Electrical conductivity of sol-gel derived nano- 8mol% yttria stabilized zirconia

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Nanosized 8mol% Yttria Stabilized zirconia (8YSZ) was prepared by the sol-gel technique. The calcination temperature of the gel powder was optimized to be around 600°C by the Thermo Gravimetric (TG) and Differential Thermal Analyses (DTA). The calcined powder was ground in a planetary mill in ethanol medium and dried at 60ºC. Powder X-ray Diffraction (XRD), Selected Area Electron Diffraction (SAED) and Transmission Electron Microscopy analyses (TEM) of the grounded sample was confirmed to be nanosized (15 nm) and cubical in structure. The nano sized 8YSZ powder sample was pelletized by adding polyvinyl alcohol as binder and sintered in a microwave furnace at 1500ºC for 15 minutes of dwelling time. The electrical conductivity and activation energy have been evaluated by a two probe A.C impedance analyser. From this study the activation energy 1.20 eV, and the electrical conductivity 1.55×10^{-3} $\Omega^{-1}cm^{-1}$of the microwave sintered 8YSZ were estimated.

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1. Introduction

Fuel cells are attracted due to its fuel flexibility at high temperature, 800°C-1000°C, 8mol%Yttria Stabilized (Zirconia) 8YSZ widely used as negative oxygen ionic conductor in Solid Oxide Fuel Cells(SOFC), and oxygen sensors [1-6], due to its super ionic conductivity at high temperature (1000°C). The Particle size reduction of 8YSZ can enhance the ionic conductivity which improve the performance of SOFC, and mechanical strength [7,8]; Further the nano sized 8YSZ will increase the life time of the material during the operation of the fuel cell at higher temperatures. Many methods are available for the synthesis of nano 8YSZ such as the hydrolysis of alhoxides, hydrothermal treatment, co-precipitation, combustion, and sol-gel processing [9-14]. Of these methods the Sol-gel process can provide the atomic homogeneity, high purity and precise chemical compositions; further, the sol-gel route [15] requires minimum processing temperature at low cost. High density, minimum sized grains, and the elimination of pores in 8YSZ can be achieved through various sintering techniques. Many researchers have suggested different sintering techniques, for improving the density and reduction of grain size. Dhal et al. [16] achieved theoretical density (96%), using conventional, spark plasma and hot press sintering techniques, and also reported the mechanical and electrical properties of 8YSZ. Razavi Hesabi et al. [17] achieved high theoretical density, and also improved the electrical conductivity studies of 8YSZ, using conventional, microwave sintering and two step sintering techniques. In conventional sintering, an external heating element is used to generate heat, and it is transferred to the sample through radiation, convection and conduction; which produces a temperature gradient and internal stresses. Further, the sintering technique needs the maximum sintering time to reach high density [18, 19]. In microwave sintering, the heat is generated internally within the test sample by the rapid oscillations of the dipole at microwave frequency. Since electromagnetic waves are used to generate the heat in microwave sintering, a large amount of heat can be transferred to the interior of the material. The salient feature of microwave sintering is it's volumetric and uniform heating, and short processing time. Microwave sintering is a non-contact technique. Many researchers performed microwave-sintering technique for different applications of 8YSZ [20-24]. In the present investigation, nano sized 8YSZ was prepared by the sol-gel route and microwave sintering was performed on the 8YSZ sample at 1500°C for 15 minutes dwelling time. The electrical conductivity was studied by a two probe A.C impedance analyzer.

2. Experimental procedure

Nano crystalline 8 mol% yttria stabilized zirconia was synthesized by the sol-gel route [15], using the precursors zirconium oxychloride $ZrOCl_2 8H_2Oz$) (CDH, New Delhi), yttrium nitrate hexahydrate ($Y(NO3)_3.6H_2O$) (CDH, New Delhi) and Oxalic acid ($C_2H_2O_{4)}$ (CDH, New Delhi). The respective salts were dissolved in 200 ml of Millipore water in the stoichiometric ratio 1 M. The Initial solutions of precursors were mixed under constant stirring until the

