Synthesis and Characterization of ceria co-doped with Samarium(Sm) and Antimony: a potential candidate as a solid electrolyte for intermediate temperature solid oxide fuel cells

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Abstract. The huge potential of solid oxide fuel cells (SOFCs) in providing a clean and reliable energy source has ignited enormous interest in them. The electrolyte is one of the key components of SOFC. Samarium doped ceria oxide is one of the promising materials as an electrolyte for IT-SOFCs. In this paper, ceria co-doped with samarium and antimony have been prepared and characterized to be used as solid electrolyte for intermediate temperature fuel cells. The composite was prepared by Solid state reaction and the effect of sintering temperature on the microstructure for a new composite based on ceria were studied. All samples were characterized using X-ray diffraction, Scanning electron microscope, FTIR, Atomic Force Microscope and Impedance Spectroscopy. Results of analysis of the structural and electrical properties of the present composite indicate that present research is good as a solid electrolyte for IT-SOFCs.

1. Introduction

Solid Oxide Fuel Cells are currently generating enormous worldwide interest due to their widespread application in power generation systems [1]. Yttrium stabilized Zirconia has been favored by researchers traditionally due to its higher ionic conductivity at its high operating temperature around 1000°C. The high operating temperature limits its application due to its degraded solid oxide fuel cell application at its low operating temperature. However, this drawback can be overcome by using electrolyte operating at moderate temperature [2]. In this context, doped ceria emerged as potential candidate operating at intermediate temperature [3]. Minimum dopant level is the main factor, which stabilizes the high temperature cubic face centered (FCC) phase which in turn results in higher conductivity. Ceria Oxide has a cubic fluorite structure with their ability to get reduced from Ce³⁺ to Ce²⁺ at elevated temperature. This leads to formation more oxygen vacancies needed for higher ionic conductivity at moderate temperature [4]. Various dopant such as Sm³⁺, Dy³⁺, Y³⁺, Pr³⁺ and Gd³⁺ showed good solubility in ceria resulting in better ionic conductivity. There was a remarkable enhancement in the ionic conductivity of doped ceria electrolyte obtained by adopting different synthesis routes [5]. Various composites such as Ce₀.₈₅Gd₀.₁₅O₂ [6], Ce₀.₈₅Sm₀.₂O₁.₉ [7], Ce₀.₇₅Gd₀.₂₅O₁.₈₇₅ [8], Ce₀.₈Sm₀.₂O₁.₉ [9], Ce₀.₈Y₀.₂O₁.₉ [10], Ce₀.₈Y₀.₂O₁.₉ [11], Zr₁₋₅Ce₀.₀₈Nd₀.₁O₁.₉ [12], Ce₀.₈Sm₀.₁Nd₀.₁O₁.₉ [13] and Ce₀.₈La₀.₁₂₅Sr₀.₀₂₅O₁.₉₁₂₅ [14] are reported having better conductivity than pure ceria.

Various synthesis routes are reported for the synthesis of samarium-doped ceria to enhance the ionic conductivity at low operating temperatures. The new composition of the electrolyte is first time...
prepared by the solid state method to attain good ionic conductivity at reduced sintering temperature. In the present investigation, detailed studies on structural and electrical properties of the new composition of the electrolyte are presented.

2. Experimental

2.1. Synthesis procedure
Solid state reaction method was used to synthesize ceria co-doped with Samarium(Sm) and Antimony sample. Stoichiometry calculated amount of CeO$_2$, Sm$_2$O$_3$ and Sb$_2$O$_3$ were weighed and mixed with acetone manually using an agate mortar to obtain Ce$_{0.8}$Sm$_{0.1}$Sb$_{0.1}$O$_2$ compositions. The mixtures were grinded using agate-mortar for 48 h to obtain uniform and finely ground powder. The prepared mixture was calcined at 600°C for 3 h to remove any carbon residues remaining in the oxide powder. The foamy, pale yellow in color, the residue was crushed and then pelletized using a hydraulic press by applying 2.5MPa pressure. The pellets were sintered at 800°C for 10 h.

