CHAPTER 1

INTRODUCTION

1.1 GENERAL INTRODUCTION TO FUEL CELLS

Fuel cells (FCs) are the electrochemical device for the direct conversion of chemical energy into electrical energy. The fundamental function of fuel cells depends mainly on two important parameters, they are fuel and oxidant. The fuel is supplied at anode side (e.g. hydrocarbon, ammonia, hydrogen), undergoes an oxidation reaction for releasing an electron to the external circuits. Oxygen or air is supplied at cathode side for the reduction mechanism to take place by accepting an electron from external circuit. The flow of an electron from anode to cathode side through external circuit is ultimately results in the production of electricity. The fuel cells have no combustion process involved in it. Hence, overall reaction inside fuel cell results in the generation of combined heat and power (CHP) (Mahato et al. 2015).

When compared to the available conversion technologies such as internal combustion engines, electrical generators and coal fired power plants, fuel cell is the most efficient electrical conversion device with high efficiency > 60% (Singhal 2000, Steel et al. 2001) and have less pollution for the better environmental impact. Fuel cell is considered as a clean energy source with less emission of CO₂, nitrogen oxides (NOₓ) and sulfur oxides (SOₓ) through
less combustion process. Hence, fuel cell is the unsurpassed energy conversion device with friendly environmental nature and also considered as future source for stationary power generation (Wachsman et al. 2012).

1.2 HISTORY OF FUEL CELLS AND IT’S BACKGROUND

In the history of fuel cell, the first cell was invented and experimentally studied by Sir William Robert Grove in 1839. Later he demonstrated the constant flow of current between the platinum electrodes immersed in sulfuric acid solution used as an electrolyte at one end and sealed at other end with a container of hydrogen and oxygen separately (Grove 1839). In 1889 Ludwig Mond and Charles Langer have coined the word FUEL CELL for the first time by generating the maximum current of 6 amp per square foot at 730 mV Mond et al. (1889). In 1890, Walther Nernt have demonstrated the generation of power from a solid ceramic material made of 85% of ZrO₂ and 15% of Y₂O₅. Yttrium stabilized zirconia (YSZ) act as an electrolyte material in fuel cell for the conversion of energy (Nernst 1899). In the progress of fuel cell development, Haber filed the first Patent in 1905. In the earlier of 19th century, the first successful application of fuel cell was made by providing power to space flight and drinking water to astronauts (O’hayre et al. 2006). Later in 1935, the development of state art YSZ is used as oxygen ion conducting electrolyte for energy conversion (Schottky 1935 & Baur & Preis 1937).

In 1943 Carl Wagner attributed that the electrical conductivity of doped ZrO₃ was mainly due to the presence of oxygen vacancies in such YSZ electrolyte (Wagner 1943). In 1959, Francis Thomas Bacon, constructed the first hydrogen – air fuel cell with the high power of 6 kW used for welding machine and got licensed for Apollo Project (Francis Thomas Bacon 2009). During 1980’s the development of fuel cell became narrow and focused
towards the transportation sectors of prototype vehicle for power generation. Nowadays, fuel cell finds its application in portable power electronic materials and also in auxiliary power units (APU). In addition to the generation of power through electrochemical process, fuel cell also produces heat, less carbon dioxide and water. The conversion of green energy through fuel cells becomes an alternate technology adopted by various companies and governmental organizations around the world. The conversion of energy using fuel cell will ultimately reduce the global warming. Hence fuel cell is the primary stationary source for conversion of energy required for industries and space application (Cropper 2004).

1.3 TYPES OF FUEL CELLS

Fuel cells are working on the principle of conversion of chemical energy directly into useful power, but they are differ only by means of fuel, materials used, charge carriers, operating temperature, performance and efficiency. The operating temperature and efficiency are the two essential parameters considered for resourceful energy conversion. However, solid electrolyte in fuel cell plays an important role in the conversion process. The operating temperature of fuel cells is determined by the physical property of solid electrolyte. So it became very crucial need to find a suitable or appropriate electrolyte for the conversion of energy effectively.

The electrolyte materials and the operating conditions of fuel cells with their applications are listed in Table 1.1. Based on the chemical characteristics and type of electrolyte used, fuel cells are classified into five types. They are Alkaline fuel cell (AFC)(McLean et al. 2002), Phosphoric acid fuel cell (PAFC) (Tanni et al. 2013), Polymer electrolyte membrane fuel cell (PEMFC) (Higier et al. 2016), Molten carbonate fuel cell (MCFC) (Barelli et al. 2016) and Solid oxide fuel cell (SOFC) (Yamamoto 2000).
Table 1.1  Various types of fuel cells, application and advantages

