical energy via redox reactions at the anode and cathode, instead of a combustion process. Fuel cells are the promising alternative to traditional power generation with high efficiency and low environmental impact [2, 10 -12].

The first fuel cell was invented in 1839 by Sir William Robert Grove, known as “Father of the Fuel Cell” [13]. He found that by arranging two platinum electrodes with one end of each immersed in sulfuric acid solution and the other ends separately sealed in containers of oxygen and hydrogen, a constant current would flow between the electrodes. This "gas battery" is the basis of a simple fuel cell. The term “fuel cell” was then coined in 1889 by Ludwig Mond and Charles Langer, who attempted to build the first practical fuel cell and attained 6 amps per square foot at 0.73 volts [14]. In 1959, Francis Thomas Bacon demonstrated an alkali cell stack, the first practical 6 kW hydrogen-air fuel cell to power a welding machine, and this fuel cell was licensed to provide electrical power for the Apollo project [15]. From 1980s, several types of fuel cells were developed with main focus on transportation sector as well as portable power applications.

The difference between batteries and fuel cells is related to the locations of energy storage and conversion [3]. Batteries are closed system, in which the charge transfers occur between the anode and cathode. The energy storage and conversion occur in the same compartment. Fuel cells are open systems, where the anode and cathode are just charge-transfer media and the active masses undergoing the redox reaction are delivered from outside the cell, either from the environment (example:- oxygen from air) or from a tank (example:- fuels such as hydrogen and
hydrocarbons). Energy storage (in the tank) and energy conversion (in the fuel cell) are thus locally separated. The battery contains the fuel to make electricity and can only replenish by recharging whereas; a fuel cell is a device that converts incoming fuel directly into electricity.

The successful practical applications of fuel cells were for the space program in 1960s to the supply of electricity and drinking water for astronaut. The prospects for exploiting fossil fuels with higher efficiency made by fuel cell are more promising than other alternatives. The fuel cells are mainly applied on mobile or stationary applications, in which, the mobile applications primarily include transportation systems and portable electronic equipment, while stationary applications primarily include combined heat and power systems for both residential and commercial needs. On transportation application, all the world leading car manufacturers have designed at least one prototype vehicle using fuel cells. In addition, miniature fuel cells could replace batteries for electronic products such as cellular telephones, portable computers, video cameras, etc. The primary stationary application of fuel cell technology is for the combined generation of electricity and heat, for buildings, industrial facilities or stand-by generators [16]

1.3. **Fuel cell characteristics**

Fuel cell generates electricity through an electrochemical process without combusting any fuel, in which the energy stored in a fuel, is converted directly into dc [17]. So, they are extremely attractive from an environmental point of view. Some of the important fuel cell characteristics are
Efficiency - Fuel cells are generally more efficient than combustion engines as they are not limited by temperature as is the heat engine [18].

Simplicity - Fuel cells are essentially simple with few or no moving parts. High reliability may be attained with operational lifetimes exceeding 40,000 hours

Low emissions - Fuel cells running on direct hydrogen and air produce only water as the by product.

Silence - The operation of fuel cell systems are very quiet with only a few moving parts if any. This is in strong contrast with present combustion engines.

Flexibility - Modular installations can be used to match the load and increase reliability of the system.

1.4. Different types of fuel cells

There are five types of fuel cells, identified by their electrolyte, which have merged as viable systems. Fuel cells are classified due to their electrolyte and they are differs in the materials of construction, the fabrication techniques and the system requirements [1]. There are five types of fuel cells, named for their electrolyte which defines the key properties, particularly operating temperature, so each type of fuel cell requires appropriate materials and it is suitable for specific applications. These are Alkaline fuel cell (AFC), Phosphoric acid fuel cell (PAFC), Polymer electrolyte membrane fuel cell (PEMFC), Molten carbonate fuel cell (MCFC) and Solid oxide fuel cell (SOFC). Table 1.1 listed the important features of the four main types of fuel cells [19].
Table 1.1. Types of fuel cells and their features

