ORIENTAL JOURNAL OF CHEMISTRY
An International Open Free Access, Peer Reviewed Research Journal
www.orientjchem.org
Est. 1984

ISSN: 0970-020 X
CODEN: OJCHEG
2018, Vol. 34, No.(4):
Pg. 2125-2130

Preparation and Conductivity Studies of $La_{9.33}Si_6O_{26}$ (LSO) -$Ce_{0.85}Gd_{0.15}O_{1.925}$ (CGO15) Composite Based Electrolyte for IT-SOFC

ATIEK ROSTIKA NOVIYANTI[1]*, IWAN HASTIAWAN[1], DIANA RAKHMAWATY EDDY[1], MUHAMMAD BERLIAN ADHAM[1], ARIE HARDIAN[2] and DANI GUSTAMAN SYARIF[3]

[1]Department of Chemistry, Faculty of Mathematic and Natural Sciences, Universitas Padjadjaran, Indonesia.
[2]Department of Chemistry, Faculty of Mathematic and Natural Sciences, Universitas Jenderal Achmad Yani,
Jl. Terusan Jenderal Sudirman, Cimahi, Indonesia.
[3]PSTNT – BATAN, Jl. Taman Sari 71 Bandung 40132 Indonesia.
*Corresponding author E-mail: atiek.noviyanti@unpad.ac.id

http://dx.doi.org/10.13005/ojc/3404053

(Received: July 14, 2018; Accepted: August 02, 2018)

ABSTRACT

Reducing a high-operating temperature of solid oxide fuel cell (SOFC) to intermediate temperature SOFC (IT-SOFC, 500-750^{o}C) poses a great challenge in the sense of developing solid electrolyte at intermediate temperature range. In response to this, we report a novel composite $La_{9.33}Si_6O_{26}$ (LSO) - $Ce_{0.85}Gd_{0.15}O_{1.925}$ (CGO) in this study. The synthesis of LSO-CGO composite was carried out by combining LSO with CGO (9:1, 8:2, and 7:3 in weight ratio) using solid state reaction method. In order to get a dense pellet, all of the products were sintered at 1500°C for 3 hours. The X-ray diffraction pattern of sintered pellets show typical patterns for both of LSO and CGO which indicate that the composite was successfully formed. The highest conductivity was detected in 7LSO-3CGO, i.e. $2.10\times^{10-3}$ S cm^{-1} at 700^{o}C and also has low activation energy (0.60 eV). This result suggests that the LSO-YSZ composites are good oxide ion conductors and may potentially be used as an alternative solid electrolyte in IT-SOFC technology.

INTRODUCTION

One of the causes of energy crisis is due to the high usage of fossil fuel as energy source for various human activities. Fuel cell is an alternative technology not to only produce electrical energy, but for its environment friendly and efficient property. Fuel cell is an electrochemical device that converts chemical energy from fuel (usually hydrogen) and oxidant (usually air) into electrical energy[1-3].

Many types of fuel cells had been increasingly developed in many countries such as USA, Germany, England, and also developing Asian countries such as Japan, Korea, and China. Till now now, there are six types of fuel cells that depend on electrolyte material, which are Alkaline Fuel Cell (AFC), Polymer Electrolyte Membrane Fuel Cell (PEMFC), Phosphoric Acid Fuel Cell (PAFC), Direct Methanol Fuel Cell (DMFC), Molten Carbonate Fuel Cell (MCFC), and Solid Oxide Fuel Cell (SOFC)[1,2]. Solid Oxide Fuel Cell (SOFC) has attracted many researchers' attention due to its advantages compared to the others. This includes its capability of using many types of fuel not only H_2 but also hydrocarbon, while proving to be low in its maintenance cost and presents high efficiency (could reach 85% when combined with gas turbine)[1,2]. SOFC also uses high operational temperature (800-1000°C) due to the type of its electrolyte. This high operational temperature causes problem such as unexpected reactions between the materials which lead to lower efficiency. Therefore, the development of SOFC technology by lowering the operational temperature to the intermediate range which is 600-700°C is seen as a strategic move. Lowering the operational temperature of SOFC has many advantages including the usage of low cost material such as metal as interconnect material, the lowering of fabrication cost and maintenance cost, and avoiding the unexpected reactions at high temperatures that lead to short SOFC lifetime[3].