<table>
<thead>
<tr>
<th>Types of cells</th>
<th>Electrolyte</th>
<th>Operating Temperature</th>
<th>Charge Carrier</th>
<th>Anode</th>
<th>Cathode</th>
<th>Efficiency</th>
<th>Application</th>
<th>Advantages</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEMFC</td>
<td>Ion Exchange Membranes</td>
<td>50-100 °C</td>
<td>H⁺</td>
<td>Pt on carbon</td>
<td>Pt on carbon</td>
<td>50%</td>
<td>Portable, Mobile, Low power generation</td>
<td>High power density; quick start up; solid non-corrosive electrolyte</td>
<td>40</td>
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<tr>
<td>AFC</td>
<td>Mobilized or immobilized KOH</td>
<td>90-100 °C</td>
<td>OH⁻</td>
<td>Pt, transition metals</td>
<td>Pt, transition metals</td>
<td>50%</td>
<td>Mobile, space, military.</td>
<td>High power density; quick start up, low cost components</td>
<td>73</td>
</tr>
<tr>
<td>PAFC</td>
<td>Immobilized liquid H₃PO₄</td>
<td>150-200 °C</td>
<td>H⁺</td>
<td>Pt on carbon</td>
<td>Pt on carbon</td>
<td>40%</td>
<td>Medium to large scale power generation and CHP (Combined Heat and Power)</td>
<td>Heat waste; stable electrolyte characteristics</td>
<td>102</td>
</tr>
<tr>
<td>Types of cells</td>
<td>Electrolyte</td>
<td>Operating Temperature</td>
<td>Charge Carrier</td>
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<tr>
<td>MCFC</td>
<td>Immobilized liquid molten carbonate</td>
<td>600-700 °C</td>
<td>CO$_3$</td>
<td>Ni</td>
<td>NiO</td>
<td>45-50%</td>
<td>Large scale power generation</td>
<td>High efficiency; fuel and catalyst flexibility; heat waste</td>
<td>8</td>
</tr>
<tr>
<td>SOFC</td>
<td>Ceramic</td>
<td>600-1000 °C</td>
<td>O$^2-$</td>
<td>Ni/ceramics</td>
<td>perovskite</td>
<td>60%</td>
<td>Vehicle auxiliary power units, medium to large scale power generation and CHP, off-grid power and micro CHP.</td>
<td>Solid electrolyte; high efficiency; fuel and catalyst flexibility; generate high grade waste heat Very low levels of SO$_x$ and NO$_x$ emissions</td>
<td>121</td>
</tr>
</tbody>
</table>
Among the above mentioned fuel cells, the SOFC is the most prominent conversion device with 60% of conversion efficiency. These higher efficiency is achieved with the help of suitable electrolyte with cubic-perovskite structure for example barium cerate, barium zirconate. When compared with other types of fuel cells systems, SOFC shows its considerable interest for its eco friendly power generation (Mekhilef et al. 2012). SOFC convert the energy continuously with negligible deterioration in its performance for more than two decades (Zhu et al. 2015).

1.4 SOLID OXIDE FUEL CELLS DESIGN AND IT’S BASIC OPERATION

In 1930s Emil Baur and H.Preis conducted an experiment using several solid oxide electrolytes and opened the gateway for the development of SOFC as a efficient energy conversion source. The conversion of energy in solid oxide fuel cell is eventually carried out through the group of advanced ceramics materials called as electro ceramics.

(Source: https://www.nasa.gov/images)

Figure 1.1 Schematic diagram for SOFC operating condition
Figure.1.1 shows the working principle of solid oxide fuel cell. In SOFC, the electrochemical conversion takes place with the help of three major components such as anode, electrolyte and cathode. At anode region, oxide ions (O\textsuperscript{2-}) combine with the protons by means of oxidation. As a result of oxidation of hydrogen, an electron is released to the external circuit for the generation of power and also gives out the resultant by products called water. The performance of SOFC is purely depends on the diffusion rate of oxide ions (charged carriers) ionized at cathode. The oxide ion is directed towards anode side through the solid electrolyte sandwiched between anode and cathode. In such solid materials the conduction of charged atoms (ions) is preferably carried out through the defects in the internal crystal lattice of an electrolyte.

At cathode side, oxygen reduction takes place by accepting an electron from the external circuit. The oxide ions produced at cathode side is migrated through the crystallographic defects in the solid electrolyte and reached the anode-electrolyte interface. The presence of dense electrolyte between two electrodes will also serve as a physical barrier to prevent the direct mixing of fuel and oxygen during fuel cell operation for the conversion of efficient energy.

