

Electrical Properties of Sr²⁺ and Gd³⁺ Codoped Ceria Electrolyte System for LT-SOFC

P. KOTESWARARAO^{1,*}, M. BUCHI SURESH², P. VARALAXMI³, B.N. WANI⁴ and P.V. BHASKARA RAO⁵

¹Department of Physics, Geethanjali College of Engineering and Technology, Cheeryal (V), Keesara (M), Medchal District-501 301, India

²Center for Ceramic Processing, International Advanced Research Centre for Powder Metallurgy and New Materials, Hyderabad-500 005, India

³Department of Physics, Anurag Engineering College, Aushapur (V), Ghatkesar (M), Rangareddi District-501 301, India

⁴Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400 085, India

⁵Department of Physics, Wollega University, Nekemte, Ethiopia

*Corresponding author: E-mail: koteswarphysics@gmail.com

Received: 30 November 2017;

Accepted: 17 February 2018;

Published online: 30 April 2018;

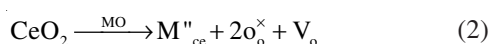
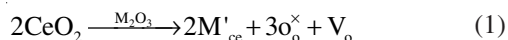
AJC-18868

This paper reports the effect of Sr²⁺ addition on electrical properties of Ce_{0.8}Gd_{0.2}O_{2-δ} (GDC) electrolyte for low temperature solid oxide fuel cell application. The Sr²⁺ (0, 0.5, 1 and 2 mol %) doped GDC solid electrolytes have been prepared by solid state method. The sintered densities of the samples are around 95 %. Among all the compositions, the highest ionic conductivity is observed in the GDC sample with 0.5 mol % Sr addition. Nyquist plots resulted in multiple redoxation process such as grain and grain boundary conduction to the final conductivity. Estimated blocking factor is lower for the GDC electrolyte with 0.5 mol % Sr²⁺, indicating that Sr²⁺ addition promoted grain boundary conduction. Activation energies were calculated from Arrhenius plot and are found in the range of 0.80 to 1.25 eV, indicating oxygen ion conduction in the doped GDC electrolyte system of samples.

Keywords: Conductivity, GDC electrolyte, Impedance, Ionic conductivity, Activation energy.

INTRODUCTION

Ceria (CeO₂) represents cubic unit cell with fluorite-type crystal structure. This structure is characteristic feature of some high performance fast-ion conductors, *e.g.* stabilized cubic zirconia. However, pure ceria is a poor ionic conductor ($\sigma_{700^\circ\text{C}} = 1.9 \times 10^{-5} \text{ S cm}^{-1}$) [1]. When partial substitution of aliovalent cations in ceria leads to incorporation of oxygen vacancies for charge compensation.



where, the symbols are used in accordance with Kroger Vink notation of defects. M'_{ce} stands for a trivalent ion on Ce⁴⁺ site, M''_{ce} stands for a divalent ion on Ce⁴⁺ site V_o is oxygen vacancy with doubly positive effective charge and O_o represents that oxygen ion on O₂ site being neutral. In order to increase the ionic conductivity, the activation energy should be minimum for oxygen diffusion, which can be achieved with the selection of proper dopants. Among rare earth elements gadolinium and samarium doped ceria have been generally used due to these lattice parameters almost equal to undoped ceria which have high solubility in ceria [2]. Their substitution creates very small strain in the lattice which reduces the activation energy for

diffusion of oxide ions [3,4]. This has also been confirmed by atomistic computer simulation studies based on the binding energy between trivalent cations and oxygen vacancies and the corresponding lattice relaxation energy [5]. Herle *et al.* [6,7] reported that GDC showed higher ionic conductivity, whereas the reverse results were reported in the literature [8]. This disagreement probably results from divergence in sample preparation. Herein, we present the effect of Sr²⁺, Gd³⁺ codoping in ceria. We have selected divalent Sr²⁺ and trivalent Gd³⁺ as codopants because average radii of the dopants will become close to critical radii and average binding energy will be lowered as proposed for multiple doping. Ce_{0.8-x}Gd_{0.2}O_{2-δ}Sr_x (x = 0, 0.005, 0.01, 0.02) system of samples were prepared by solid state method and the results of electrical properties are discussed.