Structural characterizations were carried out using X-ray diffraction analysis to determine phase purity, lattice parameter and crystalline size of the sample. Qualitative analysis regarding different functional group present in the compound are identified using FTIR images. The micron morphologies of the sintered sample were examined using Scanning electron microscope (SEM). Atomic force microscopes were employed to characterize topographical information about the topography of the sample. Electrical impedance as a function of temperature in the range 250°C-750°C was measured using impedance spectroscopy technique.

3. Results and Discussion

3.1. Characterization by XRD
The XRD pattern of the prepared electrolyte sample is shown in the figure 1. Diffraction peaks recorded at different angles corresponding to the crystallographic phases of cubic fluorite type cerium oxide phase in the space group of Fm3m with reference to the JCPDS file (34-0394). From the Scherrer’s equation [15], the average crystallite size was found to be 15 nm with a lattice parameter of 5.47334 Å. The peak of the diffraction pattern appeared broad pointing out the smaller crystallite size of the sample leading to high ionic conductivity. The prepared electrolyte sample is pure as there are no secondary phases of samarium oxide and antimony oxide in the diffraction pattern. A shift in the XRD pattern is observed in the co-doped sample compared to the samarium doped ceria oxide due to the incorporation of the samarium and antimony ions in the ceria lattice. A qualitative analysis of XRD results agrees with reported literature.

![Figure 1. XRD Pattern of (B) Ce$_{0.8}$Sm$_{0.1}$O$_{2.4}$ and (D) Ce$_{0.8}$Sm$_{0.1}$Sb$_{0.1}$O$_{2.6}$](image-url)
3.2. Characterization by FTIR
Fourier transform infrared (FT-IR) spectroscopy provide a better insight into the phase and structural transformation of the prepared sampled calcined at 600°C for 3 h. From the FTIR spectrum, the strong band near in the range 3000-3750 cm\(^{-1}\) corresponds to O-H stretching of physically adsorbed H\(_2\)O or surface -OH group. The solid peak centered at 1631 cm\(^{-1}\) corresponds to the stretching vibrations of carbonyl containing functional groups. Sharp and fine peak spotted at 1496 cm\(^{-1}\) corresponds to Sb-O bond. The band designated in the range 433 to 1120 cm\(^{-1}\) resembles the stretching mode vibrations of Ce–O bond. [16].

![FTIR Spectra](image)

**Figure 2.** FTIR Spectra (A) Ce\(_{0.8}\)Sm\(_{0.1}\)O\(_{2-\delta}\) and (B) Ce\(_{0.8}\)Sm\(_{0.1}\)Sb\(_{0.1}\)O\(_{2-\delta}\)

3.3. Characterization by SEM
SEM analysis was performed to determine the average grain size in the sintered pellet of the Ce\(_{0.8}\)Sm\(_{0.1}\)Sb\(_{0.1}\)O\(_{2-\delta}\) electrolyte. The grain is uniform in size with more agglomeration. It is evident from the reported work that for an efficient charge carrier separation of the porous structure, the particle distribution should be narrower along with a tightly packed surface. Few pores are found in the SEM images of the Ce\(_{0.8}\)Sm\(_{0.1}\)Sb\(_{0.1}\)O\(_{2-\delta}\) electrolyte.

![SEM images](image)

**Figure 3.** SEM images of Ce\(_{0.8}\)Sm\(_{0.1}\)O\(_{2-\delta}\)
3.4. EDAX analysis
The concentration of the dopant affects the electrical properties of the electrolyte. EDAX analysis report shows the presence of the element Ce, Sm and Sb. Absence of any other extra element confirms the formation of pure phase of $\text{Ce}_{0.8}\text{Sm}_{0.1}\text{Sb}_{0.1}\text{O}_{2-\delta}$ electrolyte.

