Correlation Microstructure of Triple Phase Boundary and Crystallinity in SOFC Cells NiO/LSGM/LCM

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Abstract

The electrochemical process in the TPB microstructure depends on the conductivity of the SOFC cell constituent materials. Electrolyte and electrode materials must have good conductivity. The crystallinity of an electrolyte can affect its conductivity. In this study, the electrolyte La0.8Sr0.2Ga0.3Mg0.7O3-δ (LSGM) was used and is known to have good conductivity at intermediate temperatures. The single cell of LSGM electrolyte with La0.7Ca0.3MnO3 (LCM) cathode which has high electronic conductivity and NiO anode which has low area-specific resistance (ASR) is expected to produce compatible cells.

The production of NiO/LSGM/LCM cells was carried out through the solid-solid phase synthesis method. Microstructural analysis of TPB was performed using SEM-EDS; meanwhile, crystallinity was obtained through XRD analysis. The crystallinity values of NiO, LSGM and LCM cell components above 80% allow the cells to produce high conductivity with a three-phase boundary microstructure from porous electrodes and relatively dense electrolytes which can increase the possibility of gas, ion and electron encounters in the TPB. In SOFC NiO/LSGM/LCM cells, Ni=11.08%; Ca=6.84%; Mn=9.28% and no precipitate is formed at the electrolyte-electrode boundary, so that the electrochemical process on the TPB microstructure could run well.

Keywords: Crystallinity, TPB microstructure, Single-cell NiO/LSGM/LCM, SOFC.

Introduction

Solid Oxide Fuel Cell (SOFC) is an electrochemical device that can directly convert chemical energy into electrical energy with very high efficiency (about 85%) and operates at high temperatures (600-1,200°C)5,8. The functional operation of SOFCs depends on the transport process through H⁺ and O²⁻ ions in electrochemical reactions. The conversion of chemical energy from fuels and oxidants into electrical energy depends on the three main components that make up the cell in SOFC, namely the electrolyte sandwiched between the electrodes (anode and cathode)5,15.

Electrochemical reactions occur at sites where the reaction constituents, namely ions, electrons and gaseous fuels can meet, namely the triple phase boundary (TPB)7,19. TPB plays a major role in electrochemical processes that involve combined diffusion-reaction-conduction processes of three separate phases namely gas, electron and ion species simultaneously7.

Porous NiO anode is known as a high-performance anode material which offers high catalytic activity for fuel oxidation, high electronic conductivity, good chemical stability and good thermal expansion which is compatible with electrolyte materials in SOFC4. The reaction at the anode-electrolyte interface triggers charge transfer of oxide ions and electrons at the NiO anode and transport of fuel in the pores.

Previous research has been carried out by Noviyanti et al18 combining NiO/LSGM/LSCF cells. The boundary morphology between the LSGM electrolyte – NiO anode and the LSGM – cathode LSCF electrolyte is clearly visible through SEM after sintering. The presence of pores at the NiO anode plays a role in avoiding the possibility of trapping H₂O formed, so that the evaporation of H₂O occurs more quickly and reduces cell resistance17,18. Meanwhile, the pores on the LSCF cathode play a role in facilitating the diffusion of oxygen gas to the TPB through the pore18. In contrast, the LSGM electrolyte must have a denser morphology so that the diffusion of oxygen gas from the cathode into the electrolyte can be prevented14,18. The boundary between the electrolytes does not show any chemical reactivity which is indicated by the absence of other constituent elements other than NiO, LSGM and LSCF18.

LSCF is a type of perovskite oxide which has the structural formula ABO₃ and fulfills the criteria as a good cathode. The other type of cathode that is commonly used is LCM, where this cathode has a similar structural formula to the perovskite oxide LSCF. The difference lies in the position of the manganese (Mn) atom in the LCM which is substituted by the cobalt (Co) atom in LSCF. In LCM, there is a substitution of lanthanum ions by calcium ions and makes the effective ionic radii of lanthanum and manganese ions decrease23.

The LSCF structure is analogous to LCM, making LCM a potential cathode candidate for SOFC. In addition to the similarity of the structural formula, the LCM cathode has excellent electrochemical performance compared to commonly used cathodes. This can be achieved due to the excellent oxygen reduction reaction (ORR) activity.
Preliminary results\textsuperscript{2,21} suggest that LCM can function as a cost-effective cathode, preferable to lower temperature SOFC and has a relatively high conductivity of about 264 $\text{Scm}^{-1}$.