1.5 SOLID OXIDE FUEL CELL COMPONENTS

In Solid oxide fuel cells, electric charges get enter into the electrically polarized device with the help of two electrodes namely anode and cathode. An electrolyte is a key component of fuel cell. In general, the flow of electron in the external circuit taking place from anode to cathode side apart from considering the type of device and their operating method.
1.5.1 Anode Materials

An anode electrode plays two distinct roles in fuel cells. It can acts as a positive terminal in power consuming device and negative terminal for power releasing devices. Nickel, cobalt, ruthenium are the best examples for anode materials. At anode side, oxidation of fuel takes place as per the equation (1.1)

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

(1.1)

In the present case, anode acts as power releasing electrode at negative terminal (fuel side) and leaves an electron to the external circuit by means of oxidation reaction takes place by the disperse of hydrogen gas. Due to the occurrence of oxidation, electron is free from hydrogen molecule and results in power generation at the external circuit. The example for anode type material is Nickel –YSZ cermets.

In Ni-YSZ electrolyte, the presence of YSZ improves the mechanical stability at high temperature and provide suitable thermal expansion coefficient with electrolyte. However, (Trembly et al. 2006) have explained the drawbacks of these Ni-YSZ cermets in carbons containing atmosphere and poisoning of this materials with hydrogen sulfide. The chemically adsorbed H₂S reacts with nickel and forms nickel sulfide at high temperature (>1000°C). Hence this high temperature is its main drawback. (Zha et al. 2007) suggested that the presence of nickel sulfide on the surface of cermet will reduces the electro-oxidation of hydrogen and carbon monoxide which degrade the materials durability and instability at high temperature (Fu et al. 2011).

Hence it became an massive challenge to find a new material free from Ni for anode to behave as electronic and ionic conductor at low
temperature (400-600°C) as discussed by (Abbas et al. 2014). The other class of anode material is platinum used with hydrogen as fuel for lower temperature SOFC operation (<650°C) (Xu et al. 2007). Traditionally, platinum is used as an active anode electrode for barium cerate and strontium cerate based electrolyte operated at intermediate temperature (Iwahara et al. 1990).

### 1.5.2 Cathode Materials

Cathode is the electrode at positive terminal of fuel cell. The oxygen molecule undergoes reduction to create oxygen ions. On cathode side, there are two main exchange reaction taking place, they are the positively charged cations are directed to move towards the cathode side and the negatively charged anions are observed into solid electrolyte to maintain the charge balance of electron coming from the external circuit.

Cathode electrode must be a porous to permit the oxygen molecules to reach cathode-electrolyte interface and thus the reduction of oxygen is carried out through the following reaction mechanism

\[
\frac{1}{2}O_2 + 2e^- = O^{2-}
\]  \hspace{1cm} (1.2)

In SOFCs, the cathode material is considered as a positive terminal and plays an important role in the distribution of the pure oxygen from the external atmosphere. Metals and metal oxides are considered as the best cathode materials for fuel cell application (Hirabayashi et al. 2004). For example, mixed electronic and ionic conducting (MEIC) materials with pervoskite structure such as lanthanum doped strontium ferrite ((La,Sr)FeO₃), lanthanum-doped strontium manganite ((La,Sr)MnO₃) Huang et al. (1996),
lanthanum-doped strontium cobaltite ((La,Sr)CoO$_3$) (Li et al. 2007), are the most studied cathode materials with high catalytic activity at cathode-electrolyte interface at high temperature and faced serious of unavoidable problems. The oxidation resistance of these cathode materials in the oxygen rich atmosphere is extremely good, but the high temperature operation hampers their practical applications.

1.5.3 Electrolyte Materials

The main heart component of solid oxide fuel cell is an electrolyte sandwiched between two electrodes. A solid electrolyte is the class of solid state material with a mobile ionic species present inside the rigid frame structure for the conduction of oxide ions as like liquid electrolyte. In SOFC, electrolyte is a solid membrane acts as a physical barrier to prevent the direct mixing of fuel and oxidant. The mobilization of oxide ions takes place through this highway of electronic insulator. The solid electrolyte in fuel cells must be more stable in both oxidizing and reducing atmosphere. At cathode-electrolyte interface, electrolyte behaves as oxidizing species and at anode-electrolyte interface it acts as reducing species.

An electrolyte must have the following important requirement for its long term successful operation. They are

- Good ionic conductivity (0.1S/cm at 800°C)
- High dense microstructure
- Stable at high temperature
- Electronic insulator
- Higher passage rate of oxygen ions
- Low materials cost and highly compatible with interconnectors
A solid electrolyte must be a good ionic conductor. Ionic conductors are the materials with enough oxygen vacancies through which the conduction of oxide ions takes place. In order to facilitate the transport of oxygen ions from cathode-electrolyte interface to the electrolyte-anode interface, the solid ceramic material must have the large number of oxygen vacancies with dense microstructures. An ideal electrolyte shows higher ionic conductivity of >0.1S/cm at lower operating temperature. The solid electrolytes in fuel cell must have either mobile anions (or) mobile cations, the existence of large number of vacancies in the crystal lattice is the prerequisite for the hopping mechanism to take place between the electrodes.