gelation was completed under room temperature conditions; the obtained gel was dried in a hot air oven at 45º C for five days. The TGA and DTA (PERKIN ELMER 1700 model) analyses were carried out on the 8YSZ dried gel at the heating rate of 10°C/min in a nitrogen atmosphere over the temperature range of 50° C – 1000°C. The dried gel was calcined at 600˚C for 3 hrs in a conventional furnace. The calcined 8YSZ powder was well ground in a planetary mill for 5 hrs in ethanol, using zirconia balls as the grinding media at a rotational speed of 300 rpm. The milled powder was dried in air at 60˚ C for 24 Hrs. The sol-gel derived 8YSZ powder was characterized using an X- ray diffractometer (XRD, Seifert 3000P) with Cu - Kα radiation (λ = 1.5406 Å). The XRD patterns were recorded in the 2θ scanning range of 10° – 80° degrees. The particle morphology of the nano 8YSZ was investigated by the X–ray diffraction analysis (XRD). The transmission electron microscope (TEM) and SAED [JEOL-1200 EX II operated at 120 kV (max)].

The nano sized 8YSZ milled powder was mixed with PVA (Poly Vinyl Alcohol) as binder and uni-axially pressed in to pellets (10 mm in diameter) at a pressure of 3 ton using a 10 ton press. The 8YSZ Sample was sintered in a Microwave Furnace (V. B. C. C India) at 1500 °C in a 1.1 kW at, 2.45 GHz frequency, at heating rate of 100 ˚C / min and dwelling time of 15 minutes. In a Microwave sintering furnace, a special susceptor is designed to generate heat against the microwave at a heating rate of 100 ˚C/min. A non- contact optical sensor (RAYTEK, U. S. A) is used to measure the temperature in the range of 600 ˚C-1600 ˚C; the time temperature profile is programmed by the Eurotherm temperature indicator cum programmer. The density of the microwave sintered 8YSZ sample was measured by the Archimedes method. The Microstructure of the polished 8YSZ sample was analyzed by the Scanning Electron Microscope (SEM) (HITACHI Model S-3400 N, JAPAN) A.C Impedance analyzer (Material mates two probe) was used to measure the electrical conductivity of the microwave sintered 8YSZ sample, at a frequency of 1Hz-10 M Hz. in the temperature range of 500˚C - 900 ˚C. In order to obtain the electrical contact in the sample, platinum paste was applied on both sides, and it was cured at 700 ˚C for 1hr.

3. Result and discussion

3.1 TG/DTA analysis

Fig. 1 Shows the TGA-DTA plot of the precursors of the sample. The Thermal curve shows that a slight weight loss was observed from 100°C to 250 °C, which is due to the evaporation of water in the dried precursor gel. The exothermic and endothermic peaks at 275ºC and 330ºC in the DTA and the weight loss from 250ºC to 375ºC in the TGA were due to the removal of oxalate and the structural hydroxyl group. The broad exothermic range of 375ºC to 475ºC and the corresponding weight loss may be due to the crystallization of 8YSZ. There is no considerable weight loss above 600ºC. This analysis therefore illustrates, that the optimum calcination temperature for 8YSZ is around 600 ºC [25,26].

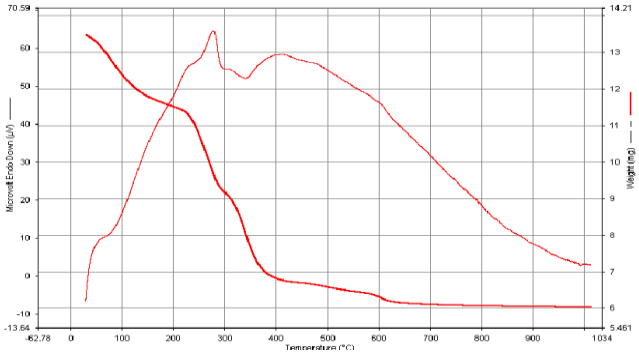

Fig. 1. Thermogravimetric and Differential Thermal analysis of 8YSZ dried-gel at 45ºC.

