



## **Summary and future work**

### 6.1 Summary

In this thesis, I have tried to develop superior electrolyte and electrode materials for SOFCs applications having lower thermal expansion coefficients (TECs) and favourable compatibility with SOFC components along with reduced operating temperature, cost effectiveness and easy fabrication processing. For electrolyte applications, a series of compositions of Ga<sup>3+</sup> and Cu<sup>2+</sup> co-doped ceria within 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) system were synthesized and the effects of co-doping on structural, morphological and conductivity properties of the materials were investigated. The second electrolyte system investigated in the present thesis is alkali carbonates (Li<sub>0.52</sub>-Na<sub>0.48</sub>)<sub>2</sub>CO<sub>3</sub> (LNC)-tri-doped ceria 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) nanocomposites synthesized in various weight fractions. The effect of addition of different content 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 properties of tri-doped ceria 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) electrolyte nanocomposite were examined. The role of microstructure and space charge layer formation on ionic conductivity and charge transport properties of the nanocomposite electrolyte is systematically studied. Additionally, for intermediate temperature IT-SOFCs cathode applications, Mo and W co-doped SrFeO<sub>3</sub> based perovskite structured composition is developed and investigated in detail.

The important findings resulting from the present thesis work is summarized below:

**(i) Structural, Morphological, and Electrical Properties of Ga<sup>3+</sup> and Cu<sup>2+</sup> co-doped Ceria Ceramics as Solid Electrolyte for IT-SOFCs**

High quality samples of Ga<sup>3+</sup> and Cu<sup>2+</sup> co-doped ceria 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 along with Rietveld

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analysis of all the co-doped systems were carried out to confirm the formation of the crystalline cubic fluorite structure of cerium oxide with Fm-3m space group. Then various characterization techniques were used to analyze the samples which reveal attractive properties of this system 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 the all compositions. The 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.

**(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 the structure, microstructure, conductivity and ion transport properties of nanocrystalline  $\text{Ce}_{0.76}\text{Pr}_{0.08}\text{Sm}_{0.08}\text{Gd}_{0.08}\text{O}_{2-\delta}$  (CPSG) electrolyte materials have been investigated to exhibit the most promising performance at lower as well as intermediate temperature ranges. The most remarkable outcome of the present work is the formation of core-shell like structural morphology between doped ceria and alkali carbonates facilitating induced space charge layers which provide 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 region and multi-ion conduction leading to long-range conduction mechanism along the interface region. The 65CPSG-35LNC nanocomposite

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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 SrFe<sub>0.8</sub>Mo<sub>0.1</sub>W<sub>0.1</sub>O<sub>3</sub> Perovskite Structured Cathode for SOFCs Applications**

We successfully synthesized Mo and W co-doped SrFeO<sub>3</sub> based perovskite structured, SrFe<sub>0.8</sub>Mo<sub>0.1</sub>W<sub>0.1</sub>O<sub>3</sub> [SFMW] by applying high energy ball milling method for solid oxide fuel cell cathode applications. Rietveld structural refinement of X-ray diffraction (XRD) pattern reveals single phase with cubic structure (*Pm-3m*). The SEM image of calcined sample exhibits porous, homogeneous nature as well as the good particle connectivity. The developed SFMW cathode shows no further 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 heat treating with them at 1200°C for 6 hours. The average thermal expansion coefficient (TEC) of SFMW sample is  $16 \times 10^{-6} \text{ K}^{-1}$  between room temperature to 1000°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 material. The SDC electrolyte-supported symmetrical cell was fabricated and characterized that gives the value of area specific resistance as  $1.67 \text{ } \Omega\text{-cm}^2$  with activation energy to be 1.13 eV. This performance demonstrates that SrFe<sub>0.8</sub>Mo<sub>0.1</sub>W<sub>0.1</sub>O<sub>3</sub> can be a potential candidate of cathode material for IT-SOFCs.

### **6.2 Suggestions for future work**

My investigations on developed electrolyte and electrode materials in this work have resulted into promising properties for SOFC applications. There are many things that needs to be looked into in future investigations. Few important suggestions of further work on the developed electrolyte and electrode systems are listed below:

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- The performance of the developed electrolyte materials should be tested in actual configuration of SOFCs.
  - Ionic conductivity of electrolyte material also depends on partial pressure of oxygen. The conductivity of prepared electrolytes should be examined under various atmospheric conditions to find out the pressure range in which the conductivity is pure ionic.
  - To ionic conductivity of developed electrolytes should be also examined by the measurement of transference number.
  - The performance of the developed  $\text{SrFe}_{0.8}\text{Mo}_{0.1}\text{W}_{0.1}\text{O}_3$  cathode material should be tested in actual configuration of SOFCs.
  - The developed cathode material shows mixed ionic electronic conductivity and it can also work as anode material. To study its potential use as anode material, conductivity measurement in wet air, electrochemical performance and I-V measurement of symmetrical cells with various electrolyte materials can be investigated in future.
  - In future, it would be interesting to perform EIS measurements at room and lower temperatures also on the  $\text{Ga}^{3+}$  and  $\text{Cu}^{2+}$  co-doped Ceria samples. The analysis and modeling of the EIS spectra will help to understand the contributions from grain, grain boundaries and interfaces at lower temperatures. This may give additional insight into the contributions from different sources to the conductivity and activation energy.
  - EIS measurements at lower temperatures on Alkali Carbonates and tri-doped Ceria Nanocomposites samples can also be done in future to determine contributions from grain, grain boundaries, and interfaces. It could help elucidate on the space-charge contribution to conductivity at lower temperatures.

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- Hall measurements and transference number studies can also be performed in future on the samples investigated in the thesis. It will help to understand in more detail the conduction mechanism in the developed materials.