

1.1 Overview of the Field

The Energy development is a most promising intuition in the evolution of science. The development of any country is also governed with the consumption of energy by the population. As per the rise of population, energy demand is also increasing continuously. Until date, the energy demand is fulfilled by combustion of fossil fuels through which the global warming increases with air pollution by the emission of toxic gases along with depleting fossil fuels [1]–[3]. Fossil fuel will not be able to preserve world energy demands with electricity consumption for different sectors, beyond 2030 as shown in fig. 1.1. In order to solve these issues, some clean energy sources are required to fulfill the energy demands. However, there are several alternative energy sources that are being developed such as solar, wind, tidal, biomass, hydro-electric, ocean and geo-thermal technologies etc. but these alternate energy sources have some limitations [4] as cloudy day, windless day etc. Due to these limitations, it is essential to look for sufficiently developed renewable energy sources. Among the available renewable energy sources with energy conversion devices, a fuel cell is an emerging technology for efficient and clean power generation [5].

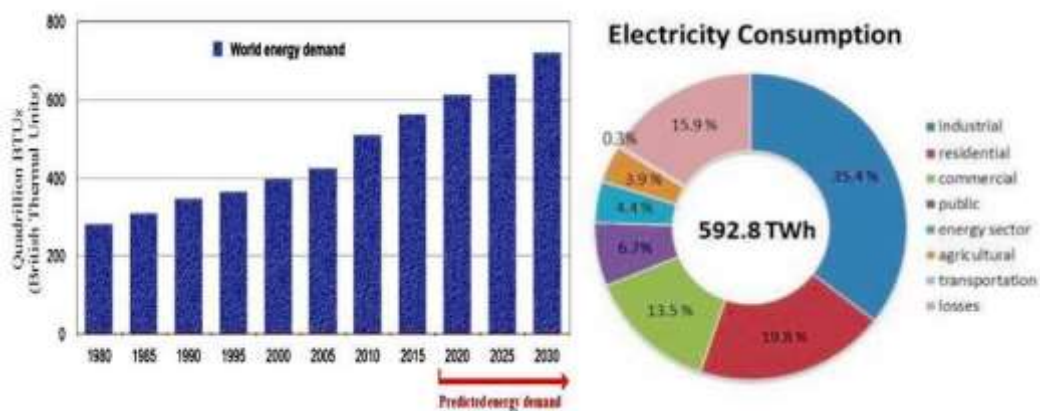


Figure 1.1: World energy demand (in BTUs) and its electricity consumption for different sectors [www.flickr.com].

1.2 Fuel Cell

A fuel cell is an electrochemical energy conversion device, which converts chemical energy of the fuels directly into the electricity. It is considered to be a promising energy conversion technology owing to its high efficiency, low environmental impact, and excellent fuel flexibility [6]. It offers a clean, pollution free technology to electrochemical generation of electricity with high efficiencies. The concept of fuel cell was suggested in 1802 by Sir Humphrey Davy. In 1839 Sir William Grove demonstrated first in laboratory and used first time for its practical applications in Gemini and Apollo space crafts in 1960 [7]. Fuel cells work in the same way as conventional batteries, having the major advantage that it will go on producing electricity as long as fuel is supplied to it. The basic components of a typical fuel cell are cathode, an ion conducting electrolyte and an anode. In fuel cell, an electrolyte is in intimate contact with a porous anode (negative electrode) and a porous cathode (positive electrode). Together these three are often referred to as membrane electrode assembly (MEA) or simply a single cell.

A fuel cell produces electricity by means of an electrochemical reaction much like a battery. Moreover there is an important difference i.e. rather than extracting the chemical reactants from the plates inside the cells, a fuel cell uses hydrogen fuel and oxygen to produce electricity. Practically fuel cells are not operated as single unit; rather, they are connected in electrical series to build voltage. A series of cells is referred as a stack. A component called as interconnect, connects the anode of one cell to the cathode of the next cell in a stack. Fuel cell stacks can be configured in series, parallel, both series and parallel or as single unit, depending on the particular application. A fuel such as hydrogen is brought into the anode compartment and an oxidant, typically oxygen into the cathode compartment. In general, chemical driving force for the oxygen and the hydrogen to react electrochemically at gas-electrolyte-electrode interface to produce water. Direct chemical

combustion is forbidden by the electrolyte that separates the fuel (H₂) from the oxidant (O₂). The electrolyte serves as a barrier to gas diffusion, which finally allow the ions to migrate across it [8].

The number of fuel cells in the stack determines the total voltage, and the surface area of each cell determines the total current. Multiplying the voltage by the current yields the total electrical power.

$$\text{Power (Watts)} = \text{Voltage (Volts)} \times \text{Current (Amps)} \quad (1.1)$$

Fuel cell emits less carbon dioxide and nitrogen oxides per kilowatt of power generated due to its high efficiencies and low fuel oxidation temperatures. Noise from fuel cell power plants has been considered as 55 dB at 90 feet [9]. Since fuel cells have no moving parts (except essential parts for the pumps as blowers and transformers), noise and vibration are practically non-existent. An additional advantage of fuel cell is its increase in efficiency at part-load conditions, unlike steam and gas turbines, fans and compressors. Finally, fuel cells can be used in many different types of fuels such as hydrogen, ethanol, methanol or gaseous fossil fuels like natural gas. This versatility ensures that fuel cells will not become obsolete due to the unavailability of certain fuels. A comparison of power output efficiency is depicted in fig. 1.2.

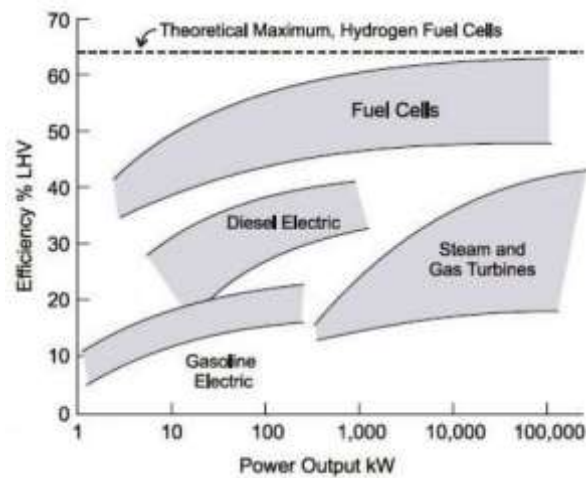


Figure 1.2: Comparison of power output efficiency [www.ags-energy.com].