The research in fuel cell for the past two decades is mainly to explore the development of a suitable oxygen ion conducting electrolyte for lower temperature operation. Zirconia based material has been studied for the first time as the best oxygen ion conducting electrolyte with fluorite structure for SOFC application. Nernst demonstrated yttria stabilized zirconia as an electrolyte by doping 8% of Yttria into 92% zirconia lattice (Nernst 1899). Doping of $\text{Y}_2\text{O}_3$ into the $\text{ZrO}_2$ can stabilize the cubic structure of zirconia based electrolyte.

Yttria stabilized zirconia (YSZ with 8%yttria), is a polycrystalline ceramic material added with zirconia as dopant exhibited good mechanical stability in both oxidizing and reducing atmospheres as pointed out in the work of (Li et al. 2014). However, the YSZ based electrolyte shows higher ionic conductivity only at high operating temperature >1000°C with 40% efficiency in energy conversion (Yamamoto 2000). (Singhal 2000) have studied these YSZ materials as oxygen ion conductor with ionic conductivity of 0.1 S/cm at 1273 K and 0.02 S/cm at 1073 K. They also reported that this higher temperature operation may results in the degradation of YSZ material,
limits its consideration for mass production of electricity and in commercialization.

The oxygen ion conducting electrolytes have faced many problems such as thermal deprivation, thermal expansion variance and interfacial reaction between the electrodes and electrolyte. It become a great deal of challenge to find an alternate oxygen ion conductor with good thermal behavior, without compromising the ionic conductivity at intermediate temperature (Dong et al. 2010) and also suitable for large scale application (Atkinson 1997 & Milliken et al. 1999). Hence reducing the operating temperature becomes a very essential need to explore the new developments in SOFC research and applications.

1.6 INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELL (IT-SOFC)

The discovery of suitable electrolyte material can convene the increasing demand of energy for future generations. In order to achieve the efficient energy conversion, researchers adopted two main approaches.

The first approach is by reducing the operating temperature of fuel cell to intermediate temperature (500°C–700°C) Huang et al. (2000). Lowering the operating temperature of fuel cells to intermediate temperature becomes a long term goal in the development of the fuel cell system toward the public usage (Will et al. 2000) & Wachsman et al. (2011). The main advantages of reducing the operating temperature of fuel cell will results in the cost reduction of ceramic interconnectors with flexible and inexpensive stainless steel materials (Mah et al. 2016).
In order to increase the efficiency of fuel cell and to reduce the materials cost for fabrication, the operating temperature of the solid electrolyte must be reduced below 700°C. The temperature range between 500°C-700°C are practically called as intermediate temperature. By reducing the operating temperature to this range will ultimately results in extending the life time of fuel cells. Very recently, intermediate temperature SOFC (IT-SOFC) established its more significant attention for the economical replacement of metallic interconnectors. The usage of low cost sealing materials for the fabrication of fuel cells Steele BCH et al. (2001) & (Mah et al. 2016) is also made passable by the reduction of temperature to this intermediate range. Brett et al. 2008 have fabricated a fuel cell with improved oxygen ion conductivity at intermediate temperature in an electrolyte.

The second approach is by reducing the thickness of the solid electrolyte from 10 to 100 microns (0.01 to 0.1 mm) for decreasing the ohmic resistance of the cell and to achieve high ionic conductivity (Fan et al. 2013). Decreasing the thickness of solid electrolyte through thin film technology can recover the rate of transport of oxide ion in solid ceramic and results in the reduction of overall cell resistance. As discussed in the work of (Wu et al. 2008) that the ionic transport is much higher in thin electrolyte with the area of specific resistance (ASR) of 0.21Ω cm² at 800°C. The ionic conductivity of thin electrolyte is same as measured for thicker one at high temperature (1000°C). However, Huang et al. (1996) & (Ishihara et al. 1995) have studied and reported that the decrease in thickness of electrolyte below 10μm will drastically decreases the mechanical strength of the electrolyte and reduces its performances. Hence, a novel research in finding a new solid electrolyte with appropriate thickness for high ionic conductivity is prerequisite for the most profitable lower temperature operation.
Overall, the benefits in dropping down the operating temperature to intermediate temperature and reducing the thickness are summarized as follows:

- Easy start-up and shut down operating response of less than 10 minutes (Choi et al. 2006).
- A broad opportunity to select the low cost materials as interconnectors (Mah et al. 2016).
- Increase the mechanical strength and durability of the product (Sun et al. 2011).
- Reduces the overall cost to fabricate the device Steele BCH et al. (2001).