The microstructure of SOFC cells is in the form of a dense electrolyte between the porous electrodes structure (anode and cathode)\textsuperscript{2,15}. The cavities in the electrodes and solid electrolytes can increase the probability of encounters among gases, ions and electrons in the TPB\textsuperscript{1}. Based on the resulting microstructure at the TPB limit, it will affect the electrochemical reactions that occur. Electrochemical reactions on the microstructure of the components that make up SOFC cells depend on the conductivity of each component. Electrolyte and electrode materials need to have good conductivity\textsuperscript{9}.

The conductivity can be affected by the crystallinity of the components that make up the cell, that is, the crystallinity is directly proportional to the resulting conductivity\textsuperscript{16}. Further research is needed to determine the microstructure of the triple phase boundary and the crystallinity of NiO/LSGM/LCM cells. This was done as a first step to determine the compatibility of NiO/LSGM/LCM as SOFC cells.

**Material and Methods**

**Materials:** The materials used in this research include apatite Lanthanum gallate, strontium and magnesium doped/LSGM (99% trace rare earth metal basic) as electrolyte, LCM cathode ($\text{La}_0.7\text{Ca}_0.3\text{MnO}_3$) solid phase synthesis from Lanthanum (III) oxide. / $\text{La}_2\text{O}_3$ (Aldrich, 99.999%); calcium carbonate/ CaCO$_3$ (Merck, 99.9%); and manganese dioxide/ MnO$_2$ (Merck, 99.9%), Nickel (II) oxide/ NiO (99.999% trace metals basic) as anode, DMF and cellulose acetate as binder.

**Methods:** Cell fabrication was carried out through solid phase synthesis and characterized to obtain the correlation of microstructure of TPB with crystallinity in SOFC cell. Cell characterization was carried out by SEM-EDS (SEM: JEOL JSM-6360LA, SEM-EDS: Hitachi-EDAX Team) to observe the morphology and composition of the electrolyte and XRD (Rigaku: MiniFlex600) to characterize the structure.

**Results and Discussion**

**XRD Analysis:** XRD analysis was conducted to determine the structure of each material. Analysis of XRD data was carried out using HighScore Plus software, the resulting diffractogram was adjusted with reference to the Inorganic Crystal Structure Database (ICSD). LCM diffractogram shows compliance with ICSD No. 96-017-4484, there is a typical LCM peak at $2\theta$ of 32.62°. The highest peak in the LCM sample at $2\theta$ is 32.46° and the second highest peak is at $2\theta$ at 32.43°. Perovskite has an orthorhombic structure with a $P_{nma}$ space group and has a value of $a = 5.4832$, $b = 7.7566$ and $c = 5.4621$. The unit cell volume of the synthesized LCM cathode was 232.3209 Å$^3$, larger than the standard LCM (230.36 Å$^3$).

![Fig. 1: XRD Diffractogram of LCM, LSGM and NiO](image-url)
The single-phase sample diffractogram Gd$_{0.8}$La$_{0.8}$Mg$_{0.2}$O$_{2.2}$Si$_{0.2}$ shows conformance to ICSD No. standard 98-009-8170 and has a typical peak at 20 = 32.3383°; 57.6501°; and 46.3715°. There is an expansion in the unit cell volume wherein the unit cell volume of the LSGM in the study is 60.02 Å$^3$ which is larger than the standard (60.01 Å$^3$). Diffractogram of single-phase NiO showing conformance to ICSD standard no. 98-064-6098. The NiO anode has a typical peak of 20 = 43.093°, 37.0569° and 62.7038°. The unit cell volume of NiO in the study was 72.72 Å$^3$, smaller than the standard unit cell volume (72.88 Å$^3$).

The suitability of the lattice parameters on all materials indicates the atomic coordinates, particle size and occupancy as the same as the standard, except that the unit cell parameters such as the angle and distance of the crystal lattice are not significantly increased or decreased. From the XRD results, there is no indication of the formation of a new phase in NiO/LSGM/TCM.

**Crystallinity and Crystal Size**: The determination of the crystal size was carried out using the HighScore Plus software and then using the Debye-Scherrer equation:

$$B = \frac{K \lambda}{D \cos \theta}$$

where B is the crystal size, K is the Scherrer constant (0.9), $\lambda$ is the wavelength of X-ray radiation, D is the value of the peak FWHM (full width at half maximum) and $\theta$ is the diffraction angle.