Today fuel cells under development contain electrolytes in which protons, hydronium ions, hydroxide ions, oxide ions and carbonate mobile ions which are the basis for the many categories of fuel cells. Since ion conduction is a thermally activated process and its magnitude varies drastically from one material to the next, the type of electrolyte, which may be either liquid or solid, determines the temperature at which the fuel cell is operated. State-of-the art fuel cell electrolytes, along with the mobile ionic species, temperatures of operation and fuels typically utilized [8] have been discussed in the following section.

1.3 Types of Fuel Cell

Fuel cell technologies, currently being developed for power generation applications, can be categorized on the basis of following aspects:

- Temperature of operation (low, medium and high temperatures).
- The nature of the electrolyte (liquid or solid electrolytes).
- The mode of conduction (ionic or protonic conduction).

Generally, fuel cells have been classified into five categories [6]. These include solid oxide fuel cell (SOFC), molten carbonate fuel cell (MCFC), phosphoric acid fuel cell (PAFC), alkaline fuel cells (AFC) and proton exchange membrane fuel cell (PEMFC). Among the various fuel cell technology, SOFC utilizes the solid ceramic oxide components and is predominant energy conversion device that generates electrical power by continuously converting chemical energy of fuel into electrical energy through electrochemical reaction at high temperature (700-1000 °C) [10].

SOFC systems are efficient upto 50-55% and in combination with heat regeneration and co-generation technologies, the overall efficiency can be boosted upto 60-65% [11], [12]. Pollution levels are substantially reduced with 20-40% reductions in

CO₂ levels per kW of electricity produced. The summary of a few types of the fuel cell is shown in the fig. 1.3.

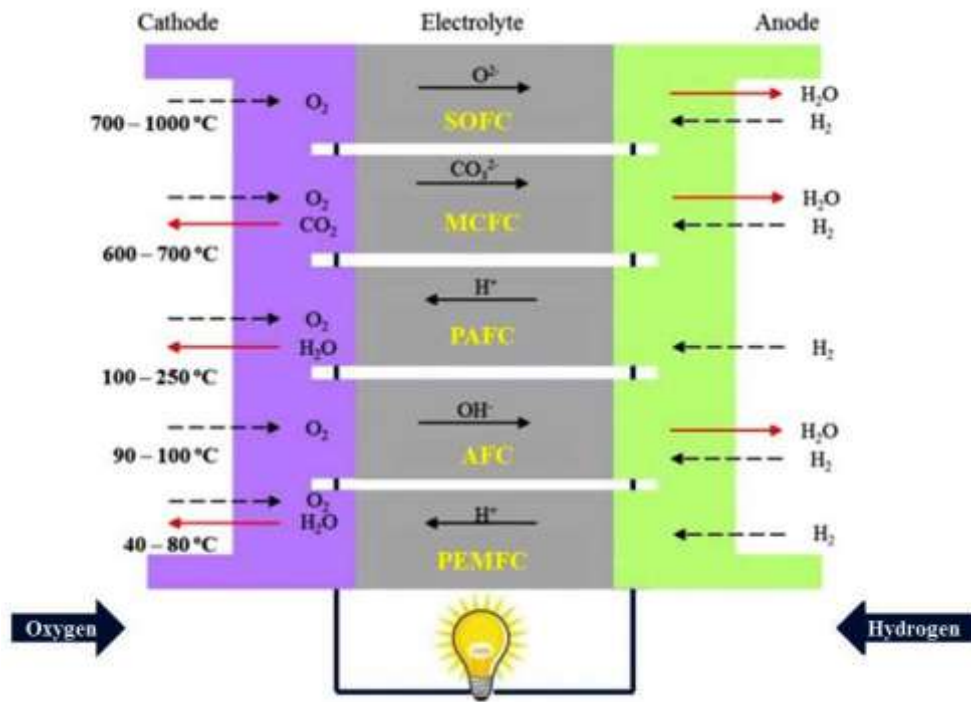


Figure 1.3: Summary of different types of fuel cell [www.ceb.cam.ac.uk].

The reactions at anode and cathode in each type of fuel cell are listed in table 1.1.

Table 1.1: Reactions occurring at anode and cathode for all five types of fuel cell [13].

Fuel Cell Type	Electrolyte	Electrode Reaction
SOFC	Ceramic Oxide	Anode: $\text{H}_2 + \text{O}^{2-} \longrightarrow \text{H}_2\text{O} + 2\text{e}^-$ Cathode: $\frac{1}{2} \text{O}_2 + 2\text{e}^- \longrightarrow \text{O}^{2-}$
MCFC	Molten alkaline NaHCO_3	Anode: $\text{H}_2 + 2\text{CO}_3^{2-} \longrightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$ Cathode: $\frac{1}{2} \text{O}_2 + \text{CO}_2 + 2\text{e}^- \longrightarrow \text{CO}_3^{2-}$
PAFC	Phosphoric acid	Anode: $\text{H}_2 \longrightarrow 2\text{H}^+ + 2\text{e}^-$ Cathode: $\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2\text{O}$
AFC	KOH	Anode: $\text{H}_2 + 2\text{OH}^- \longrightarrow \text{H}_2\text{O} + 2\text{e}^-$ Cathode: $\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow 2\text{OH}^-$
PEMFC	Polymer membrane	Anode: $\text{H}_2 \longrightarrow 2\text{H}^+ + 2\text{e}^-$ Cathode: $\frac{1}{2} \text{O}_2 + 2\text{e}^- \longrightarrow \text{O}^{2-}$

1.4 Solid Oxide Fuel Cell (SOFC)

Solid Oxide Fuel Cell (SOFC) is an encouraging and potential revolutionize device for the low cost production of electricity as compared with currently available their fossil fuels counterparts because of increased demand for high quality and reliable energy with increasing expectations for eco-friendly, low-pollutant energy with superior electrical efficiency [10]. In SOFCs, it is possible to achieve an electrochemical reaction at the electrodes by simply supplying fuel and air without using expensive noble metal catalysts. Solid oxide fuel cells (SOFCs) are comprised of a layered structure of a dense electrolyte sandwiched between porous and permeable electrodes (anode and cathode) [10]. Electrical power generation systems based on SOFC have the following advantages:

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

Furthermore, SOFC system efficiencies can be improved by the internal reforming of natural gas within the fuel cell stack [14]. With modular construction, it is possible to adapt SOFC systems to suit the load required and, as long as fuel is present, the SOFC is able to continually operate in almost any environment.