EXPERIMENTAL

Ce_{0.8}Gd_{0.2}O_{2-δ} (99.9 % pure, 40 nm particle size, Cotter International, India) and SrCO₃ (AR grade Sigma Aldrich USA, 99.9 % purity) were used as starting materials. The powders of GDC and SrCO₃ were mixed in required stoichiometric proportion (0.5, 1 and 2 mol % of SrCO₃). The mixture was ground in agate and mortar for 2 h and calcined at 800 °C for 2 h. 2 wt % of poly(vinyl pyrrolidone) was added to the powder as binder and was mixed thoroughly. All the samples were

uni-axially pressed to obtain a disc shaped pellets and sintered at 1400 °C for 2 h in air at a ramp rate of 2 °C/min and cool down to room temperature by the same ramp. The synthesized pellets were characterized using AC Impedance analyzer (SI1260A, Solatron UK).

RESULTS AND DISCUSSION

AC impedance spectroscopy is used to study the grain, grain boundary and electrode contribution to the overall ionic conductivity. Normally the total conductivity is the sum of ionic conductivity and electronic conductivity. But in air electronic conductivity ($\sigma_e \approx 10^{-5}$ S/cm) being negligible below 800 °C, as compared to ionic conductivity ($\sigma_i \approx 10^{-2}$ S/cm) for rare earth.

Fig. 1(a-d) shows Cole-Cole plots of (a) GDC (b) 0.5, (c) 1 and (d) 2 mol % Sr^{2+} doped GDC pellets recorded at 300, 500, 600 and 700 °C. Generally AC impedance of an ionic conductor measured by the two-probe method contains the contributions from grain interior, grain boundary and electrode-electrolyte interface polarization, which are reflected in a complex plane with three well successive arcs. It is observed that the change in the area of semicircular arcs with temperature represents the variation in relaxation. At lower temperatures, the samples are fairly resistive as evident from Z'' - Z' plots.

The (Z') and (Z'') values decrease with temperature in the present samples of Sr^{2+} -GDC.

The effect of grain and grain boundaries contributes on the conduction mechanism is studied by using impedance at different temperatures. The plots between Z'' and Z' have shown two semicircles and a spike. The diameter of the semicircle gives the resistance of grain and grain boundaries. Grain resistance is observed to be higher than the grain boundary resistance and it indicates that the conduction mechanism in Sr^{2+} doped GDC is due to grain boundaries. At higher temperatures, the semicircle starts intercepting at high frequency side indicating the role of series resistance in the standard material system and the time constants of the relaxations resulting from the individual polarizations are decreased and it results in successive disappearance of the arcs corresponding to the grain and grain-boundary contributions.

High frequency semi-circle corresponds to grain resistance (R_g), intermediate frequency semi-circle corresponds to grain boundary resistance (R_{gb}) and low frequency incomplete arc corresponds to electrode resistance (R_e). All these arcs will be observed depending on the nature of samples and the testing conditions. At 500 °C, the grain boundary conductivity was substantially increased with Sr^{2+} addition from 0-0.5 mol % Sr^{2+} -GDC. This might be due to the addition of Sr^{2+} affecting