Electrolyte material is the key in order to determine the operational temperature of SOFC. Apatite-based electrolyte has a great potential to be used as electrolyte at Intermediate Temperature SOFC (IT-SOFC) due to its high conductivity. Apatite has the general chemical formula $M_{10}(SiO_4)6O_{2\pm y}$, in which M is usually derived from rare earth metal group or alkaline earth. Lanthanum is one of elements in rare earth metal groups which has large atomic radius and has a potential in obtaining good conductivity in apatite. Apatite with La called lanthanum silicate-based apatite becomes one of the apatite-based research that attracts many researchers' attention[4].

In our previous works, $La_{9.33}Si_6O_{26}$ have been successfully synthesized via hydrothermal method using La_2O_3 and Na_2SiO_3 as the precursors and NaOH as the base which is heated at 240°C for 3 days[5]. The highest conductivity of the obtained apatites was 2.95 x 10^{-4} S cm^{-1} at 500°C. However, that value is still low to be used as IT-SOFC electrolyte. Chao-feng *et al.,* reported that the mechanical properties of apatites were unstable, brittle, and hygroscopic[6]. These weaknesses made the apatite-based electrolytes to be unsuitable for IT-SOFC electrolyte.

Yttria Stabilized Zirconia (YSZ) is the common SOFC electrolyte and is already commercially available. YSZ worked optimally at high-operating temperatures at 800-1000°C. YSZ has also good mechanical properties that could support the SOFC cell and has suitable thermal expansion coefficient (TEC) with the other SOFC components especially electrode. However, YSZ could react with nickel-based anode at high operational temperature that effects the efficiency of the cell.

In general, there are two ways to improve the quality of electrolyte so that it can be used as IT-SOFC electrolyte. The first way is finding the other type of metal oxide which has high conductivity within the IT range. The first way of generating process is by modifying the microstructure of metal oxide. The second way is the use of composite material which is an easier way compared to the first one[6].

In our previous work, composite apatite and YSZ had been successfully synthesized[7]. The conductivity of composite increased when the weight percentage of YSZ increased. The highest conductivity of composite was reached at a composition of 70% LSO (lanthanum silicatebased apatite) and 30% YSZ which is 1.72x10^{-4} S cm^{-1} at 500°C.

Another oxide which has a great potential to be used as IT-SOFC electrolyte is ceria-based electrolyte. Doped cerium oxide (Ceria) has higher conductivity at intermediate temperature range compared to the commercial SOFC electrolyte, i.e. Yttria Stabilized Zirconia (YSZ). Doped ceria also has good mechanical properties and suitable thermal expansion coefficient (TEC) with the other SOFC component especially electrode. In our previous research, we worked with ceria-based electrolyte, whereby Gadolinium Doped Ceria (CGO) was successfully synthesized via sol gel method using nitrate salt as the precursor and citric acid monohydrate as the chelating agent[8]. The conductivity of the obtained CGO15 ($Ce_{0.85}Gd_{0.15}O_{1.925}$) was 4.57x$10^{-2}$ S cm^{-1} at 700°C, which is suitable to be used as IT-SOFC electrolyte.

Ceria-based electrolyte also has good mechanical properties.

In other work, the use of doped ceria in composite strategy could increase the conductivity and the mechanical properties simultaneously of the obtained composite[6]. Therefore, the composite strategy is good in order to create new electrolyte material which has high conductivity and good mechanical properties.

In this work, we report the synthesis and the electrical properties of CGO-LSO composited based electrolyte. The effect of weight percent through the crystal structure, morphology, density, and conductivity of CGO-LSO composite based electrolyte were also discussed.