<table>
<thead>
<tr>
<th>Features</th>
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<tbody>
<tr>
<td>Name</td>
<td>Polymer Electrolyte fuel cell</td>
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<tr>
<td>Electrolyte</td>
<td>Phosphoric acid fuel cell</td>
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<tr>
<td>Operating Temperature (°C)</td>
<td>Molten Carbonate fuel cell</td>
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<td>Charge Carrier</td>
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<td>Electrolyte State</td>
<td>Yttria-stabilized Zirconia</td>
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<td>Cell Hardware</td>
<td>Solid</td>
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<td>Catalyst, Anode</td>
<td>Immobilized liquid</td>
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<td>Feed For Fuel Cell</td>
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<td>Reforming</td>
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<td>Oxidant for cell</td>
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<td>Co-generation Heat</td>
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<td>Cell Efficiency (%)</td>
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<td>Electrical Power</td>
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1.5. **Solid oxide fuel cell**

Solid oxide fuel cell (SOFC) has been consider as one kind of green energy device in 21st century, because, it has high energy conversion efficiency than other fuel cells and ultra-low emission of air pollution [20,21]. Solid oxide fuel cells (SOFCs) have grown in recognition as a viable high-temperature fuel-cell technology [22-30]. The high-operating temperature (up to 1000 °C) in the SOFCs allows internal reforming, promotes rapid kinetics with nonprecious materials, and produces high quality by product heat for cogeneration. Due to the high temperature operation, high reaction rates are achieved without the need for expensive catalysts and also gases such as natural gas can be internally reformed without the need for fuel reforming. A number of different fuels can be used from pure hydrogen to methane and carbon monoxide. The major advantage of SOFC lies in its efficiencies, ranging from 55% to 60% [1]. The most striking quality of SOFCs is that the electrolyte is in solid state and is not a liquid electrolyte. Solids on use for all components of the SOFC can eliminate possibilities of materials evaporation and outflow, and there are neither corrosions of peripheral materials due to the electrolytic solution nor the performance declaration due to immersion of electrodes.

Solid oxide fuel cell (SOFC) is characterized by having a solid ceramic electrolyte (hence, the alternative name, ceramic fuel cell), which is usually a metallic oxide. The basic components of SOFC are, cathode, anode and electrolyte. The cathode and anode are electrodes, where half-cell reactions take place. Fig 1.1 shows the schematic diagram of the solid oxide fuel cell. At the cathode, where oxidant, normally oxygen in the air is supplied, oxygen is reduced to oxygen ions. Then the oxygen ions are transported through the solid electrolyte under electrical load, to the
anode, where they react with the hydrogen fuel to form water. Thus, the final products of SOFCs are electricity, heat and water.

![Schematic diagram of the solid oxide fuel cell.](image)

**Fig 1.1. Schematic diagram of the solid oxide fuel cell.**

The reactions of the solid oxide fuel cell system are:

Reaction at Cathode: \( \frac{1}{2} \, O_2 + 2 \, e^- \rightarrow O^{2-} \)

Reaction at Anode: \( H_2 + O^{2-} \rightarrow H_2O + 2e^- \)

Overall reactions: \( \frac{1}{2} \, O_2 + H_2 \rightarrow H_2O \)

**1.6. Advantages of solid oxide fuel cell**

Solid oxide fuel cell (SOFC) offers a clean, pollution free technology to electrochemically generate electricity at high efficiency. Solid oxide fuel cell presents
a number of advantages over other types of fuel cells and distributed powder generation systems. In particular advantages are given [31].

**Greater efficiency:** SOFCs operate at high temperatures which is enable their integration with other new energy technology such as micro-turbines or PEM fuel cells to create electricity generation products with over 60 percent efficiency cannot be obtained by any other technologies.

**Solid state devices:** All components of SOFCs are made from ceramic materials, which are unlike as corrosive liquid. These features allow for the development of electricity generation systems that are rugged, highly reliable and require low maintenance [32].