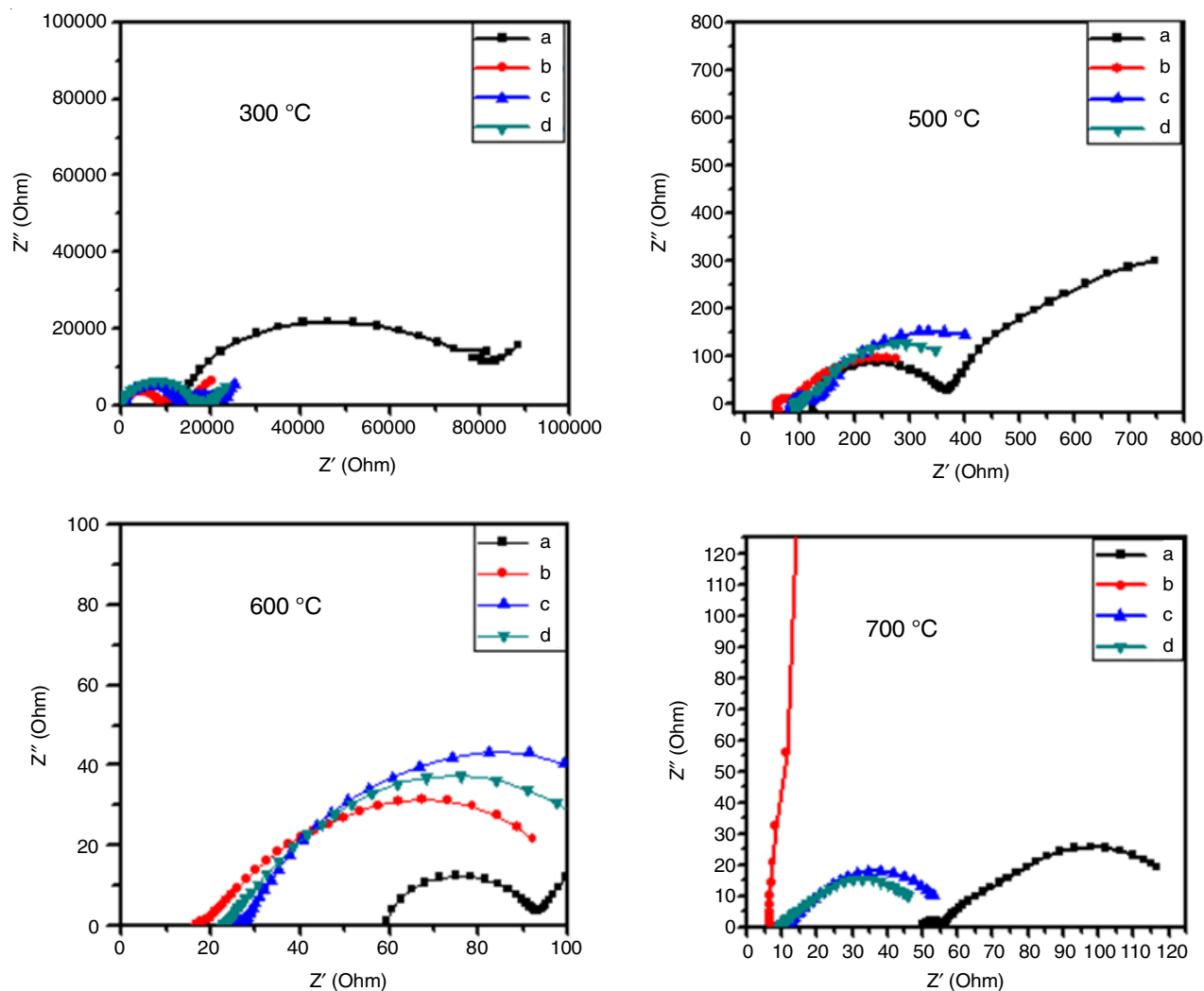


Fig. 1. Cole-Cole plots of (a) GDC (b) 0.5, (c) 1 and (d) 2 mol % Sr^{2+} doped GDC pellets recorded at 300, 500, 600 and 700 °C

the grain boundary conduction by acting as a grain boundary scavenger. Therefore, a material with low grain boundary resistance, *i.e.*, high grain boundary conductivity, is ideal for practical applications. Moreover, the size of bulk and grain boundary semicircles decreases with an increase of temperature from 300 to 700 °C and all semicircles shift towards high frequency side. The size of bulk and grain boundary semicircles decreases with an increase of temperature and finally only the electrode contribution will be seen at higher temperatures.

The sample total resistance, R_t can be obtained from impedance spectroscopy at different temperatures as:

$$R_t = R_g + R_{gb}$$

$$\sigma_t = \frac{1}{R_t} \times \frac{t}{A} \quad (3)$$

where t is the thickness and A is the cross sectional area of the sample.

The total ionic conductivity σ was calculated by using above equation. Fig. 1 shows ionic conductivity with respect of mol % of dopant at 700 °C.

Fig. 2 shows that highest conductivity (electrical or ionic) is obtained at 0.5 mol % Sr²⁺ doping concentration. However, above 0.5 mol %, Sr²⁺ concentration total conductivity decreases due to defect association and it leads to lowering the effective concentration of oxygen vacancies and their mobility. Hence increase in Sr²⁺ content to high values leads to decrease in the overall conductivity. The ionic conductivity depends mainly on the mobile oxygen concentration and their mobility. The fact is attributed to the presence of impurities located in grain boundary, which lower the ionic mobility. It is observed that there is a decrease in grain boundary resistivity by increasing the grain sizes as discussed in cole-cole plots, *i.e.*, lowering the grain boundary density [9].

