Lowered Sintering Temperature on Synthesis of La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.55}$ (LSGM) Electrolyte Composite and the Electrical Performance on La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCM) Cathode

Yoga Trianzar Malik, Atiek Rostika Noviyanti, Dani Gustaman Syarif

Abstract

Solid oxide fuel cell (SOFC) is the device that can convert chemical energy into electricity with highest efficiency among other fuel cell. La$_{0.3}$Si$_{0.26}$ (LSO) is the potential electrolyte at intermediate operation temperature SOFC. Low ionic conductivity of lanthanum silicate–based electrolyte will lead into bad electrical performance on lanthanum manganite–based anode. In this study, LSO was combine with La$_{0.2}$Sr$_{0.8}$Ga$_{0.2}$Mg$_{0.8}$O$_{2.55}$ (LSMG) electrolyte by using conventional solid state reaction to enhance the electrical performance of LSO on LCM cathode. However, pre–requisite high sintering temperature on preparation of LSO–LSGM composite will lead into phase transition phase of LSGM that may affect in decreasing the electrical performance. This study resulted that lowered sintering temperature from its ideal temperature still give an improved electrical performance of LCM/LSO–LSGM/LCM symmetrical cell. The ASR value is 0.14 $\Omega$.cm$^{-2}$ which much lower than its analogous symmetrical cell, LSM/LSO/LSM that was reported before.

1. Introduction

In the recent years, electricity consumption is noted a tremendous value as 20,201,201 TWh all over the world. Besides, the emission of carbon dioxide had reached 32,294 Mt in 2015 by fuel usage [1]. This issue has led an attraction of evolutionary electrical generator that reflects an eco–friendly fueled device in which converting chemical energy into electricity such as solid oxide fuel cell (SOFC). SOFC can generate the electricity up to 10MW [2] which has the highest efficiency 40–60% among any other fuel cells [3]. SOFC itself consists of electrolyte and electrode components which was fabricated from many rare–earth elements. In order to obtain a good electrical output, SOFC must have been operated at high temperature. However, much higher temperature will lead the cell into incompatibility in physicochemical–mechanical properties that drives the cell toward electrical deficiency and even destruction due to chemical instability of components based on high–temperature reaction occurred.

Lanthanum silicate apatite (LSO) is a potential electrolyte at low temperature. On the other hand, lanthanum gallate (LGO)–based electrolytes are known as good electrical performance electrolytes at intermediate temperature. LSO had been combined with other electrolyte material such as yttrium stabilized–zirconia (YSZ) and samarium doped ceria (SDC). But this combination still showed no significant effect in conductivity. LSO–YSZ showed a low conductivity 1.72 x 10$^{-4}$ Scm$^{-1}$ at 973K [4]. LSO–SDC also showed low conductivity at 9.27x10$^{-3}$ S/cm$^{-1}$ at 1073K [5]. Low conductivity might affect the electrical performance. La$_{0.3}$Sr$_{0.2}$Ga$_{0.2}$Mg$_{0.8}$O$_{2.56}$ (LSO) relatively has low ionic conductivity as 0.002 S.cm$^{-1}$ at 1073K [6] in comparing with La$_{0.2}$Sr$_{0.8}$Ga$_{0.2}$Mg$_{0.8}$O$_{1.5}$ (LSGM) electrolyte which has a good conductivity value as 0.166 S.cm$^{-1}$ (1073K) [7]. The combination of those electrolytes was expected to obtain a good electrical performances of its bulk material and the interaction with lanthanum manganite (LaMnO$_3$)–based cathode such as a La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCM). LCM itself has a magnificent electrical conductivity as ~200 S.cm$^{-1}$ at 1173K [8]. Both lanthanum silicate apatite and lanthanum...
gallate-based electrolytes were known having good chemical stability with LaMnO$_3$ cathode [9, 10].

On the other hand, Shi et al. [5] reported high temperature sintering on the preparation of LSO–SDC electrolyte composite as 1823K. While Noviyanti et al. [4] also showed high sintering temperature on LSO–YSZ electrolyte as 1673K. LSO is melting at above 2273K based on its phase diagram [11], while LSGM starts to melt at ~1773K [12]. In order to fabricate a good combination of LSO–LSGM, the solid state reaction must take place above 1673K based on Tamman’s rules for ideal sintering temperature [13]. However, this temperature will lead the phase conversion of LSGM at high temperature [14] which lead a tendency of the lowering electrical performances of individual components. Hence, lowering the sintering temperature below 1673K was designated to decrease the effect of this phase transition. This research aimed to synthesize the electrolyte composite of LSO–LSGM at below its Tamman’s temperature and study the electrical performance of LSO–LSGM electrolyte composite on LCM cathode.

