

STUDY OF SrTiO_3 BASED ANODE MATERIALS FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELL



Thesis submitted in partial fulfillment for the
Award of Degree
Doctor of Philosophy

by

Saurabh Singh

DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY)
VARANASI- 221005

Roll No: 13171005

July, 2018

7.1 Conclusion of the Present Investigation

The primary goal of this research work was the study of conduction mechanism in SrTiO₃ based materials and development of promising anode for Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs). Undoped SrTiO₃ cannot be used as anode due to its low electrical conductivity. Therefore, it was planned to synthesize and study various rare earth element doped SrTiO₃ systems and to check their suitability as an anode material for IT-SOFC. The chemical stability, structural and micro-structural characteristics of the investigated systems have been explored in correlation to electrical conductivity, which are the necessary requirements for the anode materials. The conductivity spectroscopy and impedance spectroscopy techniques were employed to explain the electrical conductivity behaviour. On the basis of result obtained, the whole thesis has been summarized as:

1. The structural, micro-structural and electrical properties of La_xSr_{1-x}TiO_{3-δ} (with x = 0, 0.1, 0.2, 0.3 and 0.4) system have been studied. The conductivity spectra at the measured temperatures of this system were explained by using Jonscher's power law and Ghosh scaling model. The remarkable change in conduction mechanism has been observed on the basis Polaron tunnelling model for the compositions. Therefore, undoped SrTiO₃ and La-doped SrTiO₃ demonstrated small polaron and overlapping large polaron conduction mechanism, respectively. The composition La_{0.1}Sr_{0.9}TiO₃ was found to exhibit highest electrical conductivity among the other compositions. Thus, the composition La_{0.1}Sr_{0.9}TiO₃ may be proposed as a promising anode for IT-SOFCs.
2. The structural and electrical conduction behaviour in air and hydrogen atmospheres were studied for the compositions Y-doped SrTiO₃ i.e., Y_xSr_{1-x}TiO_{3-δ} (with x = 0.03, 0.05

and 0.10). The composition $Y_{0.08}Sr_{0.92}TiO_3$ was found to be highly porous i.e. 34% which may provide large triple phase boundary region for the electrochemical reactions. Different incorporation mechanisms have been explained by defect chemistry. To check the chemical stability of the compositions, the XRD measurement and FESEM micrographs have been studied for all reduced (H_2 atmosphere) samples. Therefore, found that composition $Y_{0.08}Sr_{0.92}TiO_3$, among all the investigated compositions, is the most favourable candidate as an anode material for IT-SOFC with good chemical stability and high electrical conductivity in hydrogen atmosphere.

3. The conduction mechanism for the systems $Sm_xSr_{1-x}TiO_{3-\delta}$ (with $x = 0.05, 0.15$ and 0.20) have been studied on the basis of structural and electrical properties. The conductivity spectra of the systems at different temperature have been analysed using Jonscher's power law and scaling behaviour. The composition $Sr_{0.15}Ti_{0.85}O_3$ exhibits high electrical conductivity with excellent chemical stability in hydrogen atmosphere. Hence, the composition $Sr_{0.15}Ti_{0.85}O_3$ may be considered as a suitable anode material in reducing atmosphere.

4. Dy-doped $SrTiO_3$ i.e., $Dy_xSr_{1-x}TiO_{3-\delta}$ (with $x = 0.03, 0.05, 0.08$ and 0.10) systems have been investigated and reported as suitable candidate for anodic materials. The effect of Dy on $SrTiO_3$ was explained in terms of defect chemistry by considering different incorporation mechanisms for different amounts of Dy with electron compensation. Anodic properties of these systems have been measured in both air and hydrogen atmosphere and found that the conductivity is predominantly electronic type for $x \leq 0.05$, becomes ionic for $x \geq 0.08$ in air. It is observed that, for all the compositions the conductivity increased and activation energy decreased in hydrogen atmosphere than that of air atmosphere. The composition $Dy_{0.08}Sr_{0.92}TiO_3$ was found to limited degradation

with high electrical conductivity in hydrogen atmosphere. Therefore, $\text{Dy}_{0.08}\text{Sr}_{0.92}\text{TiO}_3$ may be considered as a promising anode material for IT-SOFCs.