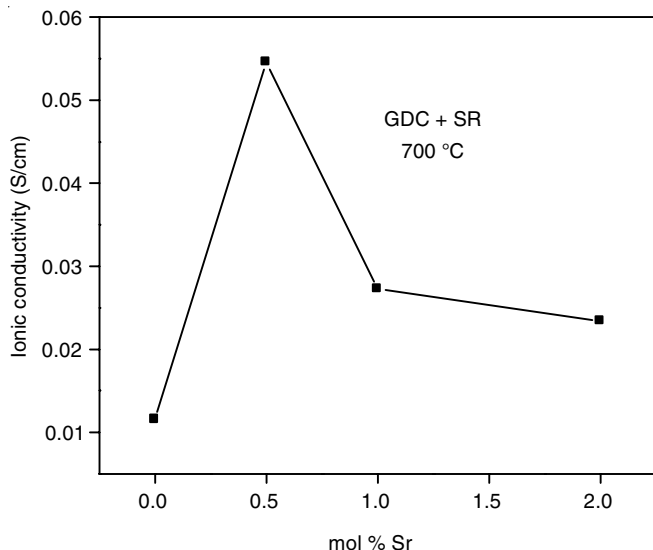


Fig. 2. mol % vs. ionic conductivity of Sr²⁺ doped GDC

Fig. 3 shows the Arrhenius plots of Sr doped GDC system of samples. The ionic conductivity of GDC was significantly enhanced by addition of strontium due to creation of oxygen vacancies. It is clear that both bulk and grain boundary impedance arcs are present in the ceramics and electrical properties are determined. According to previous reports partial substi-

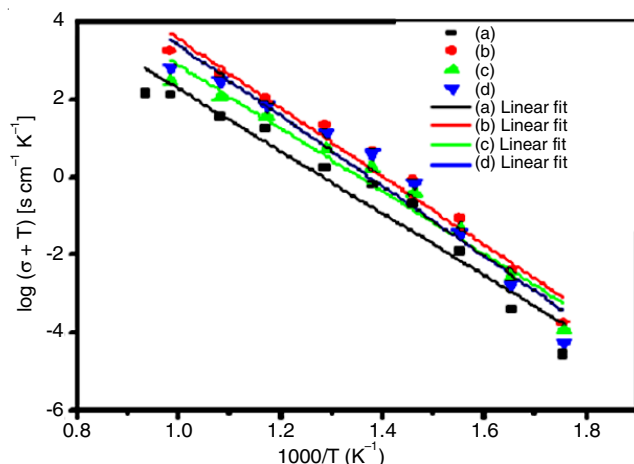


Fig. 3. 1000/T versus log (σ) Arrhenius plots of Sr²⁺ GDC

tution of gadolinia by samaria in Ce_{0.85}Gd_{0.15-x}Sm_xO₂ up to $x = 0.05$ also enhances the total electrical conductivity compared to only gadolinia doped ceria (Ce_{0.85}Gd_{0.15-x}Sm_xO₂). Because of small ionic size mismatch between the host and a dopant was reported as a factor to enhance the ionic conductivity [10,11]. As temperature increases R_{gb} decreases in all samples which indicates enhancement of the conductivity due to oxygen ions migrate easily codoping ceria system more effective than single dopant [12-15].

For a specific composition, with rise in temperature, time constants of both grain and grain boundary processes reduce and corresponding resistances decrease. Hence conductivity rises with the temperature. The temperature dependence of total electrical conductivity can be fitted into the Arrhenius relation:

$$\sigma = \frac{A}{T} \exp \frac{-E_a}{kT} \quad (4)$$

Sr²⁺-GDC samples showed higher conductivity than GDC at all temperatures with more difference in the lower temperature ranges. The activation energies of the total conductivity for GDC and Sr²⁺-GDC (0.5, 1 and 2 mol %) were estimated and shown in Table-1. These activation energies are lesser than the previous reports as presented in the literature review [16,17].

TABLE-1 ACTIVATION ENERGY OF GDC + Sr SYSTEM	
Composition	AE (eV)
Pure GDC	1.250
0.5 mol % Sr ²⁺ doped GDC	0.809
1.0 mol % Sr ²⁺ doped GDC	0.916
2.0 mol % Sr ²⁺ doped GDC	0.956

In Sr²⁺ added GDC the ionic radius of Sr²⁺ (1.26 Å) is higher than Gd and ceria (0.97 Å), so the electrostatic attraction (Sr_{ce}V_o) between Sr_{ce}V_o is stronger than that between Gd_{ce}V_o. Therefore defect Association between (Sr_{ce}V_o) is easier than Gd_{ce}V_o, so that Sr²⁺ attracts one (V_o) to form a defect complex, thereby decreasing conductivity. Strontium doping to GDC patterns results in improving the oxygen vacancies and reducing the lattice fastening power that increases the oxygen ion movement, resulting in the observed enhancement of electrical

conductivity in comparison to un-doped GDC samples. Increasing activation energy means defect complex take place between Sr^{2+} and V_o as result decrease conductivity.