1.5 Operation of SOFC

The principle of a SOFC is schematically illustrated in fig. 1.4. Two electrodes (the anode and cathode) both are highly porous and separated by a dense oxygen ion

conducting solid electrolyte. Oxidant is reduced at the cathode and fuel is oxidized at the anode. If hydrogen and oxygen are used as fuel and oxidant, respectively in an SOFC with an oxygen ion conducting electrolyte, the reactions in the fuel cell involve the oxidation of hydrogen and reduction of oxygen at the electrodes.

The operating temperature of SOFC is in the range of 700-1000 °C. This operating temperature is adequate to the oxygen ion conductivity of electrolyte. During operation, oxygen molecules are adsorbed, dissociated and reduced at the cathode surface to ionic oxygen species before incorporated into the lattice as oxygen ions, which then diffuse through the electrolyte to the anode and combine with H₂/C to form water and/or carbon dioxide depending on fuel. The electrons move from the anode to the cathode through an external circuit, converting chemical energy of the fuel into electrical energy [14].

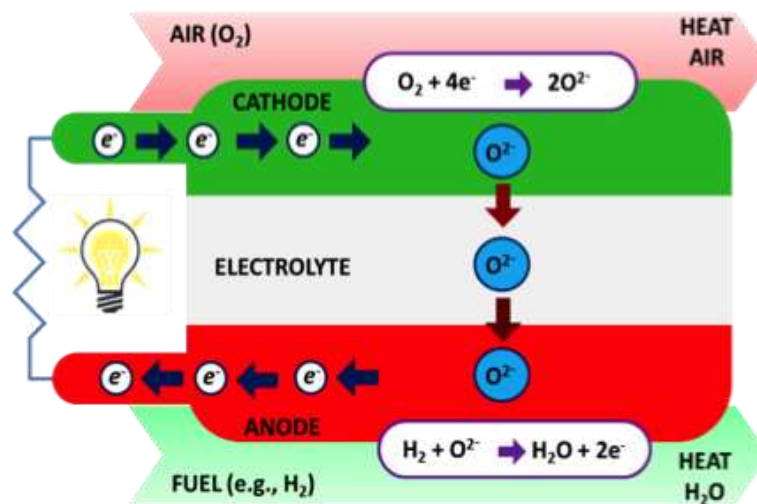
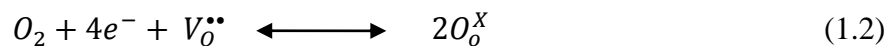
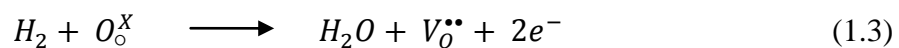


Figure 1.4: Working principle of SOFC [www.scopewe.com].

The oxygen reduction at cathode can be described by equation:



At the same time, fuel molecules (i.e. hydrogen) are oxidized at anode by combining with oxygen ions and release electrons:



The combination of these reactions yields the overall reaction of the SOFC,



The electrons released during oxidation reaction, flow through an external circuit called an electric load (any electric power consuming device). The total current at each point of the electric circuit must be the same. The current through electrolyte is due to the migration of ions while, flow of electron constitute current through external circuit. Thus, the electrodes are sites, where the charge carrying species is converted from electron to vacancies or vice versa.

1.6 Types of Solid Oxide Fuel Cells (SOFCs)

On the basis of the operating temperatures, SOFCs are categorised into two types:

(a) *High Temperature Solid Oxide Fuel Cell (HT-SOFC)*: The SOFC operates in the temperature range of 700-1000 °C, termed as HT-SOFC.

(b) *Intermediate Temperature Solid Oxide Fuel Cell (IT-SOFC)*: The SOFC operates in the temperature range of 500-700 °C, termed as IT-SOFC.

1.6.1 High Temperature Solid Oxide Fuel Cell (HT-SOFC)

The enhanced efficiency of SOFC in comparison with other energy conversion systems is borne out by its high operating temperature exceeds 700 °C. The components for HT-SOFCs are the following:

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

1.6.1.1 Disadvantages of HT-SOFC

Although the power output is high, HT-SOFC suffers with some serious demerits. Particularly for construction and interconnect materials, costs of material are high. For high temperature SOFC, the durability of the components decreases at high operating temperature. In addition, ceramic such as lanthanum chromite is used as interconnect, or, if the temperature is limited to $<1000\text{ }^{\circ}\text{C}$, a sophisticated refractory alloys e.g. based on mechanically alloyed Y/Cr can also be utilized for interconnect. In either case interconnect represents a major proportion of the cost of the stack. A potential drawback to the use of chromium containing ceramics and alloys is the volatility of the material, which can result in contamination of the stack components [14]. This has an increased significance for future reclamation of materials and components from using stacks where the presence of a toxic material such as Cr^{6+} would require special disposal procedures.

1.6.2 Intermediate Temperature Solid Oxide Fuel Cell (IT-SOFC)

Intermediate Temperature Solid Oxide Fuel Cell (IT-SOFC) operates in the temperatures range $500\text{-}700\text{ }^{\circ}\text{C}$ which may overcome to resolve some of the problems of High Temperature Solid Oxide Fuel Cell (HT-SOFC). By lowering the operating temperature ($500\text{-}700\text{ }^{\circ}\text{C}$), IT-SOFCs have the potential to greatly reduce the cost of interconnect, manifolding, and sealing materials, in addition to improved reliability, portability, and operational life. The new generation of materials for example such as Sr-doped LaMnO_3 (LSM), Sr and Mg doped lanthanum gallate (LSGM), La-doped strontium titanate (LST) are used as cathode, electrolyte and anode, respectively for IT-SOFC [14].

1.6.2.1 Advantages of IT-SOFC

Due to low Operating temperature below $700\text{ }^{\circ}\text{C}$, IT-SOFC offers several merits. Some of the salient features are pointed as:

- Operation at less than 700 °C means that low cost metallic materials, e.g. ferritic stainless steels or even metal-alloys can be used as interconnect and construction materials. This makes both the stack and balance of plant cheaper and more robust.
- Lower temperature operation offers the potential for more rapid start up and shut down procedures.
- Reducing the operating temperature simplifies the design and materials requirements of the balance of plant.
- Low operating temperature significantly reduces corrosion rates. In order to operate at reduced temperatures, several changes need to be made to cell and stack design, cell materials, reformer design and operation, and operating conditions.