2. Experimental

2.1. LSO synthesis

LSO was firstly synthesized from La$_2$O$_3$ (Aldrich, 99.999%, trace metal), Na$_2$SiO$_3$, 5H$_2$O (Aldrich, 95%), and NaOH (Merck, 98%) via hydrothermal method using 100 mL autoclave [15] by modification of synthesis time (7 days synthesis at 313K) based on Noviyanti et al. [16].

2.2. LSO–LSGM composite preparation

LSGM electrolyte was obtained from Sigma–Aldrich (99.999%, trace metal). Both materials with ratio 51:49 (LSO–LSGM) were mixed by using mechanical milling using zirconium ball for 24h. Then it was sintered at 1273K for 36h using gradual steps sintering temperatures as 573K, 1073K, and 1273K by milling at each step.

2.3. Characterization of LSO–LSGM composite and LCM/LSO–LSGM/LSGM performance analysis

The result was recorded using Rigaku SmartLab X-Ray Diffraction with Cu–K$_\alpha$ radiation, $\lambda$ = 0.15418nm, $\theta$ = 0.02° min$^{-1}$. The actual composition was studied using SEM–EDS analysis (Hitachi–EDAX Team). This mixed material then was uni-axially pressed into a pellet (area=1,76cm$^2$, and thickness = 0.15cm). LCM cathode was synthesized from La$_2$O$_3$ (Aldrich, 99.999%, trace metal), CaCO$_3$ (Merck, 99.9%), and MnO$_2$ (Merck, 99.9%) using conventional solid state reaction [17]. The electrolyte pellet was re-sintered at 1523K for densification. It was furthermore coated with LCM cathode slurry at both side by cellulose acetate in DMF as a binder. The sintering process was prerequisite to eliminate the binder at 1123K for 1h. The prototype of symmetrical cell LCM/LSO–LSGM/LSCM that was attained from this process then was tested for electrical performance using EIS method at ambient air atmosphere by using LCR Meter GW Instek 8105G in frequency range of 20Hz – 5MHz. In order to get ASR value, the resistance that was obtained from EIS measurement and fitted with ZView® then calculated.

3. Results and Discussion

3.1. Preparation of LSO–LSGM electrolyte composite

LSO as the precursor was successfully synthesized using hydrothermal method and then the structure was analyzed using XRD. The XRD pattern (Fig. 1) showed a good refinement of the LSO phase within 7 days synthesis time. The data analysis was using Highscoreplus®. The XRD pattern as shown in Fig. 1 was pointing a characteristic peak at $2\theta = 30.84^\circ$ (3 1 1) and $2\theta = 31.07^\circ$ (1 1 2) with the relative intensity as 100% and 71% respectively. All the peak was matched with the standard ICSD No.98–015–5624, with Gof (Goodness of fit) as 2.1522. The impurities phase as La$_2$SiO$_5$ that was found in [16] and another phase like La$_2$SiO$_5$ in Sakao et al. [6] were not found in the LSO pattern. This phenomena justified the formation of LSO crystallite phase. LSO itself has p6$_3$/m space group (a=b=9,7271(8) c=7,1863(6)) that was accorded to LSO synthesized by Noviyanti et. al. [16] with cell unit volume as 588.87Å$^3$.

![Fig. 1. XRD pattern of La$_{0.13}$SiO$_{26}$ (LSO)](image-url)

LSO–LSGM electrolyte composite was successfully synthesized using conventional solid state method at 1473K. Fig. 2 depicted distinguishable peak from each component phase of LSO and LSGM respectively while the inset represented an actual XRD pattern. The diffraction peaks do not show another peak impurity that might emerge from both materials. The diffraction denotes two main peak in which correlating with LSO at $2\theta = 30.3396$ (2 1 1) and with LSGM at $2\theta = 32.1447$ (0 1 1). The crystallinity from both peaks can be determined through a ratio calculation of peak height (h) to total peak intensity (I) [18] as shown in Fig. 3. The percentage of crystallinity for both peaks were calculated as 65.86% and 70.70%. This value confirmed the good crystallinity for electrolyte composition (51:49) which was obtained at lowered sintering temperature.
The LSO peak shifted toward lower degree rather than its ICSD standard from $2\theta = 30.71$ to 30.34 which indicated unit cell volume expansion (Table 1) while the LSGM peak shifted toward higher degree from $2\theta = 31.80$ to 32.14 that was indicating shrinkage of unit cell volume as shown in Table 1. The shifting was depicted in a zoomed diffraction peak as shown in Fig. 4. The shrinkage of LSGM peak was estimated from phase transition from orthorhombic to cubic that was occurred at 1073K [5]. In this study, LSGM phase was found in cubic crystal structure with $P m \overline{3} m$ space group in accordance with Philippeau et al. [19] and Rahmawati et al. [20] study. $La_{1-x}Sr_xGa_{1-y}Mg_yO_3-\delta$ has orthorhombic-based crystal structure and gradually change to primitive cubic structure as increasing Sr and Mg doping to La and Ga [21].