EXPERIMENTAL

To prepare the composite materials, three batches with the LSO to CGO ($Ce_{0.85}Gd_{0.15}O_{1.925}$) weight ratios of 9:1, 8: 2, and 7: 3 were designed (recorded as 9LSO-1CGO, 8LSO-2CGO, and 7LSO-3CGO respectively). CGO was synthesized by sol-gel using starting material of CeO_2 99.99% (trace metal basis. Aldrich) and Gd_2O_3 99.99% (trace metal basis. Aldrich). LSO was synthesized by hydrothermal using high-purity La_0O_3 (Aldrich, 99.999%), Na_2SiO_3 (Sigma, 97%), and a 3 M NaOH solution was used in the preparation of these apatites as mineralizer. According to the weight ratios, LSO powder and CGO powder were weighted and mixed using ball mill for 60 minutes. Three batches of mixture powders were pressed under 6000 kg m^{-2} to obtain green pellets with 8 mm diameter and ~2 mm thickness. The pellets were then sintered at 1500 °C for 3 hours. The densities of the sintered pellets were calculated using the ratio of weight and volume (based on their dimension).

The structure identification was examined by using X-ray diffraction (Rigaku SmartLab X-Ray Diffractometer using Cu-Kα radiation (λ = 1.5406 Å) at room temperature, while the morphology of the calcined powders and sintered pellets were investigated by using scanning electron microscopy (Hitachi-EDAX Team). Meanwhile, the density of the apatite was examined by using the Archimedes principle. Ionic conductivity was measured using an LCR meter (GW Instek 61056) at 600 – 700°C and a frequency range of 20 Hz – 5 MHz on the sintered pellet sample. The total resistance (R) after which the value of resistivity (ρ) is calculated by the following equation:

$$\rho = R\frac{A}{l} \quad (1)$$

The surface area (A) and thickness (l) were obtained by measuring the diameter (d) and thickness (l) pellets directly. After the value of resistivity (ρ) was obtained. Finally, the value of conductivity (σ) is calculated using the following equation:

$$\sigma = \frac{1}{\rho} \quad (2)$$

RESULT AND DISCUSSION

Figure 1 shows the XRD patterns of the as-calcined composite of LSO-CGO. Significant peaks for LSO appeared at 2θ = 21-22°; 31°; and 45°, while for CGO at 2θ = 28.5°; 33°; 47.4° and 56°. The diffraction patterns of the three sintered pellets (1.500°C for 3 h) of 9LSO-1CGO, 8LS0-2CGO, and 7LSO-3CGO exhibit typical LSO and CGO phases. The X-ray diffraction results indicate that all the composites have been successfully prepared.

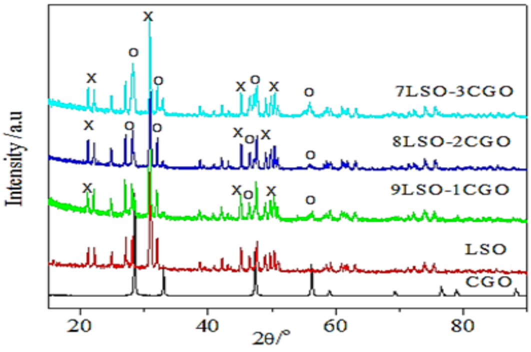

Fig. 1. Diffraction patterns of LSO-CGO composites of 9 LSO-CGO, 8 LSO-2CGO, and 7LSO-3CGO. (x) = LSO and (o) = CGO

In order to evaluate the relation between the microstructure of composite and conductivity, SEM measurements were carried out. The SEM micrographs of the sintered LSO-CGO are presented in Fig. 2. The size of grains was in the range of 3 to 7 µm. It is not clear whether the LSO and CGO phase is located at the grain boundaries or inside of grains of the main phase. The addition of CGO on

LSO reduced the reactivity of sintering powder with the atmospheric H2O and CO_2[9]. Table 1 listed the EDS data for LSO-CGO composite composition. In overall, the experimental ratio of constituent atoms in ($La_{9.33}Si_6O_{26}$-$Ce_{0.85}Gd_{0.15}O_{1.925}$) is close to the calculated ratio. There were no impurities detected and it was concluded that the LSO-CGO composite has been well-formed.

