

199. Investigations on Gadolinium doped Ceria (GDC) electrolyte prepared via sol-gel and co-precipitation routes for intermediate temperature solid oxide fuel cell (IT-SOFC) applications

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Abstract

Yttria Stabilized Zirconia (YSZ) is the common material used as an electrolyte for high temperature solid oxide fuel cells (SOFC). Due to high operating temperature, various design issues arise. Therefore, low to intermediate temperature solid oxide fuel cells (SOFCs) are actively being developed. Ceria based materials are among the best options for intermediate temperature SOFC (500-800°C). We have carried out successful synthesis of Gadolinium doped Ceria (GDC) electrolyte material with a formula $Ce_{1-x}Gd_xO_{2-x/2}$ ($x=0.15$) by two different techniques namely sol-gel and co-precipitation. Both techniques have the advantages of high phase purity, homogeneity and low processing temperatures along with strong control on crystallite size. The synthesized materials were characterized by X-ray Diffraction, Scanning Electron Microscopy with EDX etc. We have detected a cubic fluorite structure for both synthesized compounds. The co-precipitation synthesis resulted in better control on crystallite size in comparison to that by sol-gel route. The average particle size was found to be in the range of 40-70 nm. The electrical conductivity of the GDC pellet was measured in the temperature range of 220-660 °C in air by using two probe LCR meter. GDC pellet synthesized by sol-gel method was found to has highest conductivity value of 2.17×10^{-4} S/cm at 600 °C with activation energy of 0.31 keV.

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Keywords: IT-SOFC; sol-gel; co-precipitation

1. Introduction

SOFC working at high temperature causes many issues like sealing, long start up time etc., which results in high cost and maintenance problems[1]. There is a need to synthesize a low temperature electrolyte to overcome these problems. Ceria is the best option for low to intermediate temperature SOFC electrolyte. Pure ceria has low ionic conductivity and mechanical strength[2]. But, it can be increased when it is doped with some rare earth or alkaline earth materials[3]. Among various rare earth elements reported as dopant, gadolinium is one of the most suitable dopant[4]. Conductivity value mainly depends on the ionic radius, material that has closed the ionic radius with ceria exhibit high conductivity value[5]. According to literature a smaller mismatch in size between host and dopant ion gives maximum value of conductivity[6]. A critical ionic radius for ceria is 1.038Å. Gadolinium Gd^{3+} has the ionic radius of $r_{Gd, VIII}^{3+} = 1.053\text{Å}$. As the Gd^{3+} ionic radius is very close to critical ionic radius of ceria, so GDC gives maximum value of conductivity and it is a suitable dopant for ceria[7]. GDC electrolyte prepared by solid state method showed the conductivity value of 0.1 S/cm at 1023 K and activation energy E_a of 0.9 eV[8]. Similarly GDC synthesized by a citrate-nitrate combustion method showed very promising results at low temperatures. GDC pellet sintered at 1300 °C had relative density of 97 % and conductivity value of 1.27×10^{-2} S/cm at 600 °C[9]. Numerous techniques have been used for the preparation of GDC electrolyte such as hydrothermal, conventional solid state, co-precipitation, spray and freeze drying and sol-gel[10], [11]. Among various synthesis techniques wet chemistry route mainly sol-gel and co-precipitation shows

very promising results with low processing temperature, homogeneity and purity[12].

The present study deals with the synthesis of GDC electrolyte by two different methods namely sol-gel and co-precipitation. The detailed analysis of morphological, structural and electrical properties of prepared GDC electrolyte was carried out.

2. Experimentation

2.1. Sol-gel method

The sample with a general formula of $Ce_{1-x}Gd_xO_{2-x/2}$ ($x=0.15$) was synthesized by sol-gel method. The precursor of cerium nitrate hexahydrate and gadolinium nitrate hexahydrate were used as starting materials. Stoichiometric amounts of $Gd(NO_3)_3 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ were dissolved in de-ionized water separately. Then $Gd(NO_3)_3 \cdot 6H_2O$ was added in $Ce(NO_3)_3 \cdot 6H_2O$ drop wise with continuous stirring. Stoichiometric amount of anhydrous citric acid was also dissolved in de-ionized water. The composition of total oxide to citric acid was 1:1. For better results, both solutions were mixed drop wise in a separate beaker with continuous stirring. To get homogenizing mixture, the sample was stirred for 10 hours. After complete mixing, the temperature was raised to 80 °C with continuous stirring to remove extra water and to form a gel. As the temperature increases, the solution become more viscous and after 4 hours a transparent gel was formed. Then put beaker in a dry place for 24 hours. Because, during aging poly-condensation continues which increase the thickness and decrease porosity[13]. The gel was then dried in an oven at 120 °C for several hours for complete drying. After drying, the sample was ground using agate mortar to get a fine powder. The fine powder was than calcined at 600 °C for 4 h.

