

# Preface

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Currently, we are facing dual challenge caused by ever increasing energy demand and environmental pollution due to fossil fuel burning with consequent greenhouse effect. Thus the need to explore advanced energy conversion and storage technologies is the most demanding research area [Steele et al., 2001; Chu et al., 2012; Ding et al., 2014]. Solid oxide fuel cells (SOFCs) are such kind of energy conversion devices, which transform chemical energy of fuel to electrical energy, with added advantages of high energy conversion efficiency, environmental compatibility and extensive fuel flexibility [Wachsman et al., 2011]. As a promising sustainable technology, solid oxide fuel cells are believed to be clean, highly efficient and environment-friendly alternative source of energy. In recent years, SOFCs have attracted extensive research interest among the existing fuel cell technologies due to their high efficiency, multi fuel compatibility, and low polluting emissions [Facci et al., 2017; Sun et al., 2017; Bi et al., 2017; Cebollero et al., 2017]. However, even with these advantages, a market development and commercialization of these devices have been mostly hindered by high operating temperature which brings several issues like fast material degradation and compatibility challenges in cell components [Steele et al., 2001; Jiang et al., 2008; Schrödl et al., 2015; Lee et al., 2010]. The traditional SOFCs mainly consist of a high oxide ion conducting electrolyte, “mixed ionic-electronic conducting” cathode and a porous anode. Use of expensive materials in cell components for high operating temperature range and associate high cell production cost poses major hindrance in commercialization of SOFC technology [Brett et al., 2008; Gao et al., 2016; Duan et al., 2015; Liu et al., 2017; Zhang et al., 2017; Fan et al., 2018]. Solid electrolyte having high oxide ion conduction with low operating temperature is one of the main requirements for the commercialization of SOFCs. Development of advanced cathode materials with high performance of oxygen reduction reaction (ORR) at intermediate/low temperatures is another important

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requirement for the commercialization of SOFCs at large scale. There is a need to develop electrolyte and electrode materials of SOFCs having lower thermal expansion coefficients (TECs) and favourable compatibility with SOFC components along with reduced operating temperature, cost effectiveness and easy fabrication processing. In this Ph.D. thesis, I have tried to address these two important concerns by development of new electrolyte and electrode materials. I have mainly focused on materials with the fluorite and perovskite structures for potential application in electrolyte and electrode for solid oxide fuel cells. The broad objectives of this thesis work are following:

- To develop novel ceria based electrolytes by co-doping of cheaper elements, and to investigate the effects of co-doping on structural, morphological and conductivity properties of the materials.
- Investigation for selection of suitable dopants and sintering aids with optimum concentration on co-doping scheme in cerium oxide to improve its conduction behavior at relatively lower temperatures.
- To develop composite ionic conductors as solid electrolyte for low temperature LT-SOFCs and study the role of microstructure and defect clusters on ionic conductivity and charge transport properties of the developed materials.
- Investigation of the influence of A- and B-site co-doping on the chemical and electrical properties of cobalt free  $ABO_3$  perovskite-type cathode for intermediate temperature IT-SOFCs.

To achieve above objectives, a series of compositions of  $Ga^{3+}$  and  $Cu^{2+}$  co-doped ceria within system  $Ce_{0.8}Ga_{0.2-x}Cu_xO_{2-\delta}$  (for  $x=0.00, 0.05, 0.10, 0.15,$  and  $0.20$ ) are synthesized and the effects of co-doping on structural, morphological and conductivity properties of the materials are investigated. Further, the effect of addition of different content of alkali carbonates  $(Li_{0.52}Na_{0.48})_2CO_3$  (LNC) on structure, morphology, ion

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conductivity and charge transport properties of tri-doped ceria  $\text{Ce}_{0.76}\text{Pr}_{0.08}\text{Sm}_{0.08}\text{Gd}_{0.08}\text{O}_{2-\delta}$  (CPSG) electrolyte are studied. The role of microstructure and space charge layer formation on ionic conductivity and charge transport properties of materials are evaluated. Subsequently, later part of the thesis is dedicated to investigate the chemical, thermal and electrical properties of A- and B-site co-doped cobalt free  $\text{SrFeO}_3$  perovskite structured cathode for IT-SOFCs. The important findings resulting from the present thesis work is briefly described below:

**(i) Structural, Morphological, and Electrical Properties of  $\text{Ga}^{3+}$  and  $\text{Cu}^{2+}$  co-doped Ceria Ceramics as Solid Electrolyte for IT-SOFCs**