1.7 Material Selection for SOFCs

The material selection requirements for SOFC are quite challenging, stubborn and well established [6], [15]. On the basis of the characteristics of cell as oxygen-ion conductor, electronic conductivity, stability in both oxidizing and reducing conditions, density and fuel flexibility there are following essential components.

1.7.1 Electrolyte Material

The sandwiched material between the cathode and anode electrodes is an electrolyte of the SOFC. The current conduction in solid electrolyte is due to the migration of oxygen ions (O^{2-}). A criterion to select an electrolyte which posses high ionic conductivity and should be temperature independent. A small number of ceramic ion conducting electrolytes are available for operating over a wide range of temperatures from 400 to 1000 °C [16], [17]. The basic requirements of electrolyte materials are:

- High ionic conductivity.

- Very high density (almost free from porosity) along with phase stability.
- Mechanical and physical strengths.
- Gas tightness with thermal shock resistance.
- Thermal expansion coefficient should be matched and compatible with the electrodes and interconnect.
- Chemical resistance to react gases (to oxidising and reducing atmosphere).

Prominent electrolyte materials: Ytria stabilized zirconia (YSZ), Sm/Gd doped ceria (SDC/GDC), Sr & Mg doped Lanthanum gallate (LSGM) etc.

1.7.2 Cathode Material

Cathode acts in oxygen atmosphere where oxygen molecules reduced in the oxygen ions. At high temperatures, it is particularly strong oxidising environment which made it difficult to use lower cost metals but favour the use of noble metal, semiconducting oxides or conducting metal oxides. Cathode must meet the following requirements [18], [19].

- High electronic conductivity.
- Chemical stability in environments during cell operation and fabrication of interconnection, electrolyte and fuel electrode layers.
- Thermal expansion coefficient should be matched with other cell components.
- Sufficient porosity to facilitate transport of molecular oxygen.

Prominent Cathode Materials: Sr-doped lanthanum cobaltite & manganite (LSC & LSM) etc.

1.7.3 Interconnect Material

The interconnect material is used to electrically connect the anodes and cathode of stacked cell in series [10][20]. The requirements of interconnect material are:

- 100% electronic conductivity, no porosity (to avoid mixing of fuel and oxygen).
- High chemical and physical stability.
- Good thermal conductivity.
- High sinterability in air.
- Good thermal expansion compatibility with other cell components.

Mostly, pure or doped lanthanum chromite (LaCrO_3) is used for interconnect material.

1.7.4 Anode Material

The anode acts in reducing atmosphere of the fuel gas and it allows for a use of a range of metals, of which porous nickel have been most widely employed. The basic requirements for a SOFC anode materials are relatively similar to those for cathodes (except reducing environment in place of the oxidizing environment), with appropriate electronic conductivity, thermo-mechanical and chemical compatibility with the electrolyte and interconnect materials, necessitated porosity to allow gas transport to the reaction sites [21], [22]. The basic properties and characteristics of anode materials:

- High electronic and low ionic conductivity.
- High porosity.
- Large triple phase boundary.
- Chemically stable in a reducing atmosphere.
- Thermal expansion coefficient should be matched with neighbouring cell components.

Prominent Anode Materials: Porous Ni, NiO/YSZ, La and Y doped SrTiO_3 etc.

This thesis work is based on the development of ceramic perovskite materials as anode for IT-SOFC, therefore, a brief survey of these systems is being presented in the following sections.

1.8 Perovskite Oxide Systems for Anode Materials

The perovskite oxides (with general formula, ABO_3) e.g., $SrTiO_3$, $BiFeO_3$, $LaMnO_3$ etc. are very significant materials for SOFC, as they have generally stable crystal structure, large free lattice volume and substitution liberty [23], [24]. Perovskite oxides are of great interest in research for their wide applicability in human life as dielectric thermistors, barrier layer capacitors, dielectric amplifier, oxygen sensor, humidity sensor and anode or cathode or electrolyte or interconnect for solid oxide fuel cells etc. An ideal perovskite has a cubic structure. From fig. 1.5, the ideal cubic structure of ABO_3 shows the BO_6 octahedron form a corner-shared network, with remaining voids filled by the cation A.

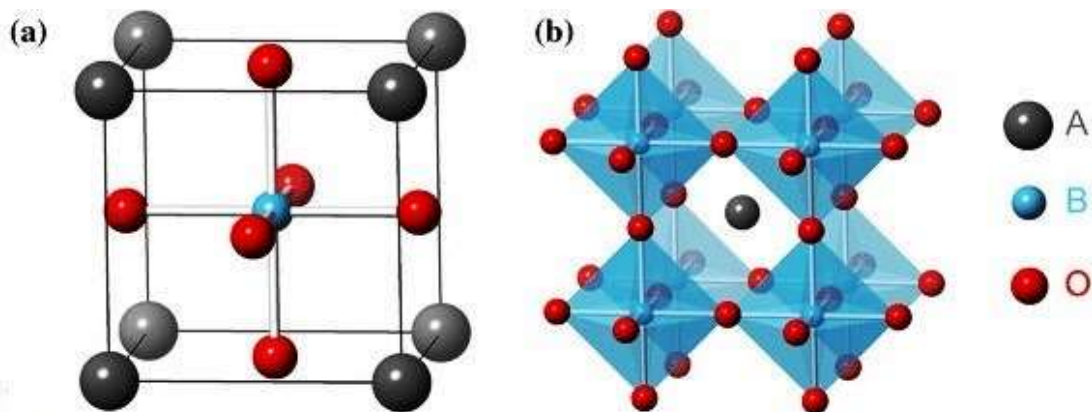


Figure 1.5: (a) Perovskite structure ABO_3 and (b) octahedron BO_6 [www.sfscientific.com].

1.9 Types of Perovskite Oxides

On the basis of cation valencies (A^{m+} and B^{n+}), perovskite oxides can be divided into five categories. The basic criteria of classification depends on addition of the valencies of cations ($A+B$) must be equal to anions (oxygen) valencies to maintain the electro-neutrality. These perovskite oxides are described with following categories.

1.9.1 $A^{1+}B^{5+}O_3$ Type Structure

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

1.9.2 $A^{2+}B^{4+}O_3$ Type Structure

In this type of perovskite oxides, A-site is occupied by divalent cations and B-site is occupied by tetravalent cations. In electro-ceramics, a number of perovskite oxides are studied by the general formula $A^{2+}B^{4+}O_3$ where A cations are alkaline earth metals (A = Sr, Ba, Co and Pb etc.) and B cations transition elements (B = Ti, Sn, Zr, Hf, Mo and Th etc.). Some significant examples of $A^{2+}B^{4+}O_3$ series are $SrTiO_3$, $CaTiO_3$ and $BaTiO_3$ are used as piezoelectric and ferroelectric materials. They are utilized as a piezoelectric transducer, phonograph pickups, air transducers, instrument transducers and ultrasonic devices. These are most promising candidates for the anode and cathode in a solid oxide fuel cell.