1.6.1 Oxygen Ion Conductors

Solid oxide fuel cells consist of two classes of electrolyte materials used as oxygen ion conductors. They are ceria based electrolyte and barium cerate based electrolyte materials. Ceria based electrolyte materials belongs to fluorite structure and barium cerate based materials belongs to perovskite structure with increased oxygen vacancies. The conduction of oxide ion takes place through the defects in the solid ceramic and increases the ionic conductivity for the efficient energy conversion. The conduction mechanism of oxide ions is carried out through the oxygen vacancies and exhibits the considerable conductivity at high temperature 1000°C.

Oxygen ion conductor consist charged oxide ions that are migrated from cathode side (oxygen rich atmosphere) to anode side (fuel rich atmosphere) rapidly when connected to an external electrical circuit. The presence of these charge carriers in certain oxidic electrolytes makes these solid oxide fuel cells as s most efficient one with increased ionic conductivity.
1.6.1.1 Fluorite structure Materials

Ceria based electrolytes come under the fluorite structure oxide materials with the general formula of AO\textsubscript{2} where ‘A’ represent the tetravalent cations with larger ionic radius (for example cerium, zirconium). The crystal structure of ceria based materials basically consists of a cubic oxygen lattice with alternating body centers which are unavailable by eight coordinated cations. The cations are arranged into a face centered cubic site and the tetrahedral sites are occupied by anions results in creation of large octahedral interstitial voids with open structure for conduction of oxide ions.

Undoped cerium oxide (CeO\textsubscript{2}) is considered as alternate material with the cubic fluorite structure of Fm\textoverline{3}m space group and has a low ionic conductivity at 800°C (Huang et al.1997). As well as, this ceria based system exhibits a serious of drawbacks is operated at intermediate temperature (<700°C). The reduction of Ce\textsuperscript{4+} ions to Ce\textsuperscript{3+} ions cannot maintain its fluorite structure for the generation of oxygen vacancies and results in undesired electronic conductivity. Hence, the addition of lower valence (allovalent) cations can produce oxygen vacancies, resulting in improved oxygen ion conductivity at 800°C Skinner et al. (2003). Therefore, this ceria based system is doped with lower valance cations like gadolinium or samarium into the host lattice of cerium (Jadhav et al. 2007).

The ionic radius of allovalent cations (Gd and Sm) is much closer to the ionic radius of cerium oxide. Introduction of lower valence cation in the ceria host lattice will results in the creation of oxygen ion vacancies by maintaining the charge neutrality and thereby facilitate the migration of oxide ions through its crystal lattice for better ionic conductivity as pointed out by (Forrat et al. 1964). Doped ceria based electrolyte such as GDC and SDC have shown its higher ionic conductivity of 0.016 S/cm and 0.034 S/cm respectively.
at 1000°C when compared with the ionic conductivity of YSZ is 0.005 S/cm at 1000°C (Steel 2000).

Even though the required high ionic conductivity was found in ceria based oxide ion conductor with cubic fluorites structure, there are some unresolved problems for this type of systems Tao et al. (2006). Under low oxygen partial pressure, this doped ceria system will tends release an electron by the reduction of cerium from Ce$^{4+}$ ions to Ce$^{3+}$ ions. This reduction process will increases the undesired electronic leakage and further decreases the output efficiency of fuel cell (Steele 2000). The overall cell performance of the cell is decreased due to high temperature operation (Im et al. 2008). Hence it becomes an essential need to find an alternate electrolyte to act as oxygen ion conductor for higher ionic conductivity at intermediate temperature.

1.6.1.2 Perovskite structure Materials

In 1839, Gustav Rose discovered the mineral called perovskite from the calcium titanium oxide samples found in the Ural mountains. The name perovskite was named after Count Lev Aleksevich von Perovski, a Russian mineralogist. A Perovskite material belongs to a group of oxides with the general formula of ABO$_3$. Barium cerate based electrolytes are another class of oxide ion conductors with perovskite structure. The crystal structure of perovskite materials is highly stable at higher temperature operation. In perovskites materials, the crystal lattice is extremely tolerant for the creation of vacancy by accommodating the various mixtures of aliovalent cation with different ionic radius like Gd$^{3+}$ (1.07Å) and Sm$^{3+}$ (1.09Å) (Kato et al. 2003).

