

This thesis represents a culmination of work and better understanding in the field of solid oxide fuel cell (SOFC) that has taken place in the last couple of years. Energy markets are dominated by a substantial increase in energy demand due to the strong economic growth in the developing countries in all over the world. Ecological degradation and limited fossil fuel have compelled the governments and industries around the world into considering renewable energy technologies as alternatives to fossil fuels for power and electricity production. Elimination of pollutants, pollution of air by releasing toxic gases and compounds, and the groundwater by leaking fuel tanks with toxic-fuel additives (used to reduce pollutants) are also the subject of concern. Alternate energy resources are considered a long-term solution to the world's future energy demands, as they are environment-friendly and independent of our declining limited natural resources. All the issues that are associated with the burning of fossil fuels and hydrocarbon fuel sources can be under control by the fuel cells. Among the available renewal energy resources, a fuel cell is an emerging field for power production.

A fuel cell is an electrochemical device that converts chemical energy into electrical energy by utilizing the natural tendency of oxygen and hydrogen to react. Fuel cells are classified on the basis of electrolytes and operating temperatures. Among the various fuel cell technologies, SOFC utilizes the solid ceramic oxide components and is an important energy conversion device that generates electrical power by continuously converting chemical energy of fuel into electrical energy along with high energy conversion efficiency. There are mainly three components of SOFC: Anode, Cathode and Electrolyte.

In the present research work, the development of ceramic perovskite materials as anode for intermediate temperature solid oxide fuel cell (IT-SOFC) has been selected for

further investigation. Anode material is an essential component of SOFCs which exhibits high electrical conductivity in both atmospheres namely oxidizing and reducing. There are four primary requirements as given below, that any anode material in a SOFC must exhibit.

- The material must be porous enough to allow fuel to flow towards the electrolyte.
- The material must possess electronic conductivity to transport electrons throughout the electrode and the external circuit.
- It must have ionic conductivity too so that the O^{2-} anions are able to migrate throughout the electrode.
- Catalytic activity is necessary in order to facilitate the dissociation of oxygen and the oxidation of fuel.

However, in anode material, ions coming from the electrolyte flow through the anode and combine with fuel (H_2) and release electrons at the region where the last three properties meet. It is often referred to as the triple phase boundary (TPB). Therefore, the large triple phase boundary is also required for anode materials for SOFC application. Further, an anode should have compatible thermal expansion coefficient (TEC) to that of other components of SOFC with the chemical stability.

On the basis of the above requirements, perovskite oxide with structure ABO_3 is of great interest of research for their wide applicability in various device applications such as anode materials for solid oxide fuel cells. Therefore, in the investigation of low cost and widely stable materials, perovskite structured $SrTiO_3$ has also been proposed as a potential anode for SOFCs under doping with rare earth elements. Its electronic conductivity is sufficient for the use as an anode at operating temperature of SOFC. This material offers not only high electronic conductivity but also optimum ionic conductivity.

Thus, SrTiO₃ with suitable doping has been proposed as promising nickel-free anode material for solid oxide fuel cell to resolve the issue of carbon and sulphur tolerance.

In order to synthesize SrTiO₃ based anode materials, solid state reaction and chemical reaction routes have been opted. Citrate-nitrate auto-combustion method of chemical reaction route is very important synthesis techniques over others to get particle in nano range and to reduce operating temperature. Structural, microstructural and elemental analyses have been carried out using XRD, FESEM and XPS techniques. Differential impedance analysis technique has been implemented to study the electrical behaviour and to understand the conduction mechanism.

In order to enhance the conductivity of SrTiO₃, it was planned to synthesize doped SrTiO₃ at Sr-site with various rare earth elements (i.e. La, Y, Sm, and Dy). It is reported that the acceptor doping in the perovskite materials enhances the ionic conductivity whereas, the donor doping increases the electronic conductivity. Various rare earth element ions (i.e. La³⁺, Y³⁺, Sm³⁺ and Dy³⁺) 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 between Ti⁴⁺ and Ti³⁺ that also occurs in the system contributes to improving the electrical conductivity under reducing atmosphere and shows an n-type semiconducting behaviour.

The main emphasis of the present work is to develop cost effective novel anode materials for IT-SOFC with high 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 SrTiO_3 systems and correlate it with the structural characteristics of the systems to make it more suitable as anode materials for IT-SOFC.

The present thesis is divided into seven chapters as per the brief description given below:

Chapter-1 of this thesis illustrates motivation of the work, backgrounds of solid oxide fuel cell (SOFC), essential requirements of the anode for SOFC, present scenario of ceramic-perovskite anodes, strontium titanate based anode materials on the basis of the literature survey. This chapter includes also the main objectives of the present work.

Chapter-2 represents the details of the employed experimental instruments and analysis techniques. Solid state reaction and chemical reaction technique were used to synthesize the rare earth doped SrTiO_3 systems. A detailed description of the employed instruments like XRD, FESEM, XPS and Impedance Spectroscopy etc. along with important analysis techniques like Rietveld refinement, differential impedance analysis have been discussed in this section.

Chapter-3 describes the large polaron hopping phenomenon in La-doped SrTiO_3 anode material with a few compositions of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_{3-\delta}$ (with $x = 0.0, 0.1, 0.2, 0.3,$ and 0.4) system which were synthesized via solid state reaction route. In order to study the conduction mechanism, the conductivity spectra of the system at different temperatures have been analyzed using Jonscher's power law and Ghosh scaling model along with the experimental verification of small and large polaron conduction using polaron tunneling model.

Chapter-4 describes the structural and electrical conduction behaviour of Y-doped SrTiO_3 anode material for SOFC application in which $\text{Y}_x\text{Sr}_{1-x}\text{TiO}_{3-\delta}$ (with $x = 0, 0.03, 0.05, 0.08$ and 0.1) compositions were synthesized via citrate-nitrate auto-combustion route. In order to propose the promising anode, the electrical conductivity and phase stability in air and hydrogen atmospheres were investigated through electrochemical

impedance spectroscopy and XRD measurements with corresponding FESEM micrographs, respectively.

Chapter-5 describes the conduction mechanism in Sm-doped SrTiO₃ anode for SOFCs along with correlation between structural and electrical properties. The various compositions of Sm_xSr_{1-x}TiO_{3-δ} (with x = 0.05, 0.15 and 0.2) system were synthesized by citrate-nitrate auto-combustion route. The effect of Sm³⁺ doping on electrical conductivities was studied for promising anode. The conductivity spectra of the system at different temperatures have been analyzed using Jonscher's power law and conduction mechanism has been explained qualitatively in terms of scaling behaviour.

Chapter-6 describes the structural and electrical properties of Dy-doped SrTiO₃ as a promising anode material for SOFCs. In this chapter, Dy_xSr_{1-x}TiO_{3-δ} (with x = 0.03, 0.05, 0.08 and 0.1) compositions were synthesized by citrate-nitrate auto-combustion route. To understand the effect of Dy-content, anodic properties are measured in both air and hydrogen atmosphere, and explained in terms of defect chemistry.

Chapter-7 describes the summary of the present thesis and future perspectives of the present research work. It has been concluded that SrTiO₃ based materials are cost effective and highly conductive and found that their suitability as an anode material for Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs).