

Comparative Study of Structural and Ionic Properties of Doped Zirconia Electrolytes for Solid Oxide Fuel Cells

Kanchan L. Singh¹, Payal Sharma^{1,3,*}, Anirudh P. Singh², Chetan Sharma³

¹Department of Applied Sciences and Humanities, D.A.V. Institute of Engineering and Technology, Jalandhar, Punjab, India

²Dean RIC, IKG Punjab Technical University, Kapurthala, Punjab, India

³Ph.D. Scholar, I.K. Gujral Punjab Technical University, Jalandhar, Kapurthala, Punjab, India

Abstract

The current study looks at yttria and scandia doped zirconia electrolytes for application in solid oxide fuel cells. Samples with (i) 10 mol% yttria, (ii) 5 mol% yttria and 5 mol% scandia, and (iii) 10 mol% scandia in zirconia host lattice were prepared by mixed oxide method and were sintered by conventional heating at 1400°C for six hours. The samples were then analysed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) for structural and microstructural studies. The conductivity study was done using impedance spectroscopy. It was found that sinterability of 10 mol% scandia in zirconia (10ScSZ) is highest and of 10 mol% yttria in zirconia (10YSZ) is less. Also the sample with highest scandia content was found to be having highest conductivity. Activation energies for these samples have also been calculated from their Arrhenius plots drawn between room temperature to 500°C.

Keywords: Electrolyte, stabilized zirconia, XRD, SEM, electrical conductivity

*Author for Correspondence E-mail: psharma.daviet@gmail.com

INTRODUCTION

A fuel cell is a promising energy conversion device that directly converts chemical energy of a fuel into electricity. Among different types of fuel cells available, a solid oxide fuel cell (SOFC) has shown great potential for commercial scale production [1]. These are increasingly recognized as a next generation clean technology devices for electrical energy conversion due to their high energy conversion efficiency. It consists of three parts, anode, cathode and the electrolyte. The electrolyte acts as a barrier between the electrodes and helps in transferring the O²⁻ ions in between the electrodes [2–4]. The most commonly used electrolyte material is zirconia (ZrO₂) doped with trivalent oxides (called stabilized zirconia) to introduce vacancies into the oxygen lattice through which the O²⁻ ions can be transported [5]. Ionic conductivity occurs by means of ions hopping from a lattice site to other site in the vicinity through the crystal structure. So, there must be some defects or vacancies in crystal for successful hopping of ions. The conduction mechanism in these solid electrolytes is vacancy migration, in which an ion adjacent to vacancy may be able to hop into it leaving its own site vacant.

This stabilized zirconia has improved mechanical and thermal properties such as high strength, toughness and thermal-shock resistance etc. and the electrical properties depend upon the crystal structure and morphology of the material. With respect to electrical conductivity, cubic fluorite and tetragonal phases are the most desirable phases. Further, the ionic conductivity of stabilized zirconia also depends upon the size and concentration of the dopant [6, 7].

For the SOFC electrolyte, amongst the various candidates, the yttria (Y₂O₃) and scandia (Sc₂O₃) doped zirconia are the two most commonly used materials. This is because of their high ionic conductivity in a given temperature range. [10,11]. The high temperature phases can be partially or completely stabilized at room temperature by doping with aliovalent oxides such as yttria (Y₂O₃), calcia (CaO), scandia (ScO) or magnesia (MgO), etc. The addition of Y₂O₃ and Sc₂O₃ in zirconia stabilizes the zirconia cubic fluorite structure to room temperature and changes the non-conducting zirconia into an ion conducting material [8, 9]. Further, it

has been reported that the ionic conductivity of scandia stabilized zirconia (ScSZ) is twice that of YSZ due to similar ionic radius of Sc^{3+} (0.087 nm) and Zr^{4+} (0.084 nm) that leads to lower internal stress during dissolution in the zirconia lattice [12]. The significantly higher oxygen-ion conductivity of ScSZ than the 8 mol% yttria-stabilized zirconia (8YSZ) opens up the possibility to reduce the operational temperature of SOFCs because high operating temperature have various limitations like short service life of the cell and higher cost for metallic interconnectors [13]. High operating temperature of SOFCs also causes thermal degradation, thermal expansion mismatch and even the interfacial reaction between electrodes and electrolyte. So, lowering the SOFC operating temperature down to the intermediate temperature (IT) range 500–700°C is one of the major targets in recent past [14]. The reduction of the cell working temperature to 600°C or even lower will lead to use of cheap stack materials, cell stability and will also increase the range of potential applications [15]. Therefore, it is important to develop new electrolyte materials with higher ionic conductivities at low temperatures. In the present work, we have studied the stabilized zirconia electrolytes in the low temperature range for their electrical properties.