Pervoskite materials are considered as the best candidate materials for SOFC applications. In these type of materials, two cation lattice sites are readily available for doping the aliovalent cation and thus results in
the creation of large number of oxygen vacancies in oxygen sub lattice. Those vacancy sites are utilized for the fast migration of oxide ions through the lattice (Bonanos et al. 1995). The migration path for oxide ions through the oxygen vacancies in the crystal lattice is shown schematically in Figure.1.2

![Oxide ion migration paths through perovskite lattice](image)

**Figure 1.2 Oxide ion migration paths through perovskite lattice (indigenous)**

In this type of perovskite structures, the cubic corners are normally said to be called as A-Site occupied by the divalent larger cations like barium, strontium, lanthanum and calcium. On the other hand B-site cubic centers are filled by higher tri or tetra valence cation like cerium, zirconium. (Boukamp 2003) have reported that the six oxygen ions are co-ordinated at octahedral site which gives a corner shared strings of BO₆ octahedra and are surrounded to A-site and B-site. The presence of BO₆ octahedra in the
structure made contact with each other by means of their vertices and form a three-dimensional network. Takahashi et al. (1971) have studied first the presence of oxide-ion conductivity in ABO$_3$ structured pervoskite materials by creating the larger quantity of oxygen vacancy (usually denoted as $\delta$) when doped at B-site with lower valance cations (Gd or Sm) by maintaining the charge neutrality in the crystal structure. La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{3-\delta}$ (LSGM) materials has been identified as the pure oxygen ion conductor under dry O$_2$ atmosphere. In the presence of water vapour containing atmosphere, these LSGM materials exhibited mixed ionic (i.e) ionic and proton conductivity of $10^{-2}$ S/cm at 600°C (Ma et al. 2006).

In order to have higher ionic conductivity in ABO$_3$ pervoskite materials, it is necessary to have the lower electro negativity in A site and simple reduction in the B site. For example doped barium cerate with the general formula of BaCe$_{1-x}$M$_x$O$_{3-\delta}$ ($M$ = rare-earth ions such as Gd$^{3+}$, Sm$^{3+}$, Eu$^{3+}$ Nd$^{3+}$, and Yb$^{3+}$, $\delta = x/2$ oxygen vacancies) have shown highest ionic conductivity at 1000°C when compared with that of the undoped BaCeO$_3$(Forrat et al. 1964).

The creation of oxygen vacancies in the structure are purely depends on the size and type of material used as dopant cations (Garbova et al. 2008). In doped barium cerate materials, the concentration of trivalent dopant is limited to 20 mol % to increase the creation of oxygen vacancies and other charge defects. The concentration of charge carrier is further increased to enhance the ionic conductivity (Ishihara 2009). The carrier’s (intrinsic defects) concentration in doped barium cerate system can be determined by oxygen defect structures in the form of vacancies. The oxygen vacancies are created on the oxygen sub lattice stoichiometrically by means of Frenkel defects. The Kroger –Vink notation for Frankel defects is given in equation (1.3)
The concentration of oxygen vacancy increase with increase in the concentration of aliovalent dopant until the dopant reaches its solubility limits (20 mol%) in the host oxides. But at certain level of dopant concentration, the defect are interacted with each other and creates defect associates. Hence, the formation of defect associates will decreases the conductivity in perovskite materials (Norby 1999).

The crystal lattice in such pervoskite materials consist of a triangular space between two large A-sites and one small B-site cation for the fast movement of oxide ions Kilner et al. (1982) & (Cherry et al. 1995). The size of the critical triangle space strongly depends on the ionic radius of the dopant cation at A-site for the easy mobilization of oxide ions from cathode to the anode side through the defects in solid electrolyte. Introduction of dopants with larger ionic radius into the host lattice of pervoskite material will expand the unit cell dimension in the crystal.

The pervoskite materials having the large ionic radius (r_A) at A-site and smaller ionic radius (r_B) at B-site can create the number of vacancy site and give higher ionic conductivity due to the variation occurred in its lattice dimension. It is evident from the work of (Ishihara et al. 1994) studied that PrAlO_3 electrolyte have shown higher ionic conductivity while pronium (Pr) with larger ionic radius as a dopant and observed the high unit cell dimension by the expansion of crystal lattice. Whereas at high temperature, BCY electrolyte shown low ionic conductivity. The reason for the decrease in ionic conductivity has been attribute as the formation of high basicity in the solid electrolyte which leads these barium cerate to react with CO_2 and moist atmosphere. The decomposition of BaCoO_3 into BaCo_3, Ba(OH)_2, and CeO_2

\[ \text{O} = \text{O}'' + \text{V}_0 \]

(1.3)
was observed for yttrium doped barium cerate based electrolyte operated at intermediate temperature as per equation. (1.4) and (1.5) and hampers the practical application.

\[
\text{BaCe}_3 + \text{CO}_2 \rightarrow \text{BaCO}_3 + \text{CeO}_2
\]  

(1.4)

\[
\text{BaCe}_3 + \text{HO}_2 \rightarrow \text{Ba(OH)}_2 + \text{CeO}_2
\]  

(1.5)

Very recently in the development of SOFC electrolyte (Li et al. 2013) have reported that the barium cerate based composite electrolytes can have low basicity by doping them with different trivalent cations like Gd\(^{3+}\),Sm\(^{3+}\),Yb\(^{3+}\),Y\(^{3+}\) ions of lower valence and are stabilized in CO\(_2\) and H\(_2\)O atmosphere. As well as in the work of Ryu et al. (1999) have observed that the partial substitution of cerium in BaCeO\(_3\) using higher electronegative elements like Zr and Nb, can decrease the rate of decomposition of barium cerate by reducing the basicity of these oxides at intermediate temperature. So it is necessary to find an effective way to increase the chemical stability of barium cerate based solid electrolyte operated at intermediate temperature for SOFC application Tanner et al. (1996).