1.9.3 $A^{3+}B^{3+}O_3$ Type Structure

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

1.9.4 A⁴⁺B²⁺O₃ Type Structure and A⁵⁺B¹⁺O₃ Type Structure

These categories of perovskite are not easily available in previous reported literatures. Several investigations have been focused on the conductivity of perovskite oxide structure due to their relatively open structure. Ionic conductivity of perovskite oxides is discussed in terms of structurally related parameters, such as tolerance factor, specific free volume and oxygen deficiency. The Goldschmidt tolerance factor [25] is given by the formula

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (1.5)$$

where r_A , r_B , and r_O are the ionic radii of A, B and O ions respectively in ABO₃ perovskite, t is the tolerance factor. For ideal perovskite, $t = 1$. Such types of materials are typically the source of electrical conductivity.

Also, several authors have reported that if tolerance factor $t \sim 1$, the perovskite oxides (ABO₃) may be enhanced the electrical conductivity[26]. In the present overview, basic characterizations (structural and electrical conductivity) of perovskite material for a SOFC application as a function of compositions and the type of magnitude which affect their properties have been studied. The importance of perovskite is summarized in terms of structural and electrical conductivity and classified the perovskite based anode materials for SOFC. Perovskite is a most important unit of materials that represents the suitable properties for several technological applications. These are being extensively studied over the last few decades for their rich multiplicity of electrical, dielectric, magnetic and optical properties [27]. During the last two decades, studies on the electrical properties of perovskite materials have produced enormous information on electro-ceramic materials [28]. Perovskite structure can stand for wide-ranging modifications by substituting the A and/or the B-site cations of the ABO₃ to improve specific properties

such as electrical conductivity, catalytic activity, thermal compatibility and stability, respectively. These activities promote to several substances which are considered to be potential anode materials for solid oxide fuel cells. Perovskite compounds such as SrTiO₃ [33], BaTiO₃ [30], [31] and LaCrO₃ [32] are generally used as electro-ceramic compounds. Therefore, perovskite oxides (A²⁺B⁴⁺O₃) are promising candidates as anode for SOFCs due to their mixed ionic/electronic (electrical) conductivity with good catalytic activity [33]–[35]. Perovskite structures can go through broad variations of the doping elements at the A and B sites with much more complex compositions. Our study is especially concerned with the electrical properties in perovskite systems under investigation. However, undoped SrTiO₃ perovskite cannot be used as anode due to its low electrical conductivity, whereas donor doped SrTiO₃ systems are proposed to be suitable to anodic conditions due to their chemical and thermal stability, high electrical conductivity and carbon/sulphur tolerance [36]. It is well known that in SrTiO₃ based systems, the oxidation of fuel occurs at anode and mixed conductivity feature provides oxidizing reaction sites that decrease the polarization and accelerate the anode reaction [37]. However, the combination of ionic and electronic conductivities could not fulfil the requirements for the electrode materials, therefore, many efforts have been made to enhance the electronic conductivity of the SrTiO₃ materials. It is reported that the acceptor doping in the perovskite materials enhances the ionic conductivity [38], [39] whereas, the donor doping increases the electronic conductivity [37]. Rare earth elements (like La³⁺, Y³⁺, Sm³⁺ and Dy³⁺ etc.) may act as donor dopant at Sr²⁺ site of the SrTiO₃, and suitable for substitution due to less difference between ionic radii. As the results of doping, two phenomena occur simultaneously, first maintain electro-neutrality in lattice defect structure due to charge imbalance and second improve the electrical conductivity of SrTiO₃ *via* the formation of oxygen-rich planes. In addition to that, redox coupling of

Ti⁴⁺/Ti³⁺ that also occurs in the system contributes to improving the electrical conductivity under reducing atmosphere and shows an n-type semiconducting behaviour [40]–[42].

1.10 The Essential Requirements of Anode Material in SOFC

There are four primary requirements that any anode material in a SOFC must exhibit. First, the material must be porous to allow fuel to flow towards the electrolyte. Second, the material must possess electronic conductivity to transport electrons throughout the electrode and to or from an external circuit. Third, it must have ionic conductivity so that the O²⁻ anions are able to migrate throughout the electrode. Finally, catalytic activity is necessary for the dissociation of oxygen and for the oxidation of fuel [43]–[45]. Regarding the anode, ions coming from the electrolyte flow through the anode, thus combining with fuel (H₂) and releasing electrons at the region where the last three properties meet is often referred to as the Triple phase boundary (TPB) [46], [47]. Consequently, electrons flow towards the anodic current collector. The TPB exists in the approximately 10-20 μm thick active region near the anode-electrolyte interface [44]. It is at the TPB that the reaction occurs, as depicted in fig. 1.6. However, the ionically conductive electrolyte transports oxygen anions to the TPB of the anode where the anions encounter fuel which has diffused through the porous anode. At catalytically active sites within the TPB, the fuel and O²⁻ undergo the oxidation reaction which releases electrons [48]. Electronic conductivity is, therefore, also required to transport electrons away from the TPB to the external circuit. Therefore, anodes are typically comprised of mixed electronic and ionic conducting materials [44], thus both electrons and ions can flow through them. If any one of these critical properties is not present in sufficient levels within the anode, the anode will be inactive and suffer from poor electrochemical performance.

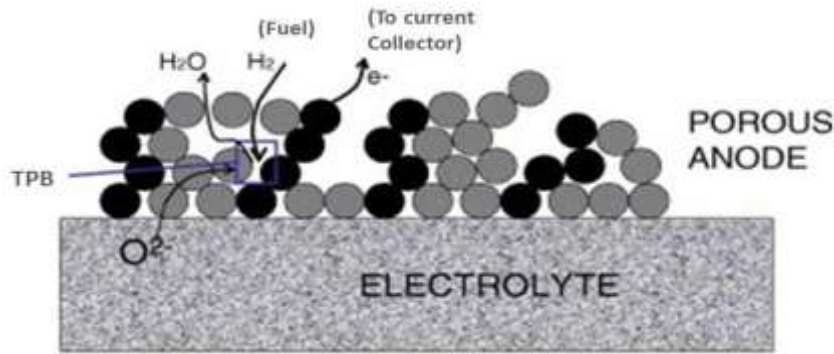


Figure 1.6: Triple phase boundary (TPB) and anodic reaction [49].