Table 1. LSO and LSGM lattice parameter

<table>
<thead>
<tr>
<th>Phase</th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
<th>V (Å$^3$) theoretical</th>
<th>V (Å$^3$) practical</th>
<th>Annotation</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSO</td>
<td>9.722(8)</td>
<td>9.722(8)</td>
<td>7.337(9)</td>
<td>587.92</td>
<td>592.57</td>
<td>Expansion from standard</td>
</tr>
<tr>
<td>This study</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LSO [16]</td>
<td>9.722(1)</td>
<td>9.722(1)</td>
<td>7.486(1)</td>
<td>-</td>
<td>588.219</td>
<td></td>
</tr>
<tr>
<td>LSGM</td>
<td>3.896(7)</td>
<td>3.896(7)</td>
<td>3.896(7)</td>
<td>60.01</td>
<td>59.17</td>
<td>Densification from standard</td>
</tr>
<tr>
<td>LSGM [19]</td>
<td>3.999(4)</td>
<td>3.999(4)</td>
<td>3.999(4)</td>
<td>-</td>
<td>60.19</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. XRD peaks of LSO–LSGM and the inset pointed the bare data of LSO–LSGM XRD pattern

Fig. 3. Peak diagram for crystallinity percentage ratio calculation. This figure showed the peak height ($h$) and the peak total intensity ($I$) of LSO–LSGM peak at around $2\theta = 32^\circ$. This figure is also denoting the peak data for crystallinity percentage calculation as explained before.

The SEM–EDS analysis at cross-sectional LSO–LSGM electrolyte pellet was carried out to study the actual composition of LSO–LSGM in the composite. Fig. 5 showed relatively a dense LSO–LSGM electrolyte with low porosity. The porous that was formed reflects a small diameter as $0.67\pm0.25\mu m$ at 15 points based on the length calculation technique by using parallel dimension tool in CorelDraw ©2018. This porous might refer as discontinued macroporous which lead to a relatively dense electrolyte.
composite was formed as expected in such composition. This value took no significant effect to the composition, as diffraction data showed no additional peak of impurity and EDS spectrum (Fig. 6) showed every single component in LSO–LSGM.

Table 2. Percentage of EDS composition in LSO–LSGM electrolyte composite

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass from EDS/ %</th>
<th>Theoretical mass/ %</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>25.76</td>
<td>58.00</td>
<td>0.04</td>
</tr>
<tr>
<td>Si</td>
<td>5.47</td>
<td>4.58</td>
<td>0.16</td>
</tr>
<tr>
<td>O</td>
<td>22.04</td>
<td>21.19</td>
<td>0.04</td>
</tr>
<tr>
<td>Ga</td>
<td>10.05</td>
<td>11.58</td>
<td>0.15</td>
</tr>
<tr>
<td>Sr</td>
<td>4.29</td>
<td>3.64</td>
<td>0.16</td>
</tr>
<tr>
<td>Mg</td>
<td>2.39</td>
<td>1.01</td>
<td>0.58</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>-</td>
</tr>
</tbody>
</table>

3.2. Electrical Performance of LCM/LSO–LSGM/LCM

Area specific resistance (ASR) is value of total resistances (R_{tot} = R_1 + R_2 + R_3) with geometrical factor-dependent (A) at which being obtained from value fitting of Nyquist plot using 2View. The ASR value was calculated using an equation ASR_{elec} = R_{tot} \cdot A/2; R_{tot} = R_1 + R_2 + R_3 [22]. The Nyquist plot itself was obtained from EIS measurement. Fig. 7 depicted Nyquist diagram for symmetrical cell LCM/LSO–LSGM/LCM. From the diagram, increasing in temperature led to shrinking in semi-circle which indicated the decreasing of total polarization resistance (R_{tot} = R_s + R_p) as expected. At lower frequency, R_p was pointed as a small ‘tail’ that may refer to the second semi-circle as the existence of an electrode on the electrolyte [23]. That was confirmed that polarization resistance could occur at this symmetrical cell that was containing LCM cathode. R_p was pointed by R_1, R_2, and R_3 symbols as at its equivalent circuit in Fig. 7 and noted in Table 3.