EXPERIMENTAL DETAILS

For this study samples of (i) 10 mol% yttria doped in zirconia, (ii) 10 mol% Scandia in zirconia, and (iii) 5 mol% Yttria and 5 mol% Scandia co-doped in zirconia were considered. Here, the ternary system, 5 mol% Yttria and 5 mol% Scandia co-doped in zirconia (5Y5SZ) is chosen because scandia stabilized materials show large aging effects as transformation from cubic to rhombohedral phase occurs in scandia stabilized zirconia with time. This leads to degradation of the cell, and it is expected that codoping of zirconia with Sc_2O_3 and Y_2O_3 will enhance the electrical conductivity of the electrolyte and will reduce the degradation property [16–22]. The precursor of 10 YSZ, 10ScSZ and 5Y5SZ samples were prepared by mixed oxide method. Powders of Y_2O_3 (99.99% purity), ZrO_2 (99.0% purity), Sc_2O_3 (99.9% purity) were used as starting material to prepare target materials using mixed oxide method. These

powders were taken in stoichiometric ratios in plastic bottles in acetone medium and were ball milled for 6 hrs and were subsequently filtered. These filtered powders were then dried and pelletized into cylindrical pellets after mixing with 2% PVA solution by uniaxial pressing at 310 MPa in a cylindrical die of 10.2 mm diameter. These green pellets (five in number, of each composition) were then conventionally sintered at 1400°C for six hours. The structural and microstructural analyses of these samples were done using XRD and SEM techniques respectively. Then to make out the conductivity behaviour of these samples impedance spectroscopy was done in (1000 Hz to 1000 kHz) range of frequency from room temperature to 500°C. The ionic conductivity (σ) was calculated from impedance data and the activation energy, E_a , was calculated by using Arrhenius equation.

RESULTS AND DISCUSSIONS

Characterization of Crystal Structure

The XRD patterns of the sintered samples are shown in Figure 1. These patterns revealed that the cubic phase is the main phase present in these samples. In 10 YSZ (Figure 1a) monoclinic and tetragonal phases are also seen as secondary phases. Further, in 10 ScSZ (Figure 1b) as well as in 5Y5SZ (Figure 1c) samples peaks of lesser intensities corresponding to tetragonal phase were seen but there was absence of monoclinic phase, thus, indicating that both the scandium and yttrium are well incorporated in the zirconia lattice. This result is in agreement with the findings of several researchers [23–25] who reported only pure cubic phase for samples sintered from 1300°C and above.

Crystallite Size Analysis by Scherrer Equation

The crystallite size of these sintered samples was determined by Scherrer equation:

$$D=0.9\lambda/\beta\cos\theta$$

Where, D is the thickness of the crystal (in angstroms), λ is the X-ray wavelength and θ is the Bragg angle. The line broadening, β , is measured from the extra peak width at half the peak height [26, 27].

It is believed that the incorporation of Sc^{3+} and Y^{3+} in the zirconia stabilizes the cubic phase

and effectively increases the ionic size in the cubic fluorite structure which in turn would create more sites for ionic conduction when the oxygen vacancies are formed within the crystal lattice [28]. A unit cell parameter of cubic lattice as well as crystallite size increases as yttria content increases because of larger ionic radius of yttria as compared to scandia. Increase in the lattice parameter in 5Y5SZ and 10YSZ samples as compared to

10ScSZ samples shows that all of Scandia cations were substituted by Yttria cations or vice-versa (Table 1).