Several other important considerations must also be formulated when selecting a material for use in SOFC anodes. The first is the coefficient of thermal expansion, also called the thermal expansion coefficient (TEC). The TEC of the anode material must be similar to that of the electrolyte and cathode, otherwise fuel cell will fail during sintering and while heating to normal SOFC operating temperatures [43]. Solid state reactions must also be avoided. An anode material should not react with the electrolyte or with other materials under anodic reaction because other phases or compounds may form which do not meet the four primary anode requirements [50]. The presence of such additional phases would promote to decreased anode performance. Moreover, the anodes are most commonly incorporated into SOFCs fail during oxidation and reduction cycling at elevated temperatures, therefore, they should be thermally and chemically stable [51].

1.11 Ceramic Perovskite over Ni-Cermet Anode Materials

For IT-SOFCs, a second generation of planar SOFC was developed in the mid-1990s. As most planar fuel cell developers switched to the anode supported cells [52]. The main advantage of this design is that a very thin electrolyte (~10 μm) can be used, significantly reducing the cell resistance and, consequently, lowering the operating temperature. As a consequence, a wider range of inexpensive materials could be used for cell fabrication. Due to the low cost, good mechanical properties, high electrochemical

activity, and electronic conductivity, Ni-YSZ cermets are the most common SOFC anode material nowadays. Cell performances of up to 2 W/cm^2 at $700 \text{ }^\circ\text{C}$ using humidified hydrogen as fuel and air as oxidant have been reported [53]. However, when operating the cell using less expensive hydrocarbon fuels or on redox cycles that occur during cell or stack maintenance, the use of Ni-cermets becomes problematic: firstly, nickel can catalyse the direct carbon formation from hydrocarbons on its surface, blocking the catalytic active sites and secondly, the oxidation-reduction process is accompanied by a volume change in around 70% [54] that can irreversibly damage the cell. Moreover, nickel is sensitive to potential fuel impurities such as sulfur and all these disadvantages led to a search for more robust alternatives for replacing Ni-cermets. As the anode-supported cell design typically requires a $250\text{-}500 \text{ }\mu\text{m}$ Ni-cermet support, replacing it with a more robust support material less prone to the above-mentioned problems seems sensible. The most likely candidates are the ceramic perovskites (ABO_3) such as titanates [55] or chromites [56] as they present interesting features such as low catalytic activity toward hydrocarbon cracking, chemical and thermal compatibility with the other cell components, insensitivity to fuel impurities such as sulphur [57], [58] and dimensional stability upon oxidation/reduction cycles. Some specific titanate and chromite-based perovskite ceramics are being appreciated as a potential candidate for anode materials in SOFCs as shown in table 1.2.

Among these alternatives, donor doped SrTiO_3 are feasible candidates as anode materials and conductive supports due to the fact that they exhibit metallic conduction when exposed to reducing atmospheres and high temperatures, as Ti^{4+} reduces to Ti^{3+} effectively freeing electrons for conduction and creating oxygen vacancies. The defect chemistry of these materials and, herein their electronic conductivity can be manipulated through appropriate doping. Replacing Sr^{2+} with higher charge cations such as La^{3+} or

Y^{3+} on the A-site is charge compensated most commonly either by introducing extra oxygen (oxygen excess compositions) or by creating A-site vacancies. Titanates can also be doped on the Ti site with elements such as Nb^{5+} or Mn^{4+} to increase their conductivity [59], [60].

Table 1.2: Electrical conductivity of some chromite and titanate based perovskite ceramic materials in reducing atmosphere.

Compositions	Electrical conductivity($S\text{cm}^{-1}$) (Reducing atmosphere)	References
$\text{La}_{0.7}\text{Ca}_{0.3}\text{TiO}_3$	~2.7	Pudmich et al.(2000)
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_{0.5}\text{Ti}_{0.5}\text{O}_3$	~0.02	Pudmich et al.(2000)
$\text{La}_{0.1}\text{Sr}_{0.9}\text{TiO}_3$	~3	Marina et al. (2002)
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$	~1.3	Tao et al. (2003)
$\text{La}_{0.7}\text{Mg}_{0.3}\text{CrO}_3$	~0.17	Jiang et al.(2008)
$\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$	~0.22	Jiang et al.(2008)
$\text{La}_{0.4}\text{Sr}_{0.4}\text{TiO}_3$	~96	Neagu et al. (2010)
$\text{Y}_{0.07}\text{Sr}_{0.895}\text{TiO}_3$	~7–64	Vozdecky et al. (2011)

Cerium incorporation into these materials significantly improved the electrocatalytic activity for hydrogen oxidation, although the presence of ceria/perovskite assemblage was revealed in which a ceria-rich phase enhances this activity [61]–[63]. The robustness of doped strontium titanate ceramic makes it a suitable conductive backbone and the lack of catalytic activity and oxide ion conduction can be compensated by impregnation with an oxide ion conducting electrocatalyst such as ceria [64] and/or with nickel [65].

1.12 Donor-doped SrTiO_3 Systems as Anode Materials

In order to sizeable interest for use in SOFC anodes, donor-doped strontium titanates (Sr_xTiO_3 , where “x” is the dopant as rare earth elements) have been observed to

possess good electrical conductivity [43], [66], [67]. These materials also render several other crucial properties, including chemical inertness when sintered with YSZ and a TEC similar to that of YSZ, which is the main constituent of most SOFCs [68]. Donor (i.e. negatively) doped Sr_xTiO_3 are ceramic materials which have a portion of the strontium or titanium atoms replaced with other elements that contain a greater number of electrons. When Sr^{2+} is doped with rare earth elements such as La^{3+} , Y^{3+} , Sm^{3+} and Dy^{3+} etc., the new materials are called A-site doped Sr_xTiO_3 . In order to achieve the high conductivities observed in the literature, most Sr_xTiO_3 ceramics must first be subjected to a pre-reduction step at a temperature much higher than SOFC operating temperatures [67]. For these materials, the reduced state exhibits conductivities which are two to three orders of magnitude greater than the oxidized state. One disadvantage of this approach is that the good electrical conductivity gained from the reduction step can be lost during the oxidation and reduction cycles encountered during operation, resulting in unacceptable high ohmic losses [43]. Oxidation usually occurs at a lower temperature than reduction, so the normal operating temperatures of SOFCs are often sufficient to partially or fully oxidize the pre-reduced Sr_xTiO_3 . When the anode is exposed to fuel and a reducing atmosphere is re-established, complete re-reduction does not occur at the lower temperature. In fact, a portion of the material remains in the oxidized state decreases the overall conductivity of the material. Therefore, determining whether or not the high extent of reduction can be maintained during exposure to redox cycles at fuel cell operating temperatures becomes a critical factor in deducing the applicability of a specific doped strontium titanate for supplanting Ni-YSZ anodes. Due to the many favorable properties associated with *n*-type Sr_xTiO_3 ceramics, previous attempts have been produced to determine which dopant materials yield high electrical conductivity. A-site lanthanum-doped $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ (LST) and yttrium-doped $\text{Y}_x\text{Sr}_{1-x}\text{TiO}_3$ (YST) have been