Table 1: EDS data for LSO-CGO composite composition

Element	(9LSO-1CGO) Calculation Mass/ %	(8LSO-2CGO) EDS%	(7LSO-3CGO) Calculation Mass%	EDS%	Calculation Mass %	EDS%
Lanthanum	62.20	62.48	55.36	56.61	48.47	49.75
Silicon	8.09	7.30	7.20	7.63	6.30	7.15
Oxygen	21.80	21.76	21.38	20.58	20.95	21.29
Cerium	7.11	6.67	13.98	12.07	20.86	18.38
Gadolinium	1.41	1.79	2.77	3.11	4.13	3.43

In order to know the influence of CGO content in LSO, we attempt to calculate the density of composite by using the Archimedes principles. Table 2 shows that the higher the CGO content is, the higher the density of the composite.

It was concluded that the CGO helped to increase the electrolyte performance. In addition, the higher the density of LSO-CGO composite, the higher were their conductivities. A similar result was also presented in our previous research for LSO-YSZ composite[7,10].

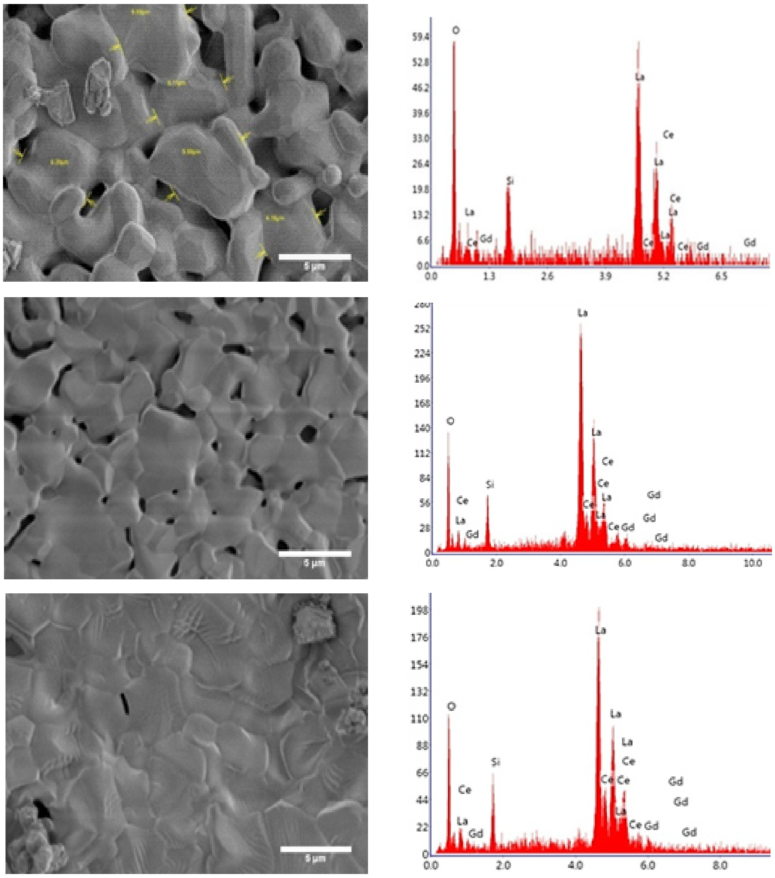

Fig. 2. Microstructure observations of the samples SEM image and EDX of (a) 9LSO-CGO, (b) 8LSO-2CGO, and (c) 7LSO-3CGO after sintered at 1.500°C for 3 hour

Table 2: Density of sintered composite of LSO-CGO

	9LSO-1CGO	8LSO-2CGO	7LSO-3CGO
Mass (g)	0.2859	0.2907	0.2957
Radius (cm)	0.3788	0.3740	0.3695
thickness (cm)	0.1565	0.1580	0.1635
Volume (cm^3)	0.0705	0.0694	0.0701
Density (g cm^{-3})	4.0557	4.1890	4.2187
Surface area (cm^2)	0.4508	0.4396	0.4291

Conductivity investigation

The Nyquist plot obtained at 600, 650, and 700°C for 9LSO-1CGO composite is presented in Figure 3.