**Flexibility of fuels:** One of the main attractions of SOFCs is their ability to handle more convenient hydrocarbon fuels whereas, other types of fuel cells have to rely only on a clean supply of hydrogen for their operation. High operating temperature of SOFCs allow them to reform hydrocarbons within the system either in a reformer or directly on the anode side of the cell. High system efficiency could be achievable with various hydrocarbon fuels such as diesel, biogas, propane, butane, methanol and liquefied petroleum.

**Low noise and air emission:** SOFCs allow for superior flexibility in locations for social community because no emission of NO\textsubscript{x} and SO\textsubscript{x} gases.

**Broad product range capability:** It generates heat and power units in the capability ranges from small residential to large Industrial as well as automotive applications.

For SOFCs application, there has not yet been commercial for large scale power generation. But it uses in 100W-1kW for military applications. SOFCs are
constructed at the 1-10kW in order to provide power to residential building and auxiliary power units in vehicles [7, 8].

1.7. Materials for solid oxide fuel cell

A solid oxide fuel cell essentially consists of two porous electrodes separated by a dense, oxygen ion conducting electrolyte. The materials for the cell components in these different designs of SOFC are similar in nature. The materials for different cell components have been selected based on the following criteria [2, 10, 33].

a) Suitable electrical conducting properties are required for different cell components to perform their intended cell functions.

b) Adequate chemical and structural stability during the cell fabrication as well as during cell operation at high temperatures.

c) Minimal reactivity and interdiffusion among different cell components.

d) Matching thermal expansion among different cell components.

1.7.1. SOFC electrodes

At cathode, oxygen molecules reduce to oxygen ions in a strong oxidation atmosphere (1000 °C) with the following reduction reaction,

\[ \frac{1}{2} \text{O}_2 + 2e^- \rightarrow \text{O}_2^- \]

Example of cathode material: metal, metal oxides.

At anode, fuel oxidation reaction takes place[2, 10], i.e.

\[ \text{O}_2^- + \text{H}_2 \rightarrow \text{H}_2\text{O} + 2e^- \]

Example of anode material: nickel, cobalt, ruthenium, etc.

The fuel cell electrodes in the SOFC have the following properties [1, 33, 34].

a) High electronic conductivity.
b) Chemical and dimensional stability in environments encountered during cell operation and during fabrication of interconnection, electrolyte and fuel electrode layers.

c) Thermal expansion matches with other cell components.

d) Compatibility and minimum reactivity with the electrolyte and the interconnection with which air electrode comes into contact.

e) Sufficient porosity to facilitate transport of molecular oxygen from the gas phase to the air electrode/electrolyte interface.

1.7.2. SOFC Interconnects

The interconnect material is used to electrically connect the anodes and cathodes of stacked cells in series [1, 2, 10, 34]. The interconnect materials should have the following properties

- High electronic conductivity
- Low ionic conductivity
- Chemical and mechanical stability (including low volatility and non reactivity with adjoining cell components in both air and fuel gas)
- Mechanical compatibility (adherence and thermal expansion) with the electrodes and electrolyte
- Absence of mass transfer effects in the presence of chemical gradients that may lead to the formation of voids or high contact resistances
- No time dependent phase changes or re-crystallization between 25 °C and 1000 °C
- Low materials and fabrication costs.

Interconnect materials range from high cost ceramic materials to low cost stainless steel depending mainly on the SOFC operating temperature.
1.7.3. Electrolyte of SOFC

The most important property of electrolyte materials is the ionic conductivity, which must have sufficient oxygen ion conductivity. The current transfer in solid electrolyte involves the movement of oxygen (\(O^{2-}\)) ion vacancies. A criteria to select an electrolyte material is based on its ionic conductivity and it should be able to operate over a wide range of temperature 450 °C to 1000 °C.