extensively studied for SOFC applications [43], [59], [66], [69], [70]. Additionally, it was demonstrated that good SOFC performance can be achieved with a several donor doped SrTiO₃ anode infiltrated with an oxidation catalyst.

1.13 Conduction Mechanism in the SrTiO₃ Perovskite Systems

The electrical conductivity in electro-ceramics is generally a summation of ionic and electronic conductivity that approaches to the applicability of ceramic perovskite materials for SOFC application. Electrical conduction also depends on charge carriers of electrons, holes and oxygen vacancies that can be summarized as the mobility of charge carriers as following Nerst-Einstein relation:

$$\sigma' = ne\mu_e + pe\mu_h + 2e[V_O^{\bullet\bullet}]\mu_{V_O^{\bullet\bullet}} \quad (1.6)$$

where μ_e , μ_h and $\mu_{V_O^{\bullet\bullet}}$ are the mobilities of electrons, holes and oxygen vacancies, respectively. The oxygen vacancies are created at higher temperatures and the electronic carriers are generated due to the charge compensation processes leading to the enhancement in conductivity with increasing temperature [71]. To explain conduction mechanism of SrTiO₃ perovskite systems, numerous defect equations can be considered [72], [73]. These are based on the structural, thermal and/or electrical properties of pure non-stoichiometric oxides, doped-stoichiometric oxides and doped-non stoichiometric oxide systems. The extensive studies have been initiated to determine the conduction progression with the help of defect chemistry that attributed mainly via effect of ionic radius, valence, and concentration.

1.13.1 Ionic Conduction

The ionic conductivity (σ_i) in SrTiO₃ perovskite systems depends mainly upon various factors, such as sample preparation, temperature, dopants concentration, defect

dissociation and oxygen partial pressure etc.. The dependence of ionic conductivity (σ_i) at temperature (T) can be represented by Arrhenius relation

$$\sigma_i T = A \exp\left(-\frac{E_a}{KT}\right) \quad (1.7)$$

where A is pre-exponential factor, K is Boltzmann constant and E_a is activation energy for ionic conduction, respectively. Ionic conductivity for any given material can be explained in terms of charge carrier concentration C_i , ionic mobility μ_i and charge q_i of the charge carriers [74]. This correlation can be given as

$$\sigma_i = C_i q_i \mu_i \quad (1.8)$$

The concentration of oxide ions in terms of oxygen vacancy ($V_o^{\bullet\bullet}$) can be written as

$$C_i = [1 - (V_o^{\bullet\bullet})] N_o \quad (1.9)$$

where N_o is number of oxide ions present in crystal lattice per unit cell volume. The ionic mobility, μ_i with ion diffusivity (D_i) may be expressed by the following Nerst-Einstein relation

$$\mu_i = \frac{q_i D_i}{KT} \quad (1.10)$$

Diffusivity is considered to be a function of activation enthalpy (ΔH_m) and activation entropy (ΔS_m), then a relation of mobility is described by the following relation

$$D_i = a^2 v_o [V_o^{\bullet\bullet}] N_o \exp\left(\frac{\Delta S_m}{K}\right) \left(-\frac{\Delta H_m}{KT}\right) \quad (1.11)$$

where a is jump distance of ion, v_o is vibration frequency of lattice. Since, C_v is represented as:

$$C_v = [V_o^{\bullet\bullet}] \{1 - [V_o^{\bullet\bullet}]\} N_o \quad (1.12)$$

From equations of (1.10), (1.11) and (1.12); Arrhenius relation can be written as the following relation

$$\sigma_i T = A [V_o^{\bullet\bullet}] (1 - [V_o^{\bullet\bullet}]) \exp\left(-\frac{\Delta H_m}{KT}\right) \quad (1.13)$$

where A is a parameter and represented as

$$A = \frac{4e^2}{k} a^2 v_o [V_O^{\bullet\bullet}] N_o \exp\left(\frac{\Delta S_m}{K}\right) \quad (1.14)$$

For less majority of $[V_O^{\bullet\bullet}]$

$$\sigma_i T = A [V_O^{\bullet\bullet}] \exp\left(-\frac{\Delta H_m}{KT}\right) \quad (1.15)$$

This relation is described the temperature dependence ionic conductivity as an exponential function [74].