Conclusion

Sr^{2+} doped GDC solid electrolytes are successfully synthesized by solid state reaction method. The conductivity is more for 0.5 mol % Sr^{2+} than pure GDC. An enhanced conductivity at 0.5 mol % is due to scavenging effect. Activation energies were calculated from Arrhenius plot and are found in the range of 0.80 to 1.25 eV, indicating oxygen ion conduction in the doped GDC electrolyte system of samples.

REFERENCES

1. W. Huang, P. Shuk and M. Greenblatt, *Chem. Mater.*, **9**, 2240 (1997); <https://doi.org/10.1021/cm970425t>.
2. V.V. Kharton, F.M. Figueiredo, L. Navarro, E.N. Naumovich, A.V. Kovalevsky, A.A. Yaremchenko, A.P. Viskup, A. Carneiro, F.M.B. Marques and J.R. Frade, *J. Mater. Sci.*, **36**, 1105 (2001); <https://doi.org/10.1023/A:1004817506146>.
3. Z. Tianshu, P. Hing, H. Huang and J. Kilner, *Solid State Ion.*, **148**, 567 (2002); [https://doi.org/10.1016/S0167-2738\(02\)00121-2](https://doi.org/10.1016/S0167-2738(02)00121-2).
4. D.-J. Kim, *J. Am. Ceram. Soc.*, **72**, 1415 (1989); <https://doi.org/10.1111/j.1151-2916.1989.tb07663.x>.
5. L. Minervini, M.O. Zacate and R.W. Grimes, *Solid State Ion.*, **116**, 339 (1999); [https://doi.org/10.1016/S0167-2738\(98\)00359-2](https://doi.org/10.1016/S0167-2738(98)00359-2).
6. J. van Herle, D. Seneviratne and A.J. McEvoy, *J. Eur. Ceram. Soc.*, **19**, 837 (1999); [https://doi.org/10.1016/S0955-2219\(98\)00327-6](https://doi.org/10.1016/S0955-2219(98)00327-6).
7. J. van Herle, T. Horita, T. Kawada, N. Sakai, H. Yokokawa and M. Dokiya, *Solid State Ion.*, **86-88**, 1255 (1996); [https://doi.org/10.1016/0167-2738\(96\)00297-4](https://doi.org/10.1016/0167-2738(96)00297-4).
8. H. Inaba and H. Tagawa, *Solid State Ion.*, **83**, 1 (1996); [https://doi.org/10.1016/0167-2738\(95\)00229-4](https://doi.org/10.1016/0167-2738(95)00229-4).
9. G. Liu, J.A. Rodriguez, J. Hrbek, J. Dvorak and C.H.F. Peden, *J. Phys. Chem. B*, **105**, 7762 (2001); <https://doi.org/10.1021/jp011224m>.
10. E. Puppini, I. Lindau and I. Abbati, *Solid State Commun.*, **77**, 983 (1991); [https://doi.org/10.1016/0038-1098\(91\)90358-3](https://doi.org/10.1016/0038-1098(91)90358-3).
11. K. Sandhya, C. Priya N.S and D.N. Rajendran, *Int. J. Eng. Trends Technol.*, **37**, 400 (2016); <https://doi.org/10.14445/22315381/IJETT-V37P267>.
12. A.S. Nesaraj, I.A. Raj and R. Pattabiraman, *J. Iran. Chem. Soc.*, **7**, 564 (2010); <https://doi.org/10.1007/BF03246044>.
13. H. Yoshida, T. Inagaki and K. Miura, *Solid State Ion.*, **160**, 109 (2003); [https://doi.org/10.1016/S0167-2738\(03\)00153-X](https://doi.org/10.1016/S0167-2738(03)00153-X).
14. N. Jaiswal, D. Kumar, S. Upadhyay and O. Parkash, *Int. J. Ionics*, **20**, 45 (2014); <https://doi.org/10.1007/s11581-013-0936-8>.
15. P. Jasinski, *Solid State Ion.*, **177**, 2509 (2006); <https://doi.org/10.1016/j.ssi.2006.04.018>.
16. F. Aydin, I. Demir and M.D. Mat, *Eng. Sci. Technol. Int. J.*, **17**, 25 (2014); <https://doi.org/10.1016/j.jestch.2014.02.003>.
17. L.P. Sun, M. Rieu, J.P. Viricelle, C. Pijolat and H. Zhao, *Int. J. Hydrogen Energy*, **39**, 1014 (2014); <https://doi.org/10.1016/j.ijhydene.2013.10.117>.