Solid oxide electrolyte materials should have the following properties [1, 2, 10, 34]

- High oxygen ion conductivity
- Low electron conductivity
- Phase stability
- Mechanical strength
- Gas tightness
- Thermal shock resistance
- Chemically resistance to reaction gases (to oxidizing and reducing atmosphere)
- Compatibility with electrode and interconnect materials
- Moderate materials and less fabrication costs.

1.8. Challenges, limitation and remedy of SOFC

High temperature SOFC (HTSOFC), which operates in the temperature region of 850–1000 °C, has been successfully demonstrated by developers such as Siemens Westinghouse and Rolls-Royce. However, the high temperature presents not only material degradation problems, but also technological complications and economic obstacles. From standpoint of cost, expensive high temperature alloys are used to fabricate the SOFC and expensive ceramics are used for the interconnections, increasing the cost of the SOFC substantially. Alongwith material degradation in
SOFC, another critical issue is prohibitive for broad commercialization. Therefore, reducing the operation temperature of SOFC means, intermediate temperature (IT) range of 600–800 °C is a grand challenge in SOFC field. By lowering the temperature of operation, a wider range of materials can be used that allow cheaper fabrication. Intermediate temperature operation also affords more rapid start-up and shut-down, reduced corrosion rate of metallic components, improved durability, more robust construction through the use of compressive seals and metallic interconnects as well as the advantage of greatly simplified system requirements [16, 35 - 37].

1.9. **Oxygen ion conductors**

The conduction mechanism in the case of ceramic oxides is identified due to the motion of the oxygen ions. These materials are finding their use in high temperature thermodynamic measurements, sensors and fuel cells, since they show the significant values of conductivity only at high temperature as 1000°C and above. Several types of the ceramic oxides, which enhance more oxygen ion conductivity, are used as solid electrolytes in solid oxide fuel cell.

1.9.1. **Yttrium – stabilized zirconia (YSZ)**

Generally, stabilized zirconia – based materials offer the best possibility choice of high oxygen ion conductivity at operating temperature and sustain ionic conduction in both oxidizing and reducing atmospheres. YSZ has been extensively used as a conventional electrolyte in solid oxide fuel cell because, it possesses an adequate level of oxygen ion conductivity and also exhibits desirable stability as well as good mechanical properties [2, 10, 34, 38].

In the stabilized zirconia \((\text{ZrO}_2 - \text{M}_2\text{O}_3)\) systems, the substitution of \(\text{M}_2\text{O}_3\) in \(\text{ZrO}_2\) creates the oxygen ion vacancies, which exhibit the oxygen ion conduction. The
high oxygen vacancy concentration provides the high ion mobility. The conductivity in ZrO$_2$ –M$_2$O$_3$ system depends on the dopant concentration and dopant ionic radius. The most commonly used stabilizing oxides or dopants are CaO, MgO, Y$_2$O$_3$, Sc$_2$O$_3$ and certain rare earth based oxides [19, 34]. These oxides exhibit a relatively high solubility in ZrO$_2$ and were able to form the fluorite structure with ZrO$_2$, which is stable over wide range of composition and temperature [10, 19].

1.9.2. Ceria based oxides

Ceria based solid materials have regarded as one of the most promising solid electrolyte for intermediate temperature [34, 38]. Unlike zirconia, pure ceria has the cubic fluorite structure up to the melting point and so, it does not need any stabilization. The ionic conductivity of ceria has been extensively investigated with respect to different dopants and dopant concentration, which is better than stabilized zirconia. However, recently, ceria based materials are not considered for the electrolytes of solid oxide fuel cell due to its electronic conductivity, particularly at higher temperatures in a reducing atmospheres [33].