The composition of  $\text{Ga}^{3+}$  and  $\text{Cu}^{2+}$  co-doped ceria within system  $\text{Ce}_{0.8}\text{Ga}_{0.2-x}\text{Cu}_x\text{O}_{2-\delta}$  (for  $x=0.00, 0.05, 0.10, 0.15,$  and  $0.20$ ) were synthesized by using most feasible auto combustion method. The powder XRD measurement along with Rietveld structure analysis of all the co-doped systems were carried out to confirm the formation of the crystalline cubic fluorite structure like cerium oxide with Fm-3m space group. Various characterization techniques were used to analyze the developed samples which reveal attractive properties for SOFC applications. The impedance spectroscopy measurement reveals that the  $\text{Ce}_{0.8}\text{Ga}_{0.05}\text{Cu}_{0.15}\text{O}_{1.825}$  electrolyte sintered for 4 hrs at  $1300^\circ\text{C}$  exhibit the highest ionic conductivity ( $\sigma_{700^\circ\text{C}} = 2.03 \times 10^{-2} \text{ S cm}^{-1}$ ) with least activation energy of conduction ( $E_a = 0.62 \text{ eV}$ ) among all the compositions. The observed experimental results reveals that the addition of  $\text{Cu}^{2+}$  in ceria ceramic promotes the formation of oxygen vacancies and helps in providing the additional oxygen ion transport path resulting in the superior ionic conductivity.

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**(ii) Space charge layer induced superionic conduction and charge transport behaviour of “alkali carbonates and tri-doped ceria nanocomposites” for LT-SOFCs applications**

The effect of addition of alkali carbonates ( $(\text{Li}_{0.52}\text{-Na}_{0.48})_2\text{CO}_3$  (LNC)) on structure, microstructure, conductivity and ion transport properties of  $\text{Ce}_{0.76}\text{Pr}_{0.08}\text{Sm}_{0.08}\text{Gd}_{0.08}\text{O}_{2-\delta}$  (CPSG) nanocrystalline electrolyte materials have been investigated to explore the most promising performance at lower as well as intermediate temperature ranges. The most remarkable outcome of present work is the formation of core-shell like structural morphology between ceria and alkali carbonates facilitating induced space charge layer, which provides the extra path and direct the mobile charge carrier groups to their preferred conduction paths in the composite electrolyte. The frequency dependent dielectric loss as well as real part of complex ac-conductivity confirms the existence of low frequency interfacial/space-charge layer polarization process along the grain boundary regions and multi-ion conduction leading to long-range conduction mechanism along the interface region. The 65CPSG-35LNC nanocomposite is recommended to be a commercial alternative of the solid oxide electrolytes having improved ionic conductivity for low/intermediate temperature solid oxide fuel cells.

**(iii) Development of Cobalt-free  $\text{SrFe}_{0.8}\text{Mo}_{0.1}\text{W}_{0.1}\text{O}_3$  Perovskite Structured Cathode for SOFCs Applications**

We successfully synthesized Mo and W co-doped  $\text{SrFeO}_3$  based perovskite,  $\text{SrFe}_{0.8}\text{Mo}_{0.1}\text{W}_{0.1}\text{O}_3$  [SFMW] by applying high energy ball milling method as the cathode for solid oxide fuel cells (SOFCs). Rietveld structural analysis of X-ray diffraction (XRD) pattern reveals the single phase cubic structure with  $Pm-3m$  space group. The SEM characterization of calcined sample reveals porous, homogeneous nature as well as the good particle connectivity in microstructure. The SFMW cathode shows no further

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chemical reactivity with the oxide ion conductor electrolyte  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_2$  (SDC) and proton ion conductor electrolyte  $\text{BaCe}_{0.8}\text{Sn}_{0.2}\text{O}_3$  (BCS) even after heat treating with them at  $1200^\circ\text{C}$  for 6h. The average thermal expansion coefficient (TEC) of SFMW sample is  $16 \times 10^{-6} \text{ K}^{-1}$  between room temperature to  $1000^\circ\text{C}$ . The activation energy  $E_a$  for SFMW sample was found to be 0.32 eV which suggests the existence of mixed ionic-electronic conductivity in the developed material. The SDC electrolyte-supported symmetrical cell was fabricated and the value of area specific resistance is found to be  $1.67 \Omega\text{-cm}^2$  with activation energy 1.13 eV. The performance demonstrates that  $\text{SrFe}_{0.8}\text{Mo}_{0.1}\text{W}_{0.1}\text{O}_3$  is a potential candidate as a cathode material for IT-SOFCs.

This thesis is organized into six chapters as summarized below.

**Chapter 1** gives a general idea of the subject matter and introduction to some basic concepts about fuel cells, types of fuel cells, with special emphasis on solid oxide fuel cells (SOFCs) and its working principle. Afterward, a brief literature review on present status in the field is discussed. The kind of improvements still needed for large scale-up production of SOFCs is discussed. Then, an introduction of ‘characteristics and main properties’ of generally used cell components in SOFCs is presented. Afterward, a detailed literature survey on advancement in functional solid electrolytes along with various aspects and deep insight into the current progress regarding ceria based solid electrolytes is discussed. Subsequently, a brief literature survey based on cobalt free cathode material is also discussed.

**Chapter 2** describes the synthesis method for the prepared samples and different experimental techniques which have been used for the characterizations of developed materials. The main techniques which have been employed for characterizations are Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD) and Energy Dispersive Spectroscopy (EDX) for the morphological and

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structural investigations. For thermal analysis of the Samples TG-DTA is used. The electrical characterization of the samples has been done using Impedance analyzer.