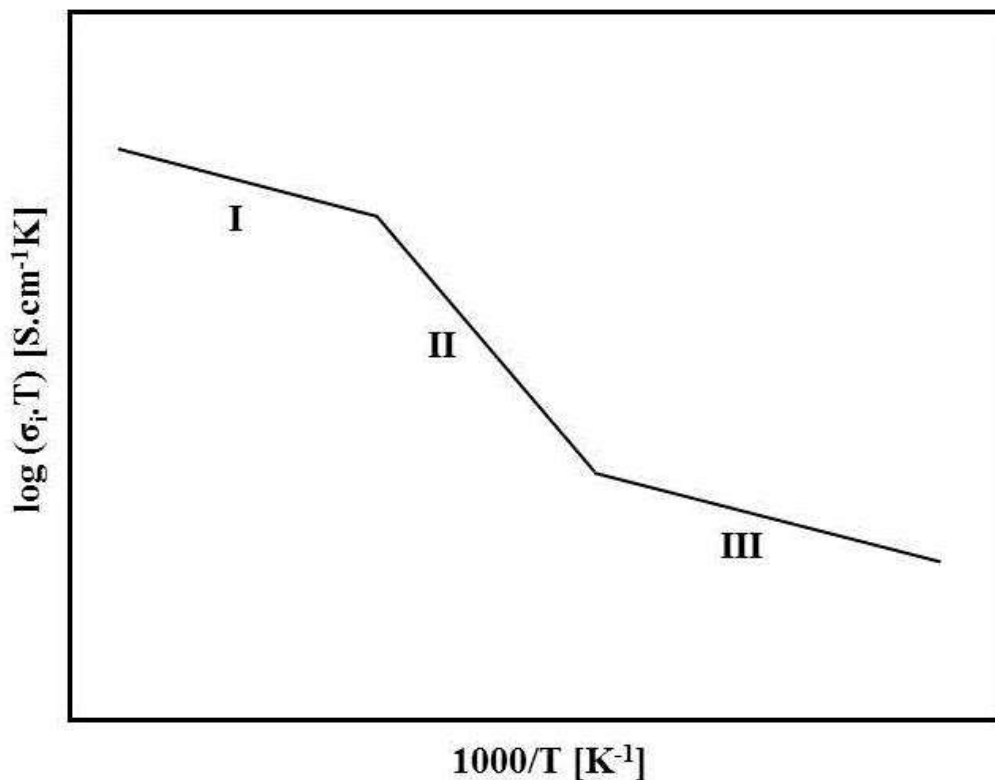


Figure 1.7: A schematic representation of the conductivity behaviour of an oxide ion conductor [75].

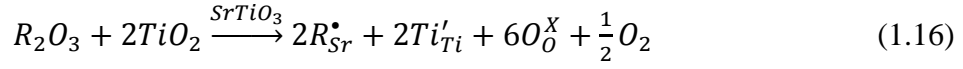
Arrhenius relation (temperature dependence) of the electrical conductivity of doped perovskite oxide cannot be expressed by a single exponential function shown in the equations (1.7), (1.13) or (1.15). Generally, the usual temperature dependence electrical conductivity can be shown in fig.1.7 as three reasonable sections according to Kilner et al. [75]. In first (I) region, which appears at high temperature, the electrical conduction is verified by the intrinsic defects (Schottky or Frenkel) in the crystal lattice. In second (II)

region, electrical conduction is directly governed by the majority of charge-carrying defects occurred by an aliovalent dopant ions or impurity. In third (III) region, as a guideline at low temperatures, the charge carrier's majority carrying defects is determined by the thermodynamic equilibrium between the free defects and the associated pairs. In view of these facts that doped perovskite oxides have a large number of oxygen vacancies, they just have the regions II and III, respectively.

1.13.2 Electronic Conduction

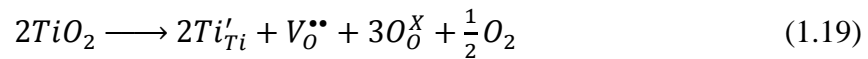
Electronic conduction is the channel of free electrons for all the way through a material. In ceramics materials, the ionic bonds gripping the atoms together do not permit for free electrons. On the other hand, in few impurities cases of different doping valence which possesses different numbers of bonding electrons in the material, and these impurities may act as donors or acceptors of electrons. In cases of rare-earth or transition metal elements of variable valency may be incorporated; such type of impurities may act as centers for polarons species of electrons that make small regions of local polarization as they move from atom to atom. Generally, electronically conductive ceramics are used in applications of resistors, electrodes, and heating elements. Defect chemistry plays a vital role to understand the electronic conduction mechanism from Kröger-Vink notation that illustrates the deviations from stoichiometry. During heating treatment, the sample may be lost oxygen and the oxygen non-stoichiometry which assigned by oxygen vacancies ($V_O^{\bullet\bullet}$). Electronic conduction is studied with similar procedure and formula as ionic that is separated by limit of activation energy. It was also reported that in perovskite structure (ABO_3), B-site transition metal is predominant for electronic conduction [76], [77]. The electronic conduction in $SrTiO_3$ perovskite enhances with trivalent rare earth cation (R^{3+}) doping at a divalent (Sr^{2+}) site.

This can be understood by the following three equations written in the Kröger-Vink notation:



Equation (1.16) accounts for the incorporation of R^{3+} at the Sr-site, with formation of positively charged defects, compensated by electrons or equivalently, by partial reduction of Ti^{4+} to Ti^{3+} . In the second case, eq. (1.17), the incorporation takes place both at Sr- and Ti-sites, with self-compensation of charges. Finally, eq. (1.18) is relevant to the case of incorporation at the Ti-site with formation of negatively charged defects, compensated by oxygen vacancies. It was already reported in case of $BaTiO_3$ [78], the most energetically favourable incorporation mechanism for rare-earth elements like La, Y, Sm and Dy is the self-compensation.

The lattice oxygen may be lost in reducing atmosphere and thus oxygen vacancies will be generated as per the following equation



in order to conserve the electro-neutrality, the following equation must be satisfied.

$$[Ti'_{Ti}] = [R_{Sr}^{\bullet}] + 2[V_O^{\bullet\bullet}] \quad (1.20)$$

Therefore, both extrinsic defects introduced by rare earth element (R) incorporation at Sr-site and intrinsic oxygen vacancies, which are formed under reducing conditions; contribute to the formation of electrons and increase of electronic conductivity.

1.14 The Main Objectives of Research Work

The main emphasis of the present work is to develop cost effective novel anode materials for IT-SOFC with high electrical conductivity at intermediate temperature range. For this purpose, strontium titanate material has been selected as a base material. The prime objective of the present thesis is to understand the electrical conduction mechanism in rare earth doped SrTiO₃ systems and correlate it with the structural characteristics of the systems to make it more suitable as anode materials for IT-SOFC. In order to meet the above objective, the following research work strategies have been planned:

- To synthesize a few series of rare earth elements (i.e. La³⁺, Y³⁺, Sm³⁺ and Dy³⁺) doped perovskite (SrTiO₃) anode materials by solid state reaction and chemical reaction routes.
- To study the phase formation and crystal structure of the prepared anode materials using powder X-ray diffraction technique.
- To determine the density and porosity of sintered samples using Archimedes' principle.
- To study effect of doping on temperature dependence conductivity behavior of prepared samples of various series using complex plane impedance spectroscopy with two and four probe methods.
- To study the microstructure employing field emission scanning electron microscopy (FESEM) and its correlation to the conduction mechanism.
- To study the oxidation state of the ions and oxygen vacancies by X-ray photoelectron spectroscopy (XPS) and its effect on the conduction mechanism.

- To investigate the temperature dependent electrical conductivity of a few promising candidate in hydrogen atmosphere.
- To study the conduction mechanism of various rare earth doped SrTiO₃ with defect chemistry.