![Nyquist plot of symmetrical cell LCM/LSO–LSGM/LCM and its equivalent circuit](image)

Ohmic resistance (R_s) refers to activity of ionic conductivity that was possessed by the bulk phase of electrolyte. The lower values indicated higher ionic activity on electrolyte. LSGM as the reinforcement in LSO–LSGM composite was estimated play a great role to lower the resistance rather than LSO. The conductivity of LSGM is 0.166 S.cm^{-1} (1073K) [7] which is much larger than LSO, 0.002 S.cm^{-3} at 1073K [6].

Table 3. ASR value of symmetrical cell LCM/LSO–LSGM/LCM at various temperature

<table>
<thead>
<tr>
<th>T/ K</th>
<th>R_s/ Ω</th>
<th>R_1/ Ω</th>
<th>R_2/ Ω</th>
<th>R_3/ Ω</th>
<th>ASR/ Ω.cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1173</td>
<td>0.054929</td>
<td>0.041686</td>
<td>0.06396</td>
<td>0.052569</td>
<td>0.142697</td>
</tr>
<tr>
<td>1223</td>
<td>0.104130</td>
<td>0.000174</td>
<td>0.013119</td>
<td>0.252582</td>
<td>0.235014</td>
</tr>
<tr>
<td>1173</td>
<td>0.154530</td>
<td>0.000167</td>
<td>0.011866</td>
<td>0.380685</td>
<td>0.347135</td>
</tr>
<tr>
<td>1223</td>
<td>0.141090</td>
<td>0.000166</td>
<td>0.023892</td>
<td>0.697891</td>
<td>0.638151</td>
</tr>
<tr>
<td>973</td>
<td>0.077042</td>
<td>0.494066</td>
<td>0.261264</td>
<td>0.624422</td>
<td>1.153608</td>
</tr>
</tbody>
</table>

ASR value denoted higher value than its ohmic resistances at all temperature as shown in Table 3. This behavior indicated the dominant ionic conduction activity of electrolyte bulk phase rather than electronic conductivity and electrochemical activity at cathode. The diffusion transfers resistance (R_d) gave a great contribution on ASR value. R_d shows diffusion transfer of oxide ion (O^{2-}) at triple phase boundary at electrolyte/electrode interface. This might correlate with low reactivity of lanthanum silicate apatite and lanthanum gallate–based electrolyte with lanthanum manganite–based cathode [10]. However, the Mn diffusion on LSO electrolyte and Si diffusion on LCM electrode [9] had a probability to block reaction site on TPB at which lowering the electrochemical activity and increasing the value of ASR.

On the other side, Cao and Jiang [24] reported ASR value of analogous symmetrical cell with the cell in this study, LSM/LSO/LSM as 1.74 Ω.cm² (1173 K) which is 12.43 times larger than was found in this experiment. It can be rationalized that the electrical conductivity might take effect on this change. The conductivity of La$_{0.3}$Ca$_{0.7}$MnO$_3$ cathode was reported as 264 S cm$^{-1}$ at 1223 K [8] which much larger than conventional cathode, La$_{0.3}$Sr$_{0.7}$MnO$_3$ (200 S cm$^{-1}$ at 1273 K) [25]. This behavior could confirm that the lowered sintering temperature on LSO–LSGM electrolyte composite preparation might have been taken no significant effect on electrical performance and it was predicted that lowered sintering temperature could resist the phase transition of LSGM.

4. Conclusion

LSO–LSGM electrolyte composite was successfully synthesized using conventional solid state method. The lowered sintering temperature was expected to sustain a phase stability of LSGM as the reinforcement material at elevated temperature. The electrical performance of LSO–LSGM electrolyte composite on LCM cathode in LSM/LSO–LSGM/LCM showed a better value than its analogous symmetrical cell LSM/LSO/LSM. ASR value of LCM/LSO–LSGM/LCM denoted as 0.14 Ω.cm² at 1173K. The value showed that the lowered sintering temperature of LSO–LSGM composite formation still give an improved electrical performance of LSO–LSGM composite on LCM cathode.

5. Acknowledgement

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