**Chapter 3** describes the results of our investigation on the Ga<sup>3+</sup> and Cu<sup>2+</sup> co-doped ceria electrolyte. A series of co-doped ceria based electrolyte consisting Ga<sup>3+</sup> and Cu<sup>2+</sup> within system Ce<sub>0.8</sub>Ga<sub>0.2-x</sub>Cu<sub>x</sub>O<sub>2-δ</sub> (for x=0.00, 0.05, 0.10, 0.15, and 0.20) were synthesized by using most feasible auto combustion synthesis method. The powder XRD measurements followed by Rietveld structural analysis of all electrolyte samples were done using cubic fluorite structure in *Fm-3m* space group. The thermal and microstructural characterization the samples have been done to evaluate the potential properties for SOFC applications. The temperature dependent ac-impedance spectroscopy measurement in air for all electrolyte samples reveals that the composition Ce<sub>0.8</sub>Ga<sub>0.05</sub>Cu<sub>0.15</sub>O<sub>1.825</sub> shows the highest value of ionic conductivity ( $\sigma_{700^\circ\text{C}} = 2.03 \times 10^{-2} \text{ S cm}^{-1}$ ) having least value of activation energy for conduction ( $E_a = 0.62 \text{ eV}$ ) among the all prepared compositions. The experimental outcomes of this chapter reveals that the incorporation of Cu<sup>2+</sup> cation in ceria based electrolyte via co-doping approach promotes the generation of oxygen vacancies and helps in providing the extra oxygen ion transport path causing in the superior oxygen ion conductivity. This work is published in Int. J. Hydrogen Energy. 2019 45 (44) 24014-24025, <https://doi.org/10.1016/j.ijhydene.2019.09.084>.

**Chapter 4** presents the results of our investigation on the role of addition of different weight ratio of alkali carbonates (Li<sub>0.52</sub>Na<sub>0.48</sub>)<sub>2</sub>CO<sub>3</sub> (LNC) on the structure, morphology, ionic conductivity and charge transport behaviour of tri-doped Ce<sub>0.76</sub>Pr<sub>0.08</sub>Sm<sub>0.08</sub>Gd<sub>0.08</sub>O<sub>2-δ</sub> (CPSG) nanopowder electrolyte materials for low/intermediate temperature SOFCs. Formation of ceria-carbonate core-shell like structural morphology that provides induced space charge layer, facilitating the extra pathways in the nanocomposite electrolyte and

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providing the pathways to mobile charge carrier groups for their preferred conduction paths is the most significant results of this chapter. The temperature dependent frequency variation of dielectric loss as well as real part of complex ac-conductivity reveal the existence of interfacial/space-charge layer polarization process along the grain boundary region in low frequency and multi-ion conduction causing long-range charge transport mechanism along the interface region. The 65CPSG-35LNC nanocrystalline composite, developed in this work with better ionic conductivity for low/intermediate temperature is proposed to be a commercial alternative of the existing solid electrolytes. This work is published in *Ceramics International* 2020 1 (47) 1218-1228, <https://doi.org/10.1016/j.ceramint.2020.08.241>.

**Chapter 5** describes the results of our investigation on novel cobalt free cathode material based on perovskite SrFeO<sub>3</sub>. The Mo and W co-doped SrFeO<sub>3</sub> cubic perovskite samples of SrFe<sub>0.8</sub>Mo<sub>0.1</sub>W<sub>0.1</sub>O<sub>3</sub> (SFMW) was successfully synthesized by applying high energy ball milling method for solid oxide fuel cells cathode applications at lower temperatures. Rietveld structural analysis of X-ray diffraction (XRD) data confirms the single phase with cubic perovskite structure (space group, *Pm-3m*). The SEM characterization of the calcined sample exhibits porous, uniform, homogeneous nature as well as the good particle connectivity and sintered sample shows dense microstructure. We found that SFMW powder sample shows no chemical reactivity with the oxide ion conductor electrolyte Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>2</sub> (SDC) and proton ion conductor electrolyte BaCe<sub>0.8</sub>Sn<sub>0.2</sub>O<sub>3</sub> (BCS) even after heating up to 1200°C for 6h. The average TEC of SFMW sample is obtained to be 16×10<sup>-6</sup> K<sup>-1</sup> between RT to 1000°C. The activation energy E<sub>a</sub> for sample SFMW was found to be 0.32 eV which suggests the existence of mixed ion-electronic conductivity in the material. Then, SDC electrolyte-supported symmetrical cell was

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fabricated and the value of area specific resistance is found to be  $1.67 \text{ } \Omega\text{-cm}^2$  with activation energy for conduction as 1.13 eV. The performance of cathode material  $\text{SrFe}_{0.8}\text{Mo}_{0.1}\text{W}_{0.1}\text{O}_3$  demonstrates that it can be potential candidate for IT-SOFCs.

**Chapter 6** summarises the conclusive remarks and lists future prospects on the subject matter.