Microstructural Evaluation

SEM micrographs of these sintered samples are shown in Figures 2–4. It can be observed from these SEMs that grains were uniform in size and shape for all these samples and the grain size is in sub-micrometer range.

Table 1: Variation in Crystallite size with Composition.

Composition	Crystallite size (Å) in nm	Lattice parameter (Å)
10YSZ	11.8	5.056
10ScSZ	7.4	5.012
5Y5SZ	23.5	5.026

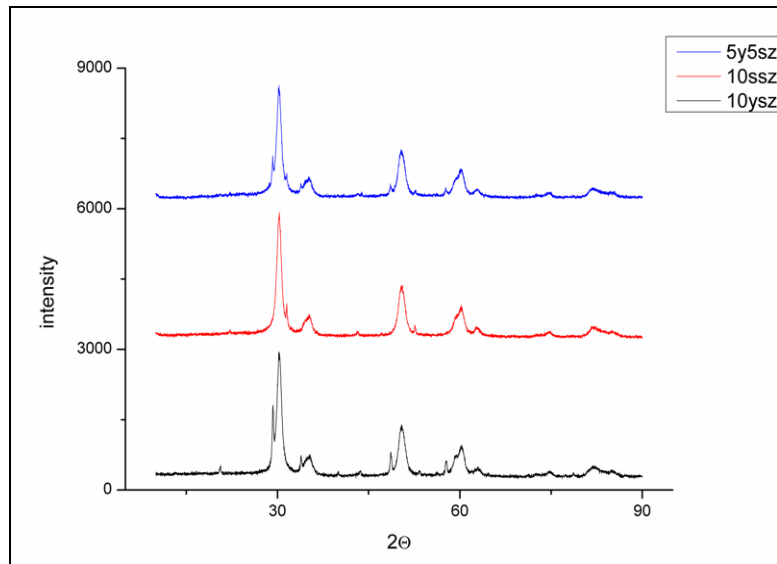


Fig. 1: XRD Patterns of Pellets after Sintering at 1400°C for 6h.

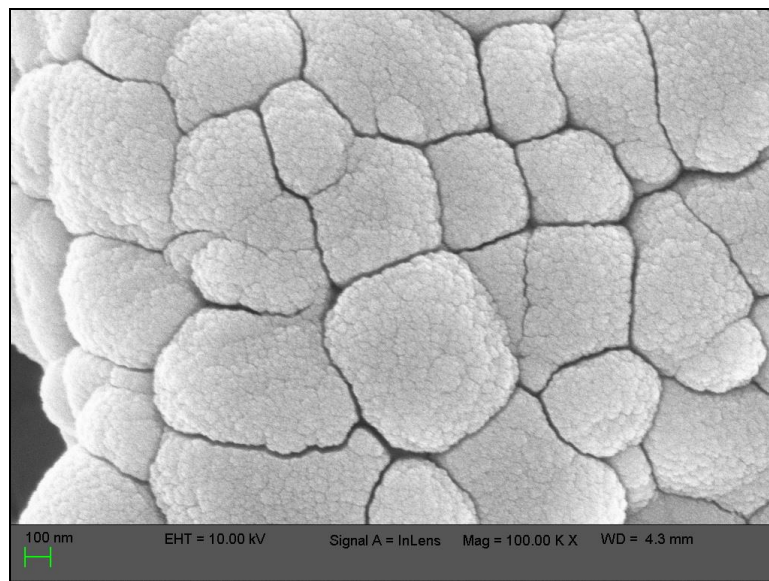


Fig. 2: SEM Image of 10ScSZ Sintered at 1400°C for 6h.