The formation of oxygen vacancy is increased by doping the pervoskite materials with trivalent cations like Gadolinium or Samarium at B-site. For example, when Gadolinium or Samarium is doped into B-site of BaCeO\(_3\) will results in the creation of crystal defects (oxygen vacancies) as per the following equations (1.6) and (1.7)

\[
\text{Gd}_2\text{O}_3 \rightarrow 2\text{Y}_\text{Ce} + \text{V}_0 + 3\text{O}_0
\]  

(1.6)
When this trivalent cation are doped with barium cerate based perovskite oxide is exposed to water atmosphere, the replacement of oxygen vacancies by hydroxyl groups takes place. In other terms crystal lattice can generate oxygen vacancies in BaCeO$_3$ structure as per equation 1.8 and further react with oxygen to produce electron holes in O$_2$ rich atmosphere shown in equation 1.9. As a result oxygen vacancies react with hydrogen to create protonic defects in the presence of moist atmosphere via the hydration reaction as per equation 1.10. The defect chemistry reactions are as follows:

\[
\text{Sm}_2\text{O}_3 \rightarrow 2Y_{\text{Ce}}^\prime + V_0^- + 3O_0^\times
\] (1.7)

When this trivalent cation are doped with barium cerate based perovskite oxide is exposed to water atmosphere, the replacement of oxygen vacancies by hydroxyl groups takes place. In other terms crystal lattice can generate oxygen vacancies in BaCeO$_3$ structure as per equation 1.8 and further react with oxygen to produce electron holes in O$_2$ rich atmosphere shown in equation 1.9. As a result oxygen vacancies react with hydrogen to create protonic defects in the presence of moist atmosphere via the hydration reaction as per equation 1.10. The defect chemistry reactions are as follows:

\[
2\text{Ce}_{\text{Ce}}^{\times} + O_0^\times + \text{Gd}_2\text{O}_3 \rightarrow 2\text{Gd}_{\text{Ce}} + V_0'' + 2\text{CeO}_2
\] (1.8)

\[
\frac{1}{2}O_2 + V_0^- \leftrightarrow O_0^\times + 2h
\] (1.9)

and

\[
\text{H}_2\text{O(gas)} + V_0 + O_0^\times \leftrightarrow 2\text{OH}_0
\] (1.10)

Therefore, from the above discussion it is clear that the dopant with larger ionic radius at B-site would expand the crystal lattice. The increase in lattice is utilized for the fast migration of oxide ions through the crystal and increases the ionic conductivity in doped barium cerate based pervoskite materials (Jacquin et al. 2007). But doped barium cerate based pervoskite shows chemical instability. Doped barium cerate phase is readily decomposing with H$_2$O and CO$_2$ atmosphere at high temperature and limits its practical application. Hence, it is necessary to find new approach in developing the concept of composite material to resolve the drawback of doped ceria and doped barium cerate based materials and also to retain their individual advantages.
### 1.7 COMPOSITE ELECTROLYTES

Composite electrolytes are the new class of oxygen ion conductors with dual phase microstructure in its crystal structure. The composite materials have shown better ionic conductivity, when compared to conventional single phase electrolyte Zhu et al. (2006). The concept of interface region between two phases has provoked the new concept for the development of this composite electrolyte. The interface region exist in between the two constituent phase of composite acts as a pathway for the effective migration of oxide ion to achieve the required ionic conductivity at low temperature. The creation of oxygen vacancies is much high in the region between two constituent phase than that of the bulk. Hence, these types of composite materials are considered as a functional electrolyte for intermediate temperature application (Zhu et al. 2001).

SDC-BCY20 composite was developed by (Zhu et al. 2004) with a hybrid oxygen and proton conductivity. This new composite technology have exhibited combined advantages of the oxygen ion conduction in SDC phase and proton conduction from 20% of Y-doped barium cerate phase and the composite electrolyte exhibited both the ionic and protonic conductivity at intermediate temperature.