3.2 X-ray diffraction studies

Fig. 2 shows the XRD pattern of 8YSZ powder calcined at 600 ºC for 3 hrs. The phase identification was analyzed with the help of the standard JCPDS data base (JCPDS#82-1246). There are six diffraction intensity peaks from planes (1 1 1) [2θ = 30.19°, d = 2.97 Å], (2 0 0) [2θ = 34.69 °, d = 2.58 Å],(220) [2θ=49.86°,d=1.82Å], (3 1 1) [2θ = 59.42°, d =1.55 Å], (2 2 2) [2θ = 62.35°, d =1.48 Å] and (4 0 0) [2θ = 73.74°, d =1.28 Å], which are confirmed and indexed in the cubic structure with the lattice parameters of a = 5.135 Å [27]. The average grain size of the 8YSZ sample has been calculated using the Debye – Scherer formula given in equation (1)

$$D=0.98\,\lambda / \beta \cos\theta \qquad (1)$$

Where D is the average particle size in nm, β is the full width at half maximum (FWHM) of X – ray reflection expressed in radians, and θ is the position of the diffraction peaks in the diffractogram. The average crystalline size of the nanocrystalline 8YSZ is found to be 15 nm.

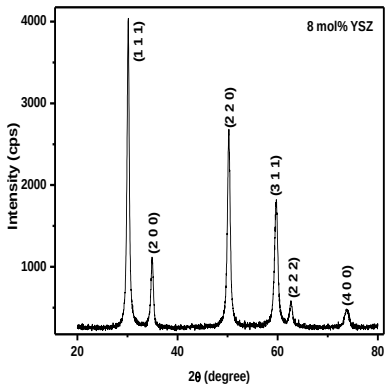

Fig. 2. X-ray Diffraction Pattern of nano-8YSZ powder Calcined at 600˚C for 3h.

Table 1. Comparison of interplanar d_{hkl} spacing and average grain size obtained from XRD and TEM studies.

2θ in degree	*d (Å)*		Diffracting plane *(h k l)*	Average grain size (nm)	
	XRD	SAED		XRD	TEM
30.19°	2.97 Å	2.977 Å	(1 1 1)		
49.86°	1.82 Å	1.835 Å	(2 2 0)	15.00	15.50
73.74°	1.28 Å	1.320 Å	(4 0 0)		

3.3 Morphological studies of 8YSZ using TEM and SEM

The TEM micrograph of the Sol gel derived nano 8YSZ sample is shown in the Fig. 3(a). It reveals better crystallinity and the crystals have an average size less than 15 nm [28] and this result agrees well with the reported results calculated from the XRD Pattern. There are three continuous diffraction ring patterns obtained in the SAED image and the corresponding to the diffraction planes (1 1 1), (2 2 0) and (4 0 0) respectively [29]. The XRD as well as SAED d-spacing (d_{hkl}) results confirm the cubic structure of nano 8YSZ. The SAED image demonstrates the well resolved diffraction fringes of the d-spacing (d = 2.97 Å, 1.82 Å, 1.28 Å) as shown in Fig. 3(b). A Comparison of the interplanar spacing (d_{hkl}) and average grain size of both XRD and SAED are presented in Table 1.

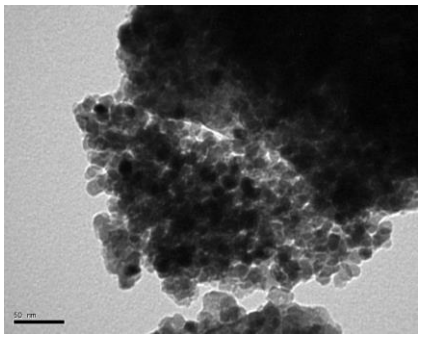

Fig. 3(a). TEM image of the Nano 8YSZ powder Calcined at 600°C for 3h.

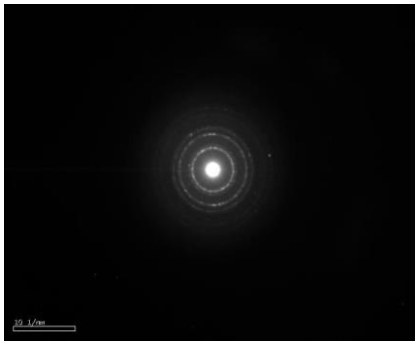

Fig. 3(b). TEM-SAED image of Nano 8YSZ powder Calcined at 600°C for 3h.