5. In the present thesis, the electrical conductivities of Y, Sm and Dy doped SrTiO_3 compositions were measured in the temperature range of 400-700 °C under hydrogen atmosphere. Among the promising anodes, the comparison of electrical conductivities at 650 °C in hydrogen is shown in fig. 7.1. Therefore, 8 mol% Dy-doped SrTiO_3 may act as the best anode material for IT-SOFCs due to highest electrical conductivity with good chemical stability among the other proposed promising anodes.

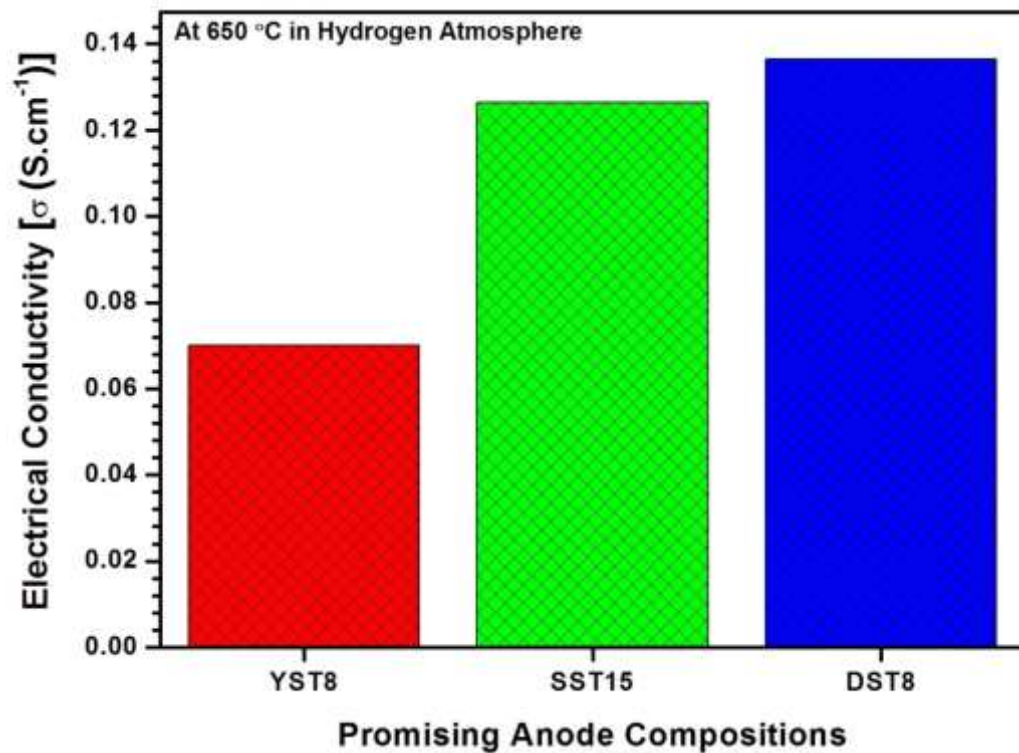


Figure 7.1: The comparative electrical conductivity of promising anodes at 650 °C in hydrogen atmosphere.

7.2 New Directions and Future Perspectives

The main requirements of anode materials for IT-SOFC such as porosity, chemical and thermal stability and electrical conductivity depend on their synthesis route and dopant concentrations. The microstructure is quite sensitive to the processing variables such as sintering temperature, atmosphere used during sintering, processing routes and

also the amount of extra phase infiltration. Therefore, a detailed study on the effect of these processing parameters on the structural, microstructural, chemical and electrical properties of the investigated compositions is required. Furthermore, the following objectives may also be considered for future perspectives.

1. The other cost-effective anode materials may be considered in perspective of improved electrical conductivity, performance, chemical and thermal stability and most importantly their operation at intermediate temperature range.
2. Thermal and chemical stability of the materials should be verified in different reducing atmosphere for their applications as anode material.
3. The thermal expansion coefficient of all the prepared compositions can be measured to see their compatibility with the other components in solid oxide fuel cell.
4. The performance of the optimized anodes may be checked their compatible with electrolytes and cathodes.
5. The conductivity behaviour of the sample at different reducing atmosphere should be studied to know the stability of the materials.
6. The measurement of transference number is an important factor to confirm both electronic and ionic contribution of conductivity.
7. The reducing stage performed was not sufficient to get equilibrium in dense perovskite materials, therefore, the porosity can be further increased by incorporation of A-site deficiency like $(R_xA_{1-x})_{1-y}BO_3$ and B-site deficiency like $R_xA_{1-x}B_{1-y}O_3$.