The pervoskite materials of ABO$_3$ group having orthorhombic structures are used as electrolyte for ionic conductivity at intermediate temperature (Raza et al. 2012 & Ishihara et al. 1994). However the barium cerate (BaCeO$_3$) phase in the composite matrix exhibits poor chemical stability and also readily undergoes decomposition or reacts with H$_2$O and CO$_2$ atmosphere at an elevated temperature which limits their practical application. On the other hand, the advantage of having barium cerate phase in the composite can effectively prevent the internal shortening (electronic
leakage) caused by the reduction of doped ceria phase and considerably improves the ionic conductivity. The oxide ion is preferred to migrate through doped barium cerate phase in the composite (Sun et al. 2011).

When compared to doped ceria based materials, doped barium cerate based materials have shown their special interest with high conductivity only at intermediate temperature. (Bonanos et al. 1989) suggested that the introduction of gadolinium in BaCeO₃ have increased the ionic conductivity of electrolyte in oxygen atmosphere at intermediate temperature.

The presence of doped barium cerate phase in the composite act as reinforcement in the matrix and suppress the reduction process occurred in doped ceria phase under low oxygen partial pressure and improve the mechanical strength of the composite electrolyte (Sun et al. 2011). The existence of doped ceria phase in the composite act as matrix and in turn improve the chemical stability of doped barium cerate phase in H₂O and CO₂ atmosphere (Mishima et al. 1998 & Zhu et al. 2004).

However, with respect to doped barium cerate based electrolyte there is only few reports available on double matrix to achieve conductivity higher than the state of art-YSZ. In the present investigation, it is favored to increase the ionic conductivity of barium cerate electrolyte by choosing the rare earth element as dopant from the group aliovalent cation such as Y, Gd, Sm, Tb, Nd, Dy, and Er. In particular heavy rare earth elements such as Gd, Sm of large ion radius than Ce has been chosen, since those elements are doped in place of Ce-site of BaCeO₃ to distort the orthorhombic perovskite crystal structure for the creation of oxygen vacancies. In recent decades, a considerable quantity of research has been employed and devoted for the development of this type of composite electrolyte as ionic conductor with cubic perovskite phase. The existence of dual phase is preferentially due to
microwave sintering of GDC-BCG and SDC-BCS composite. The concept of dual matrix phase in composite have aggravated this new concept for the initiation of the present investigation with two different aliovalent dopants in barium cerates based systems.

In order to achieve the desired dual microstructure, microwave sintering technique is adopted to reduce the sintering temperature of the solid electrolyte. From the available literature on microwave sintering, it is understood that the reduction in sintering temperature will ultimately improve the existence of double matrix in the composites (Sun et al. 2011). The oxygen ion vacancies in doped barium cerate phase can improve the ionic conductivity by the migration of oxide ions through composite matrix. The loss of barium content from doped barium cerate phase in the composite should be reduced to improve the stability performance of fuel cell during high temperature (Ebadzadeh et al. 2008). Electrolytes materials processed through microwave method can develop such a dual phase matrix with fine microstructures. The composites electrolytes sintered through this method will prevent the phase segregation and effectively block electronic conduction (Khandelwal et al. 2011). Very recently barium cerate based composites are studied as the most suitable materials for MEIC in SOFCs (Chen et al 2017 & Sun et al. 2017).

1.8 THESIS OBJECTIVES AND OUTLINE

In order to address the limitations of both doped ceria and doped barium cerate base materials, the present research approach is to fabricate the nanocomposites electrolyte for SOFCs.

Since both the single phase materials, doped ceria (GDC/SDC) and doped barium cerate based (BCG/BCS) materials cannot reach the high ionic conductivity and commercial requirement individually, a matrix phase in composite with fluorite and orthorhombic structure can improve conduction...
mechanism in electrolyte by limiting the drawbacks of individual phase (Yamoji et al. 1999). Figure 1.3 shows the matrix phase prediction with the drawback of individual phases and advantage of composite matrix phase.

Figure 1.3 Composite matrix predictions for a) doped ceria phase b) doped barium cerate phase c) matrix phase (indigenous)

The main objective of the present work is to prepare composite electrolytes

1. With two phase microstructure, where doped barium cerate and doped ceria acts as a matrix and reinforcement, respectively.
2. Operating at intermediate temperature (IT) without compromising the ionic conductivity

Two approaches were followed to achieve this target:
1. Synthesis of nano powders for the following composites through co-precipitation technique
   (a) \((1-x)\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}-x\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}\) (GDC-BCG)
   (b) \((1-x)\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}-x\text{BaCe}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}\) (SDC-BCS)

2. Microwave sintering technique was employed to achieve desired morphology

The outline of the thesis consists of five chapters. The petite description of the following chapters is presented below.

- Second chapter deals with the materials and experimental method used for the synthesis of powder and various techniques involved in the characterization of composites is discussed.
- Third and fourth chapter’s deals with the result and discussion of rare earth (Gd\(^{3+}\) and Sm\(^{3+}\)) doped composite electrolytes.
- Fifth chapter enumerate the conclusions of the present research work.