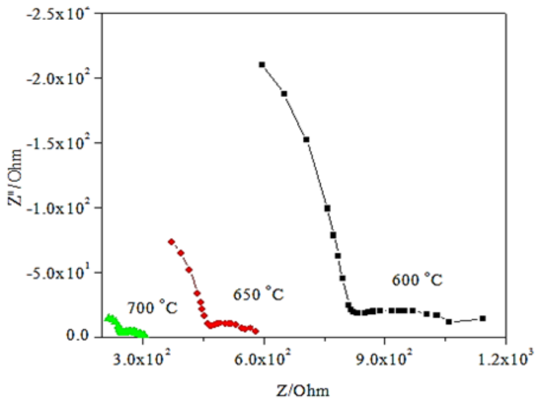

Fig. 3. The Nyquist plot of 9LSO-1CGO composite at 600°C, 650°C, and 700°C

The total resistance of composite rises about twice, when the operating temperature drops by 50 degrees. All impedance plots of an oxygen-ion conductor exhibit two semicircle parts. The third semicircle exhibit at Nyquist plot at 600°C as a response to interface electrode-electrolyte at low-frequency region. The high-frequency region corresponds to the bulk response, whereas the medium-frequency region is related to the grain boundary contribution[8,11, 12].

Impedance measurement produces two impedances (R_1 and R_2). R_1 is the contribution of its bulk phase response and R_2 is the response of the grain boundary phase. For example, the total impedance 9LSO-1CGO composite at a temperature of 700°C measurement is 263.29 Ω. which is derived from the sum of a bulk phase response and phase between the grains. The bulk resistance region is larger than that of the grain boundary resistance. The temperature effect on the conductivity of LSO-CGO composite is shown at Figure 4.

Figure 4 shows that composite conductivity is greatly dependent on both the temperature and the LSO:CGO ratio. The activation energies of 9LSO-1CGO, 8LSO-2CGO, and 7LSO-3CGO composites were 1.1 eV, 0.70 eV; and 0.60 eV, respectively. Overall, the activation energy below 1.1 eV suggests that the ionic conduction arises from the migration of interstitial oxide ions[5,13]. The slope of the curve at high temperature states of energy required to create and move the intrinsic defects, whereas the slightly more curved slope shows the energy required to remove defects only[14]. The conductivities and energy activation of the three series LSO-CGO composites are at 700°C are shown in Table 3. The composite of 7LSO-CGO shows a higher conductivity (2.10×10^{-3} at 700°C) and lower action energy compared to the other compositions.

This suggests that the higher the CGO content, the higher is the density of the composite. This is in consequence to the conductivities of series LSO-CGO composite.

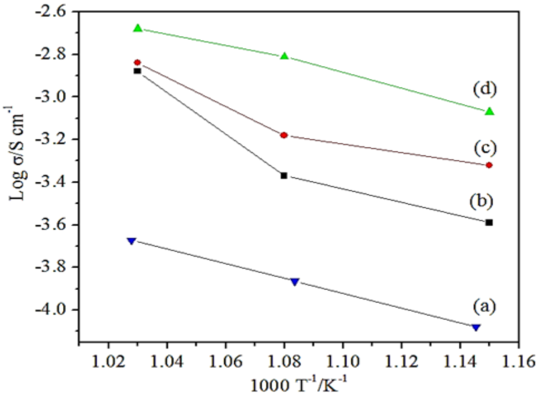

Fig. 4. Temperature dependence of conductivity of (a) LSO, (b) 9LSO-CGO, (c) 8LSO-2CGO, and (d) 7LSO-3CGO composites

Table 3: Conductivities of LSO-CGO composite at 700°C.

Composite	R / Ω	d / cm	l / cm	A / cm^2	ρ/ S^{-1}.cm	σ / S cm^{-1}	Ea / eV
9LSO:1CGO	263.29	0.7575	0.1565	0.4508	7578.01	1.32×10^{-3}	1.1
8LSO:2CGO	251.4	0.7480	0.1580	0.4396	6988.45	1.43×10^{-3}	0.7
7LSO:3CGO	181.4	0.7390	0.1635	0.4291	4756.40	2.10×10^{-3}	0.6

CONCLUSION

A novel composite electrolyte, LSO-CGO was developed and used as the electrolyte for intermediate temperature fuel cells. The results showed that when the composition was 70 wt. % LSO and 30 wt. % CGO, the electrolyte had higher electrical conductivity in the temperature of 500-750°C. The activation energy values of synthesized composites were lower than 1.1 eV. This indicates that the composite material is possible for ion oxide conductor. This composite electrolyte is a promising electrolyte material for IT-SOFC's.