1.9.3. Pervoskite type oxides

Pervoskite (ABO$_3$) type oxides have been also investigated as solid electrolyte because they also possess adequate ionic conductivity at intermediate temperatures (650 – 800 °C). The pervoskite oxides are very interesting because, there are two cations, leading to a much wider range of possible oxygen ion conducting materials. Of the pervoskite investigated to date, only the lanthanum gallate (LaGaO$_3$) based materials have been found to be suitable for ionic application [39].
Several families of oxygen ion conductors are also being investigated for intermediate temperature solid oxide fuel cells (ITSOFCs), Fluorite type (stabilized $\delta$-Bi$_2$O$_3$) oxides, Apatite type ($\text{La}_{9.33}\text{Si}_6\text{O}_{26}$) oxides, Aurivillius type ($\text{BIMEVOX}$) oxides, Pyrochlore type ($\text{Gd}_2\text{Zr}_2\text{O}_7$) oxides, Scheelite type ($\text{PbWO}_4$) oxides, etc [40].

1.9.4. Apatite type oxides

Apatite type lanthanum silicate/germinates $\text{La}_{10-x}(\text{Si/Ge})_x\text{O}_{26+z}$ represent a new class of oxide ion conductors, attracting considerable interest as potential electrolytes for SOFC applications [41 - 54]. Nakayama et al. reported high oxide ion conductivity in rare earth silicates $\text{RE}_{9.33}(\text{SiO}_4)_6\text{O}_2$ ($\text{RE} = \text{rare earth metal ion}$) with an apatite structure [55]. The most attractive feature of the conductivity of the oxide ions in apatite type rare earth silicates at a relatively intermediate temperature (~600 °C) is much higher than that of conventional solid electrolyte (yttria stabilized zirconia) [56-58]. Another important feature is that $\text{RE}_{9.33}(\text{SiO}_4)_6\text{O}_2$ does not have an oxide ion vacancy, which is essential for conventional oxide ion conductors and it has also been reported that conduction in the rare silicates is purely ionic with constant electrical conductivity across a wide range of oxygen partial pressures [59-61]. The apatite structure $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ in $\text{P6}_3\text{m}$ space group has 10 available sites for cations among both 4f and 6h sites in a unit cell. The rare earth silicates have 6.7% vacancy in their rare earth cation, which is used to enhance the ionic conductivity in the compound [54, 56]. $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ has an oxide conductivity almost three orders of magnitude larger than that of $\text{La}_8\text{Sr}_2(\text{SiO}_4)_6\text{O}_2$ [62]. The main obvious difference between these two samples is the presence of cation (La) vacancies in the former. The precise mechanistic features of oxygen ion transport in $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ and $\text{La}_8\text{Sr}_2(\text{SiO}_4)_6\text{O}_2$ at the atomic level have been recently studied using computer modelling techniques.
The atomistic modelling studies proposed that the high ionic conductivity and low activation energy of La$_{9.33}$(SiO$_4$)$_6$O$_2$ is due to an interstitial oxygen mechanism, where oxygen migration takes place along the c-axis via a sinusoidal-like pathway. In a recent computer modelling study, two kinds of oxide ion migration paths were proposed for La$_{9.33}$(SiO$_4$)$_6$O$_2$: a direct linear path through the hexagonal channel split sites and a non-linear sinusoidal-like migration through a new interstitial oxide ion site. Generally, the initial works on these apatite-type oxide ion conductors were focused on the Si system with two stoichiometries, RE$_{9.33}$(SiO$_4$)$_6$O$_2$ and RE$_{10}$(SiO$_4$)$_6$O$_3$. Nakayama and Sakamoto et al., S. Tao et al., have shown that La$_{10}$Si$_6$O$_{27}$ gives higher ionic conductivity than La$_{9.33}$Si$_6$O$_{26}$ [63, 64]. The composition without extra oxide ions is La$_{9.33}$Si$_6$O$_{26}$, which contains 6.7% of cation vacancies. If the vacancies are filled with La ions, extra oxide ions should be introduced to interstitial sites in the La$_{10}$Si$_6$O$_{27}$. The extra ions existing near the conduction channel may increase the ionic conductivity in the La$_{10}$Si$_6$O$_{27}$ compounds. Although the lanthanum silicate materials have more conductivity at lower temperature operation, the enormous amounts of the effects were found to devote for synthesis various stoichiometric compounds, including cation doping in the La site, to improve conductivity in the lanthanum silicates. By doping of cations like Sr, Ca, etc., particularly at the La site of the lanthanum silicates, the defect process is formed due to the oxygen vacancy in the La site and also formation of the interstitial oxygen ions [65, 66]. Here, our aim is to develop the pure La$_{9.33}$Si$_6$O$_{26}$, La$_{10}$Si$_6$O$_{27}$ and Ba doped on the La site of La$_{10}$Si$_6$O$_{27}$ to improve the ionic conductivity for solid oxide fuel cell applications.
1.9.5. Scheelite type oxides