2.2. Co-precipitation method

The ceramic electrolyte with the formula of $Ce_{1-x}Gd_xO_{2-x/2}$ ($x=0.15$) was synthesized by co-precipitation method. The precursor of Cerium nitrate hexahydrate and gadolinium nitrate hexahydrate were used. Stoichiometric amounts of gadolinium nitrate hexahydrate and cerium nitrate hexahydrate were dissolved in de-ionized water separately. The concentration of the precursor solution was 1M. Then mix both the solution in a separate beaker with continuous stirring at hot plate. After homogenizing mixing, added ammonium hydroxide drop wise in the solution with continuous stirring, until precipitation occurred. After precipitation raise the temperature to 200 °C to dry the slurry type sample with continuous stirring at hot plate. Pale yellow matter was obtained after complete drying. Then ground the sample by using agate mortar to obtain a fine powder. The fine powder was calcined at 600 °C for 4 hours.

Crystal structure and phase formation of the calcined samples were analysed by X-ray Diffraction equipment (STOE Germany). X-ray powder diffractogram of the calcined sample was recorded using $CuK\alpha$ radiation ($\lambda=1.5425\text{\AA}$) with 2θ values ranging from 20° to 80°. The morphology of the samples was observed by scanning electron microscopy (JEOL Analytical SEM). The average grain size was measured from higher magnification SEM images. For conductivity measurement a pellet with a thickness of 2 mm and diameter of 10 mm was formed using a hydraulic press. The pellet was sintered at 1000 °C for 4 hours for conductivity measurement the pellet was sintered at 1050 °C for 4 hours. DC conductivity was measured by LCR meter (Wayne Kerr precision analyser 6440B) in the temperature range of 200 – 600 °C.

3. Results and Discussion

3.1. XRD Patterns

Fig.1 shows the XRD pattern of Gadolinium doped Ceria (GDC) powder synthesized by two different methods, namely sol-gel and co-precipitation. The XRD pattern revealed the formation of cubic $Gd_{0.15}Ce_{0.85}O_{1.5}$ in all samples. All peaks are associated to cubic fluorite crystal structure with the space group Fm-3m (225) (PDF Card No. 75-0161). XRD peaks positioned at 2θ values of 28.40°, 32.95°, 47.28°, 56.16°, 58.99°, 69.32°, 76.51°, and 78.95° corresponding to (111), (200), (220), (311), (222), (400), (331) and (420) crystallographic planes, matching well according to the pattern JCPDS 75-0161. There are no other phases formed in sol-gel and co-precipitation methods.

From diffractogram, it can be seen that the intensity of (111) peak is maximum in all samples. The interplaner spacing d and lattice parameter of all samples are calculated by JADE 6.0 software. The reflection from (111) plane is used to measure the crystallite size D , calculated from the Sherrer formula

$$D = 0.9 \times \lambda / B \times \cos(\theta)$$

Where ' θ ' is the diffraction angle, ' λ ' is the wavelength of X-rays, and B is the full width at half maximum intensity.

Fig.1. XRD patterns of 15 mol% GDC calcined at 600 °C for 4h prepared by sol-gel and co-precipitation methods.

Table 1 shows the crystallite size 'D' of GDC prepared by both methods. From table, it can be concluded that, GDC prepared from sol-gel method has crystallite size slightly larger than that of GDC prepared by sol-gel method. There is a good agreement with SEM results of both the samples.

Method	Composition	Crystallite size (nm)
Sol-gel	Gd _{0.15} Ce _{0.85} O _{1.5}	53
Co-precipitation	Gd _{0.15} Ce _{0.85} O _{1.5}	40

The peaks of sample prepared by co-precipitation are relatively broad as compared to sample prepared by sol-gel, due to small crystallite size. The XRD pattern showed that GDC electrolyte prepared by two different methods have same phase and structure.

3.2. Surface Morphology

Fig. 2 shows the micrographs of GDC electrolyte synthesized by sol-gel and co-precipitation. SEM micrograph shows the particles are well dispersed and in a round shape. In fig. 2a the particles prepared via sol-gel method have nearly homogeneous size distribution without definite big agglomerate. The particles prepared by co-precipitation have high rate of agglomeration, but all the particles forming agglomeration are highly uniform. The particles size ranges from 50 to 70 nm by sol-gel and from 40 to 60 by co-precipitation. So by co-precipitation method, the particles are larger, fewer and denser then by sol-gel method [14]. It can also be concluded that the Ostwald's ripening is increased by increasing the pH of the solution [15].

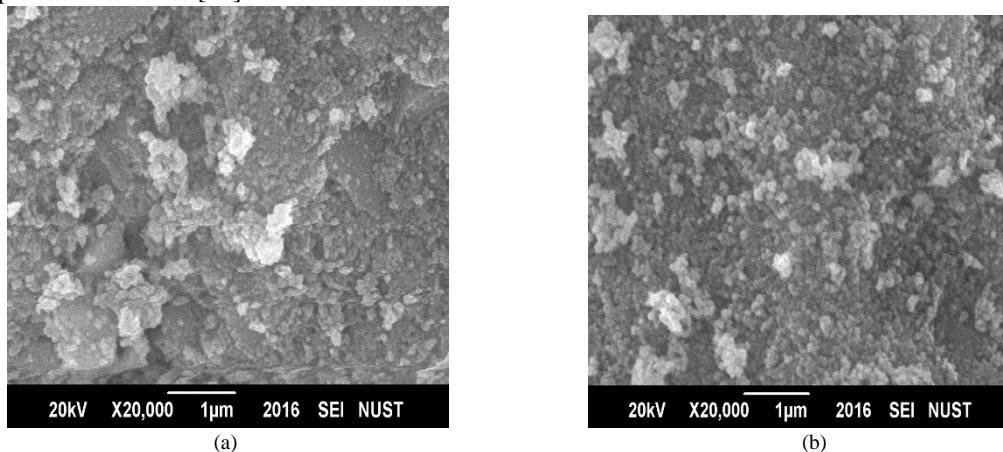


Fig.2. SEM Images of Gd_{0.15}Ce_{0.85}O_{1.5} by sol-gel (a) and by co-precipitation (b)

Fig. 2 shows the EDS analysis of the prepared samples. There is no other element found in EDS analysis except O, Ce and Gd. The intense peaks of Gd, Ce and O are present, which confirms the purity of GDC powders. The atomic percentage of cerium and gadolinium are higher in the sample prepared by co-precipitation method as shown in Fig. 3(a, b).

3.3 DC Conductivity Measurement:

The DC conductivity was measured by two probe method with LCR meter (Wayne Kerr precision analyser 6440B) in the temperature range of 200 – 600 °C. Fig.4. shows the typical Arrhenius plots of $\ln(\sigma T)$ versus $1000/T$. The changes in dc conductivity calculated from the bulk resistance and sample dimensions with temperature. The dc conductivity obeys the Arrhenius behaviour

$$\sigma_{dc} = \sigma_o \exp(-E_a / kT)$$

Where k is the Boltzmann's constant, T is the absolute temperature, σ_o is the pre-exponential factor and E_a is the activation energy [13].

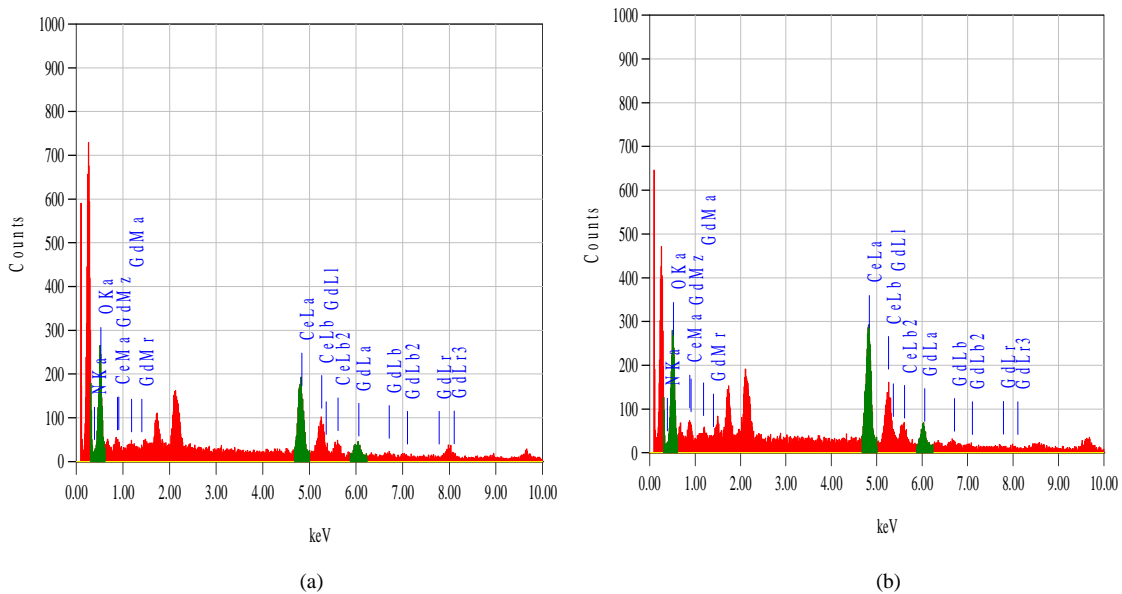


Fig.3. EDS spectra of $Gd_{0.15}Ce_{0.85}O_{1.5}$ by sol-gel (a) and by co-precipitation (b)

Conductivity curve of both the samples consist of two linear parts. Initially the conductivity value is very low form 200 to 280 °C in the sample prepared by co-precipitation method. At 280 °C, the conductivity value becomes higher.

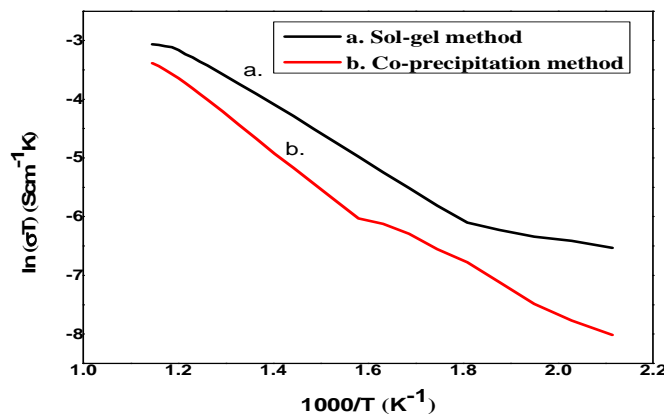


Fig.4. DC conductivity curves of $Gd_{0.15}Ce_{0.85}O_{1.5}$ by sol-gel (a) and by co-precipitation (b)

because the electrons move fast due to low resistance. After 280 to 600 °C, the conductivity curve is almost linear and it increases with the temperature increases. Similarly, GDC prepared by sol-gel method

showed very low conductivity from 200 to 240 °C and from 240 to 600 °C the conductivity curve is almost linear. GDC prepared by sol-gel method showed the conductivity value of 2.17×10^{-4} (S/cm) at 600 °C with activation energy E_a value of 0.31 keV. And GDC prepared by co-precipitation showed the conductivity value of 1.03×10^{-4} (S/cm) at 600 °C with activation energy of 0.36 keV slightly lower than by sol-gel method.

4. Conclusion

GDC electrolyte was successfully synthesized by sol-gel and co-precipitation methods. It was found that both the prepared samples have single phase with cubic fluorite structure. The co-precipitation synthesis resulted in better control on crystallite size in comparison to that by sol-gel route. DC conductivity results showed that GDC prepared by sol-gel method has slightly higher value of conductivity and lower activation energy.

Acknowledgement:

The authors would like to thank School of Chemical and Materials Engineering (SCME), National University of Science and Technology (NUST) Islamabad and COMSATS for their support in carrying out the experiments.

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