ACKNOWLEDGMENT

The authors are grateful to Universitas Padjadjaran through Unpad internal grant (Hibah Internal Unpad) No 872/UNG.3.1/LT/2017.

REFERENCES

1. Badwal, S.P.S., Foger, K.: *Solid Oxide Electrolyte Fuel Cell Review. Ceramics International.,* **1996**, *22*, 257-265.
2. Ormerod, R.M.: Solid oxide fuel cells. *Journal of Chemistry Society Review.,* **2002**, *32*, 17-28.
3. Stambouli, A.B., Traversa, E.: Solid oxide fuel cells (SOFCs): a review of an environmentally clean and efficient source of energy. Renewable and Sustainable Energy Reviews., **2002**, *6*, 433–455.
4. Sansom, J.E.H., Richings, D., Slater, P.R.: A powder neutron diffraction study of the oxide-ion-conducting apatite-type phases, $La_{9.33}Si_6O_{26}$ and $La_8Sr_2Si_6O_{26}$. *Solid State Ionics.,* **2001**, *139*(3-4), 205-210.
5. Noviyanti, A.R., Ismunandar, Prijamboedi, B., Marsih, I.N.: Hydrothermal Preparation of Apatite-Type Phases $La_{9.33}Si_6O_{26}$ and $La_9M1Si_6O_{26.5}$ (M = Ca, Sr, Ba). *ITB Journal of Science.,* **2012**, *44*((2)), 193-203.
6. Liu, C., Zhang, H., Xia, J., Li, Z.: Synthesis and characterization of $Zr_{0.85}Y_{0.15}O_{1.925}$-$La_{9.33}Si_6O_{26}$ composite electrolyte for application in SOFCs. *Journal of Advanced Ceramics.,* **2012**, *1*(4), 327-335.
7. Noviyanti, A.R., Hastiawan, I., Irwansyah, F.S., Hidayat, S., Hardian, A., Syarif, D.G., Yuliyati, Y.B.: Preparation and Conductivity of Composite Apatite $La_{9.33}Si_6O_{26}$(LSO) - $Zr_{0.85}Y_{0.15}O_{1.925}$(YSZ) In: AIP Conference Proceedings Bandung Indonesia **2016**, pp. 050002-050001-050002-050006. AIP Publishing
8. Hardian, A., Choi, G.M., Suendo, V., Ismunandar: Structure and Ionic Conductivity of Codoped Ceria for IT-SOFC Electrolytes *Journal of the Australian Ceramics Society.,* **2014**, *50*[2], 99 –109.
9. Yoshioka, H., Tanase, S.: Magnesium doped lanthanum silicate with apatite-type structure as an electrolyte for intermediate temperature. *Solid State Ionics.,* 2005, 176, 2395-2398.
10. Noviyanti, A.R., Hastiawan, I., Yuliyati, Y.B., Rahayu, I., Rosyani, D., Gustaman, S.D.: LSO apatite-YSZ composite as a solid electrolyte for solid oxide fuel cells. In: AIP Conference Proceedings 2017, pp. 040001-040001–040001-040006. AIP Publishing
11. Bechade, E., Julien, I., Iwata, T., Massona, O., Thomasa, P., Championa, E.: Synthesis of lanthanum silicate oxyapatite materials as a solid oxide fuel cell electrolyte. *Journal of European Ceramic Society.,* **2008**, *28*, 2717-2724
12. Cao, X.G., Jiang, S.P.: Synthesis and characterization of lanthanum silicate oxyapatites co-doped with A (A ¼ Ba, Sr, and Ca) and Fe for solid oxide fuel cells. *Journal of Materials Chemistry A.,* **2014**, *2*, 20739–20747
13. Islam, M.S., Tolchard, J.R., Slater, P.R.: An apatite for fast oxide ion conduction. *Chemical Communations.*, **2003**, *4,* 1486-1487.
14. West, A.R.: Solid State Chemistry and Its Applications, 2 ed. John Wiley & Sons, LTD, West Sussex PO19 8SQ, England., **1989**.