Scheelite type oxide materials exhibit high ionic conductivity, which is comparable with the conventional oxide ion conductors like yttria stabilized zirconia [67-73]. Takao Esaka et al. systematically investigated the composition dependence of electrical conductivity for scheelite type Lanthanum and Samarium doped PbWO$_4$ materials and observed high electrical conductivity $4.2 \times 10^{-2}$ Scm$^{-1}$ at 800 °C for Pb$_{0.8}$La$_{0.2}$WO$_{4.1}$ [74]. In the Pb$_{1-x}$La$_x$WO$_{4+\delta}$ ($\delta \approx x/2$) system, for example, the extra oxygen ions introduced by La doping seem to be rather localized around $z = 0.3$ of the 8e position (00$z$) of the scheelite structure with $I4_1/a$ symmetry. These positions are apparently not fully occupied and will act as possible paths for oxygen-ion migration. G. G. Zhang et al reported that the dc conductivity of the La doped PbWO$_4$ samples has a value of about the order of $10^{-3}$ Scm$^{-1}$ at ~1073K and they explained that the oxygen ion migration by short-distance diffusion of the oxygen ions (or vacancies) between the 8e sites and 16f sites in Pb$_{1-x}$La$_x$WO$_{4+\delta}$ ($\delta \approx x/2$) system [75]. V.Thangadurai et al. prepared ABO$_4$ (A= Ca, Sr, Ba; B= Mo,W) scheelite type materials and they have observed that the scheelite type PbWO$_4$ and SrWO$_4$ materials showed the high electrical conductivity between the temperatures 500 °C and 900 °C [76]. La$_2$O$_3$ is one of the rare earth oxides and it is highly insoluble and thermally stable, suitable for glass, optic and ceramic applications. Hence, our aim is to investigate the development of the scheelite type lanthanum doped Barium molybdenium oxide materials, which enhance the high oxygen ion conductivity for intermediate temperature solid oxide fuel cell applications.
1.10. Nanotechnology approach in solid electrolytes

The development of intermediate-temperature SOFC (ITSOFC) is now a world tendency for SOFC commercialization. However, with decreased operating temperature, the internal resistance of SOFC increases tremendously, which results in decrease on the performance of the cell. Therefore, it can be achieved either by reducing the thickness of the electrolyte or using alternative materials with higher conductivities. Recently, there is an increasing demand to develop fast oxide ion ($O^{2-}$) conducting materials to be applied as the electrolytes for intermediate-temperature solid oxide fuel cells (IT-SOFCs) [77, 78].