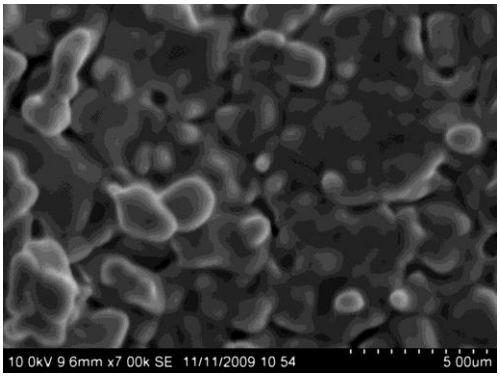

Fig. 4. SEM micrograph of the 8YSZ sample sintered in Microwave at 1500 °C for 15 minutes.

The SEM micrograph of the 8YSZ sample was microwave-sintered at1500 °C for 15 minutes of dwelling time is shown in Fig. 4. The Theoretical density of the sample was found to be 95% and it is quite significant that this level of density can be achieved without any sintering aid; The SEM studies show the presence of submicron grains with minimum pores (<900nm) [30, 31].

3.4 Conductivity studies

The high temperature complex impedance (Z' verses Z") plots were drawn for the microwave sintered 8YSZ sample.[3] The impedance measurements were taken at different temperatures 500ºC, 600ºC, 700ºC, 800ºC, and 900ºC as shown in Fig. 5(a),(b),(c),(d) and (e) respectively. Fig. 5(a) shows the complex impedance plot obtained at a measuring temperature of 500ºC for 8YSZ sample. It shows two arcs, which correspond to the grain and grain-boundary contributions, (i.e.) the oxygen ion conductors of impedance diagram is composed of two off-centers; the first centre is attributed to the grain conductivity at a higher frequency and the second one is blocking of the charge carrier at the grain boundaries at a lower frequency. These plots were for sample dimensions allowing a comparison between the semicircle diameters, which is the direct measure of the grain and grain boundaries resistivity. From Fig. 5 (b), the impedance spectrum shows two arcs corresponding to the grain boundary and electrode contributions, because the

frequency response of the grain interior lies outside the measurement range and the grain contribution was an off-set resistance. The impedance spectra collected at 700ºC, 800ºC, 900ºC in Fig. [(5(c), 5(d), 5(e)] shows, only one arc, that is due to the involvement of electrode interface contribution. In this case, the sample grain and grain boundary resistance are taken as off-set-resistance. Fig. 5(f) shows the Arrhenius plot of the electrical conductivity of 8YSZ sample plotted between the reciprocal of temperature against the conductivity. The activation energy corresponding to the temperature dependent electrical conduction can be estimated using the relation given below,

$$\sigma_T = \sigma_0 \exp(-E_a/kT) \quad (2)$$

Where σ_0 is the pre-exponential factor with dimensions of $\Omega^{-1}cm^{-1}K$, E_a is the activation energy for dc conductivity and k is the Boltzmann constant. The activation energy E_a for the grain conduction of the samples is obtained as 1.20 eV and the electrical conductivity was $1.55 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ for 900º C. M. Razavi Hesabi et al [17] used the glycine nitrate method for preparing the 8YSZ particles (25nm), and reported that microwave sintering was performed at a low heating rate of (50º C/min) at 1500º C without any dwelling time, They also obtained the grain size of 0.9 μm, and the corresponding electrical conductivity was 132.2 ms/cm for 900º C. In the present study 15nm sized 8YSZ powder was synthesized by the sol-gel technique and microwave sintering was performed at 1500°C for 15 minutes dwelling time at a heating rate 100°C/min. The SEM study revealed sub-micron sized grains of less than 900 nm and the electrical conductivity obtained was $1.55 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$, for 900°C. The activation energy has been found to be 1.20 eV. This study confirmed that the minimum electrical conductivity that was due to the nanocrystalline nature of 8YSZ, even if the sample has a high density 95%.