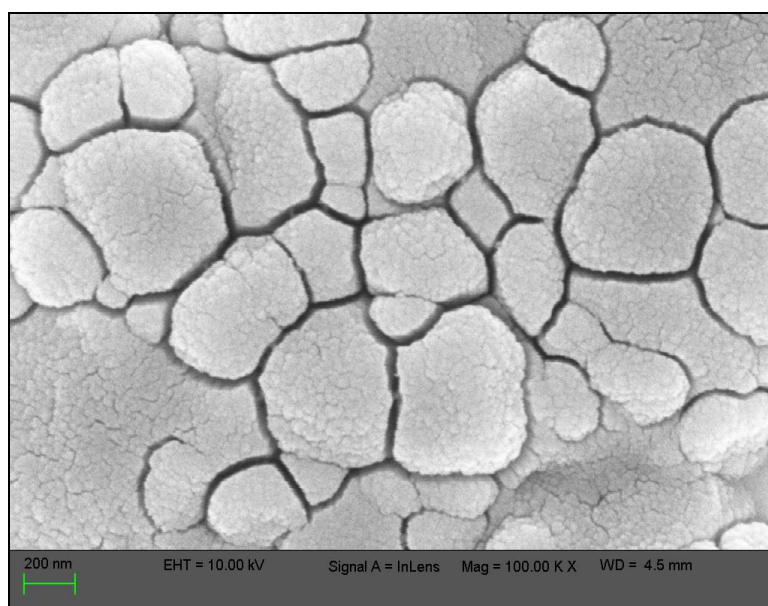


Fig. 3: SEM Image of 5Y5SZ Sintered at 1400°C for 6h.

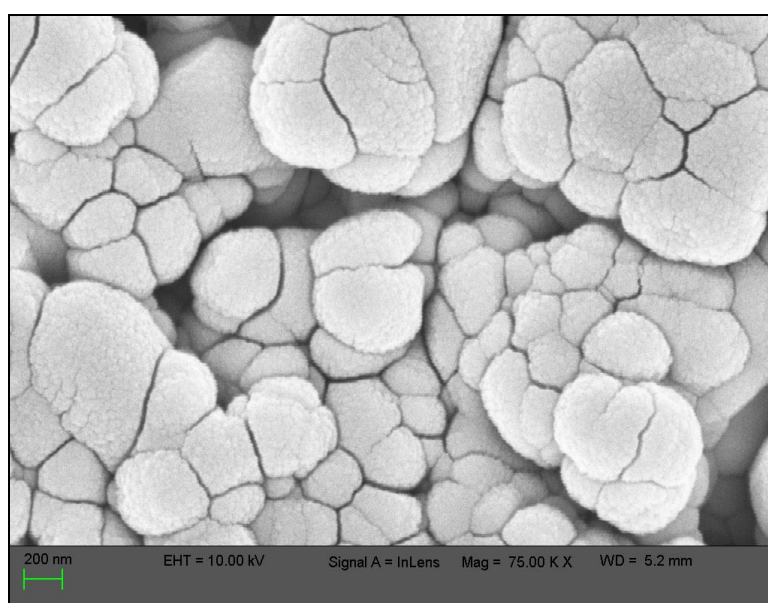


Fig. 4: SEM Image of 10YSZ Sintered at 1400°C for 6h.

As shown in the SEM micrographs of 10ScSZ and 5Y5SZ samples, the sintered samples have sufficiently high density. On the other hand, 10YSZ samples have some pores indicating low relative density. It is clear from the Figures 2–4) that the grain growth has occurred in all the samples. In the Figure 5 which shows SEM of the sample 10YSZ, there is no uniform grain growth and have poor densification. It is obvious from its density also. In the sample 5Y5SZ (Figure 4) the uniformity in the grain has increased its density has also improved. Further, it is obvious from the Figure 3 which shows SEM

of 10ScSZ that the grain growth in the sample of 10 ScSZ is the highest among the three samples with highest uniformity and the highest density. From the above observation it is clear that sinterability of YSZ system increases as the concentration of the Sc^{3+} in the YSZ increases. The poorest sinterability of 10YSZ is due to higher refractory nature of Y_2O_3 as compared to Sc_2O_3 . The sinterability of 10ScSZ is the highest. Further, Zr^{4+} has the size of 80\AA . The size of Y^{3+} (114\AA) is higher than that of Sc^{3+} (88.5\AA). As the size of Sc^{3+} is smaller than Y^{3+} and comparable to Zr^{4+} , therefore the diffusivity of Sc^{3+} in Zr^{4+} matrix

is higher and faster which leads to better sinterability of 10ScSZ. Sinterability of 5Y5SZ is intermediate between the two compositions.