The conductivity of micro-sized polycrystalline oxide ion conductors has contributed from both grain-interior and grain-boundary [79, 80]. The specific grain-boundary resistivity is known to be two to three orders of magnitude higher than the grain-interior resistivity. Therefore, many efforts have been taken on engineering of grain-boundary to lower its resistance, thus, to improve the performance of polycrystalline electrolytes. However, ion transport across or along grain boundaries in solids with nanometersized grains may differ distinctly from that in conventional polycrystalline solids [81, 82]. Nanostructured materials are distinguished from current polycrystalline materials by formation of more space in the grain boundary, which results in enhanced conductivity compared with bulk materials. The enhancement of ionic conductivity in the nanostructured solid electrolytes, known as “nanoionics”, which has been rapidly recognized as an emerging new scientific area and widely applied on rechargeable lithium-ion batteries, gas sensors and solid oxide fuel cells (SOFCs) [83, 84]. Nanoionics, as a combination of nanotechnology and ionics, have pioneered a new direction in the solid state ionic research field [84]. The enhancement of ionic conductivity in nanoionics was explained by predominance of
grain-boundary conductivity, because of faster diffusion than bulk and larger volume fraction of grain boundary in nanostructured electrolytes. Some works have been done to study the enhanced oxide ion conductivity of nanostructured electrolyte for SOFCs. For example, Martin G. Bellino et.al observed the total ionic conductivity of nanostructured, heavily doped ceria solid electrolyte increases about one order of magnitude compared to microcrystalline materials [83, 84]. Conductivity enhancement has also been found in nanostructured YSZ materials; e.g. H. L. Tuller et.al prepared YSZ thin films with nanometric sized grains and enhanced oxygen ion conductivities were observed when compared to bulk YSZ [85, 86]. In addition, oxygen diffusivity in the grain boundaries of YSZ was found to be about 3 orders of magnitude higher than in single crystals [87].

Hence, Nanocrystalline electrolyte materials having small grains, which increase the grain boundary area and showed improved conductivity, since grain boundaries have more interstitials space to transport the oxygen ions and also stabilize the crystal structure at high-temperatures.

1.11. Present Work

The literature survey in the field of solid electrolyte materials inspired to develop the nanocrystalline pure and doped apatite type oxygen ion conducting materials. Hence, in present investigation, apatite based nanocrystalline La$_{0.33}$Si$_6$O$_{26}$, La$_{10}$Si$_6$O$_{27}$ and Ba doped La$_{10}$Si$_6$O$_{27}$ [La$_{1-x}$Ba$_x$Si$_6$O$_{27-2x/2}$, where $x = 0$ (La$_{10}$Si$_6$O$_{27}$/LBS0), 0.25 (LBS025), 0.50 (LBS050), 0.75 (LBS075), 0.100 (LBS100), 0.125 (LBS125), 0.150 (LBS150), 0.175 (LBS175) and 0.200 (LBS200)] are choosen to synthesize by sol-gel process. The synthesis of nanocrystalline lanthanum silicate materials are monitored by various techniques such as TG/DTA, FTIR, XRD, SEM-
EDX and XRF. The electrical conductivities of nanocrystalline lanthanum silicate materials are studied by analysing measured impedance data at different temperatures in terms of the grain interior and grain boundary conductivity using brick layer model.

From the literature review, it is also found that the nanocrystalline scheelite type oxygen ion conductors show better conductivity than the other types of ceramic oxide materials and also sol-gel combustion method is found to be more versatile in the preparation of different types of nanocrystalline metal oxide compounds. Hence, the present investigation is aimed for the preparation of nanocrystalline scheelite type different compositions of lanthanum doped BaMoO$_4$ [Ba$_{1-x}$La$_x$MoO$_{4+x/2}$ ($x = 0$ (BaMoO$_4$), 0.1 (BLM1), 0.2 (BLM2), 0.3 (BLM3), 0.4 (BLM4) and 0.5 (BLM5))] and Lanthanum doped SrMoO$_4$ [Sr$_{1-x}$La$_x$MoO$_{4+x/2}$ ($x = 0$ (SrMoO$_4$), 0.1 (SLM1), 0.2 (SLM2), 0.3 (SLM3), 0.4 (SLM4) and 0.5 (SLM5))] samples using acrylamide assisted sol-gel combustion process and their characterization using TG/DTA, XRD, FTIR, SEM – EDX and XRF techniques. The electrical conductivities of nanocrystalline lanthanum doped barium molybdate and lanthanum doped strontium molybdate materials are studied by analysing measured impedance data at different temperatures in terms of the grain interior and grain boundary conductivity using brick layer model.
References