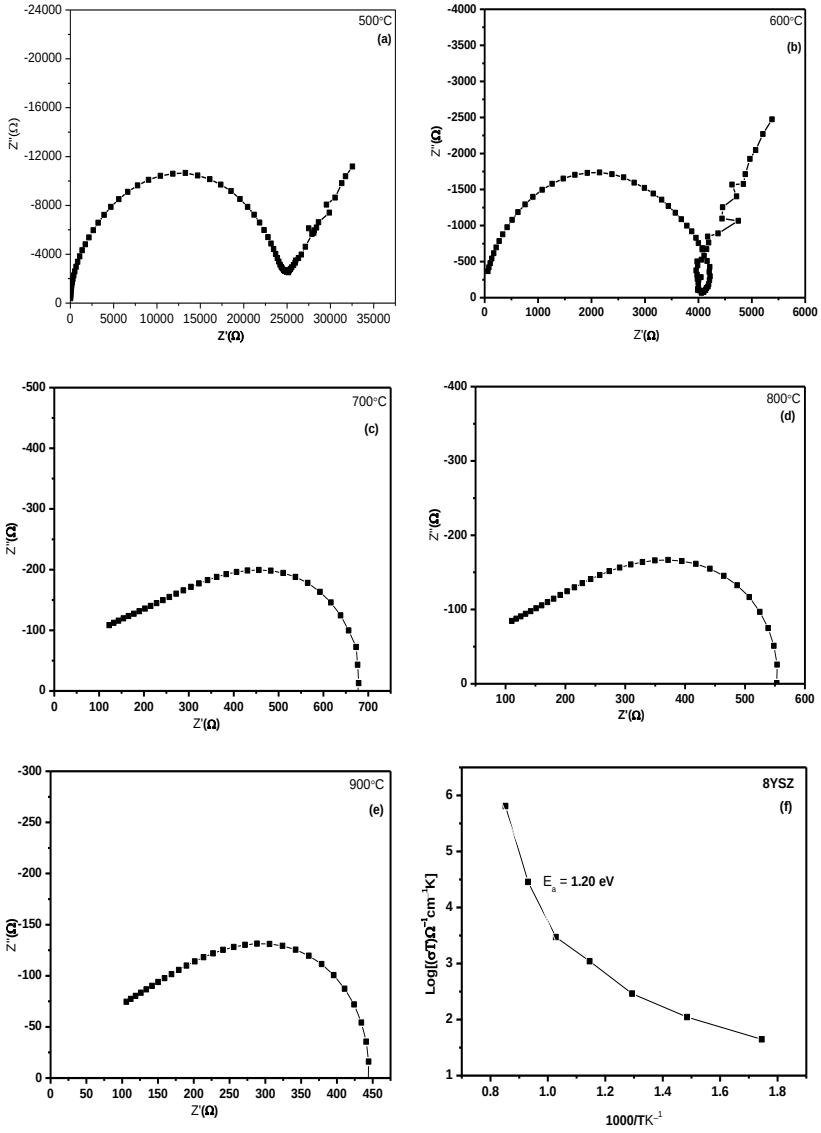

Fig. 5. Impedance plots of the 8YSZ sample sintered in a Microwave furnace at 1500 °C for 15 minutes: Impedance plots collected at (a) 500ºC, (b) 600ºC, (c) 700ºC, (d) 800ºC, (e) 900ºC (f) Arrhenius plot of the 8YSZ sample.

4. Conclusion

The 8YSZ nano-powders were synthesized by the Sol-Gel method. The thermal properties of the as-prepared gel were analyzed by using simultaneous TGA/DTA measurement; it showed that, step by step partial removal of water, oxalate and hydroxyl group in the temperature range of 50ºC - 375º, by using the TGA/DTA analyses the calcination temperature was optimized. The prepared material was calcined at 600 ºC for 3 h and its phase formation was confirmed by the XRD. The Particle size was analyzed by the TEM and SAED, and the average particle size was 15 ±0.7 nm. The microwave sintered 8YSZ Sample exhibits submicron grains (<900 nm) with less pores. High temperature impedance measurement was taken of microwave sintered 8YSZ sample at the 500ºC-900ºC temperature range, in the frequency range of 1 Hz to 10 M Hz. In this temperature range the grain, grain boundary and electrode contribution were observed. From the Arrhenius plot, the activation energy for the grain conduction of the sample is obtained as 1.20 eV and the electrical conductivity was found to be 1.55×10^{-3} $\Omega^{-1}cm^{-1}$. Thus it is found that even by using the microwave sintering technique, the electrical conductivity of nano 8YSZ has been observed to be 1.55×10^{-3} $\Omega^{-1}cm^{-1}$.

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