Electrical Conductivity

The temperature dependence of conductivity is given by the Arrhenius equation $\sigma = \sigma_0 \text{Exp}(-E_a/KT)$ where, σ and σ_0 are the electrical conductivity and pre-exponential factor respectively. E_a , K and T are the activation energy, Boltzmann's constant and temperature respectively. The above equation gives a straight line between $\ln\sigma$ and T , the slope of which is E_a/K . The Arrhenius plots for the conductivity of these samples are shown in Figure 4. These are plotted for the temperature range from room temperature to 500°C at 50 kHz frequency for all the samples. The slope of these plots gives the value of activation energy, E_a , for the conduction of oxygen ions. The conductivity of the prepared 10ScSZ samples was found to be higher as compared to 10YSZ and 5Y5SZ samples processed under same conditions. This may be due to smaller size of Sc^{3+} ions compared to Y^{3+} ions. The size of Sc^{3+} ions is closest to the host Zr^{4+} ions [29]. Due to smaller size of Scandia ions it offers lesser hindrance to flow of oxygen ions because size matched dopant induces minimum lattice distortions as compared to Y^{3+} ions having larger ionic radius (Table 2).

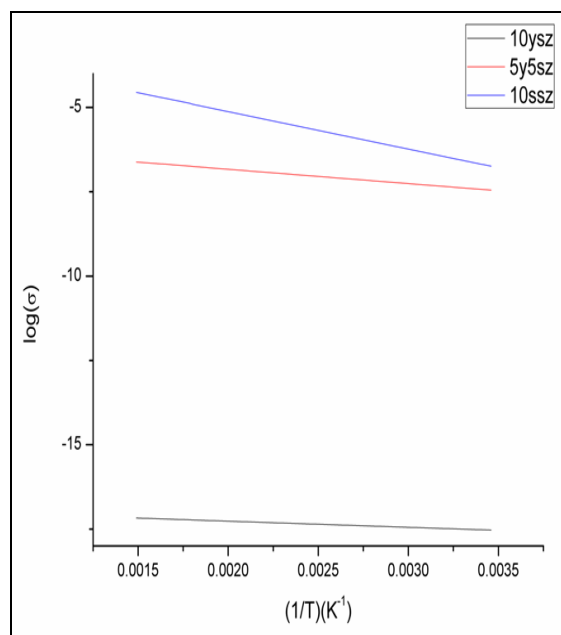


Fig. 5: Temperature Dependence of Ionic Conductivity for the Three Samples.

Table 2: Conductivity, Pre-exponential Factor and Activation Energy at 400°C and 50 kHz.

Sample	Conductivity (σ)(S cm ⁻¹)	Log σ_0 (pre-exponential factor)	U(eV)
10YSZ	3.09×10^{-6}	-7.41	0.014
5Y5SZ	4.84×10^{-7}	-5.63	0.090
10ScSZ	5.14×10^{-5}	-2.79	0.212

Straight line dependencies of the conductivities are observed in the Arrhenius plot for all the samples indicating the stabilization of cubic structure. Further, it is observed that for all the samples the higher the temperature, the higher is the conductivity. It is known that the electrical conductivity depends upon the concentration and interaction among of defects. An increase in the conductivity is due to increase in number of charge carriers at given dopant content. The electrostatic interaction among the defects always leads to increase in activation energy, which may be possible cause of increase in the activation energy of 10ScSZ in spite of its higher conductivity in our work. Further, at higher concentration of defects the content of dopant cations and vacancies are high, so vacancies are bonded to two dopant cations and are therefore jammed and this lead to decrease in the conductivity as is observed in the case of 10YSZ [30].

CONCLUSIONS

Samples with 10 mol% yttria, 5 mol % yttria & 5 mol% scandia and 10 mol% scandia in zirconia host lattice were prepared by mixed oxide method and were studied for their application in the SOFCs. Based on the consideration of the phase structure, conductivity properties it can be concluded that 10ScSZ sample is a potential candidate for application at low intermediate temperatures in SOFC as electrolytes. Further, it was found that in this low temperature range, 10ScSZ sample have highest conductivity and highest sinterability among the three compositions. Its application in IT-SOFC as electrolyte can be considered in further studies.

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