![Energy dispersive spectrum of $\text{Ce}_{0.8}\text{Sm}_{0.1}\text{Sb}_{0.1}\text{O}_{2-\delta}$.](image)

3.5. Atomic Force Microscope
The surface roughness of the electrolyte affects performance of fuel cell performance. The average AFM surface roughness of the prepared sample was measured using atomic force microscope operated in non-contact mode [17]. The sample was measured at multiple spot to determine the average grain size. Ionic hopping mechanisms are hindered with large number of grain boundaries for electrolyte material. Improvement in fuel cell performance can be obtained with a large grain with less number of grain boundaries which leads to better ionic conductivity. The topography and grain formation of the prepared sample are shown in AFM images. The agglomeration of the grains is more in the AFM images.

![AFM images.](image)
3.6. Impedance analysis

Impedance spectroscopy is an effective method to determine the distribution of the conductivity of the prepared powders. Figure 6 shows the plot of $z'$ versus $z''$ at different temperature which produces semicircles with a diameter R. As the temperature increases, it is spotted that the diameter of the arc reduces and as a result shrinking from right to left of the axis. This indicates non-Debye type of relaxation with distribution of relaxation time. The reduction in the diameter of the arc is due to the decrease of impedance at high temperature. An increase in conductivity is yielded at high temperature due to the reduction in the resistance of the sample.

Figure 5. AFM image of $\text{Ce}_{0.8}\text{Sm}_{0.1}\text{Sb}_{0.1}\text{O}_{2-\delta}$.

Figure 6. Impedance plot of $\text{Ce}_{0.8}\text{Sm}_{0.1}\text{Sb}_{0.1}\text{O}_{2-\delta}$.

Figure 7 depicts the variation of imaginary part of impedance $z''$ with frequencies at different temperature. From the plot, it can be seen there are relaxation peaks corresponding to the bulk conduction. There is a shift in the peak towards higher frequency side and broadening of peak is noted with increase in the temperature. These are the clear evidence of temperature dependent relaxation phenomena in the material. It also observed that as temperature increases, the reactance value is low.
even at low frequencies. This means that capacitance value is greater in the microfarad range which indicates grain-boundary conductivity with the rise of temperature at low frequencies.

![Figure 7. Variation of capacitive reactance with frequency for Ce$_{0.8}$Sm$_{0.1}$Sb$_{0.1}$O$_{2-\delta}$.](image)

3.7. Electrical Studies

Bulk conductivity was computed from the impedance spectroscopy by

$$\sigma = \frac{L}{RA}$$

(1)

Where L is the thickness of the pellet, A is the electrode area and R is the resistance as calculated with the impedance spectroscopy [18]. The conductivity is elucidated from the Arrhenius plot of log (\(\sigma T\)) vs 1000/T shown in figure 8. The conductivity \(\sigma\) is obtained using the equation

$$\sigma = (\sigma_0 / T) \exp \left( \frac{-E_A}{kT} \right)$$

(2)

Here \(\sigma_0\) is the high temperature limit of conductivity, \(E_A\) is activation energy and kT is associated with temperature variation in the measurement where k is Boltzmann constant and T is temperature [19]. The activation energy is figured out from the linear portion of the slope is .934 eV. From the graph 8, it is evident that the conductivity lightly deflects from the Arrhenius behavior. There is a deviation in the Arrhenius behavior due to the formation of inhomogeneity in the grain. This is caused by dopant-oxygen vacancy interaction [20]. The ac conductivity is estimated to be 3.58x10$^{-05}$ Scm$^{-1}$ for the pellet sintered at 800°C for 10 h. It is noteworthy that the better ionic conductivity is reported with the addition of trivalent ions at lower sintering temperature. Better cell performance is confirmed by high ionic conductivity at lower temperature.
Figure 8. Arrhenius plot of Ce\textsubscript{0.8}Sm\textsubscript{0.1}Sb\textsubscript{0.1}O\textsubscript{2.8}.

4. Conclusion
Nanocrystalline Ce\textsubscript{0.8}Sm\textsubscript{0.1}Sb\textsubscript{0.1}O\textsubscript{2.8} electrolyte was prepared by simple solid state reaction method capable for operating at intermediate temperature. The crystallite size of the sample is few of nanometers. In the synthesized sample, the grain appears to be round and with a uniform size in nanometer range. It is evident that the lower sintering temperature resulted change in structural and electrical property suitable for the electrolyte material in the field of SOFC applications.

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