<table>
<thead>
<tr>
<th>Cell Components</th>
<th>Crystallinity (%)</th>
<th>Crystal Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>81.1946</td>
<td>52.88</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>86.0860</td>
<td>33.11</td>
</tr>
<tr>
<td>Cathode</td>
<td>85.4043</td>
<td>54.36</td>
</tr>
</tbody>
</table>

The percent crystallinity can be determined from XRD data obtained through equation$^{12}$:

$$Crystallinity(\%) = \frac{\text{Area of crystalline peaks}}{\text{Area of all peaks}} \times 100\%$$

There is a strong correlation between the crystallinity of the sample and its electrical conductivity where the crystallinity of the sample will be directly proportional to its conductivity$^{10}$. Table 1 shows the crystallinity of the anode, electrolyte and cathode. The crystallinity obtained is above 80% from the correlation between crystallinity and conductivity that the greater is the crystallinity, the higher will be the conductivity. The components that make up NiO/LSGM/TCM cells have good conductivity in accordance with the conditions for the arrangement of cells in SOFC.

**Triple Phase Boundary Microstructure on NiO/LSGM**: The microstructure of the TPB between the anode and the electrolyte can be seen in the micrograph of the SEM cross section presented in figure 2. The boundary difference between the NiO anode and the LSGM electrolyte can be seen in the cross-sectional section. LSGM electrolyte has a fairly dense density which occurs due to densification during pelletizing and is supported by a sintering process at a temperature of 1000°C. On the other hand, the anode morphology is more porous than the electrolyte. In accordance with the criteria for electrolytes and anodes that can be used in a single SOFC cell, it consists of a porous electrode and a solid electrolyte$^{20}$.

**Fig. 2**: Micrograph on SEM cross section of anode and electrolyte in the form of NiO/LSGM with 1000 times magnification
The pore size of the NiO anode can be calculated using the parallel dimension tool in CorelDraw software. The actual size of the pore can be determined by equation:

\[
\text{Actual size (\mu m)} = \left( \frac{\text{Pore size (mm)}}{\text{Bar size (mm)}} \right) \times \text{picture} \times \text{actual bar size}
\]

The average pore size of the NiO anode is 7.1784 m, which is larger than that of the electrolyte, which is 0.6584 m. The porous microstructure protruding from the anode serves to facilitate rapid gas transport and reaction of byproducts. The electrolyte acts as a physical block to avoid direct mixing of the fuel and oxidant, so the electrolyte must be fully compacted in a narrow pore. Apart from being a physical block, electrolytes are also a block of electron diffusion to ensure that electron transport only goes towards the external circuit. This indicates that the electrolyte must be an electronic insulator (pure ionic conductor).

The porous NiO anode allows fuel in the form of H\(_2\) gas to enter and undergoes migration into the TPB boundary along with the migration of O\(^2-\) ions from the electrolyte to the TPB boundary. The meeting between O\(^2-\) ions and H\(_2\) gas then reacts at TPB, producing H\(_2\)O and electrons. The resulting electrons migrate through the porous anode to advance to the external circuit (and back into the cathode to continue the reaction), while the resulting H\(_2\)O will diffuse through the pore in the NiO anode as a by-product of the reaction.

The LSGM electrolyte has a very good conductivity of oxygen ions, so the migration of O\(^2-\) ions into the TPB adjacent to the anode is expected to accelerate the reactions that occur in the TPB. The relatively dense electrolyte allows preventing the diffusion of H\(_2\) gas into the electrolyte phase which can affect the resistance of the SOFC cell.

In this study, the boundary of the electrolyte-anode region is still relatively clear between each other. Thus, in general, chemical reactivity does not occur in NiO/LSGM/LCM cells especially at the LSGM electrolyte boundary and NiO anode. However, the anode pores look bigger than the cathode pore. Agglomeration at the anode is clearly visible where the anode grains appear larger than the cathode grains which may cause deficiency of anode-electrolyte contact.

The agglomerate cavities that may be generated from nickel agglomeration can cause a decrease in the length of the active TPB. The presence of Ni agglomeration can cause an increase in resistance at the anode (ohmic resistance). This can cause the contact between particles to be less and cause the electrical conductivity that can be generated to decrease.

To see the chemical reactivity at the anode-electrolyte boundary, an analysis of the constituent elements of the electrolyte component was carried out. The EDS spectrum in figure 3 shows the peaks of the components in the EDS component selection area. There were peaks from the manufacture of components, namely La, Sr, Ga, Mg, Ni and O and the absence of other elements besides the anode and electrolyte composition in the EDS selection area. This is in accordance with the morphology that clearly separates the boundary between NiO and LSGM.

![Fig. 3: The EDS spectrum in the selected area of the LSGM electrolyte layer in the LSGM/NiO cross section](image)

| Table 2 |
|-----------------|------|------|
| **Element**     | **Mass/ %** | **Atom/ %** |
| O               | 25.08 | 63.19 |
| Ni              | 16.13 | 11.08 |
| Ga              | 17.27 | 9.98  |
| Mg              | 1.42  | 2.36  |
| Sr              | 10.36 | 4.77  |
| La              | 29.72 | 8.62  |
Table 2 shows the percentages in the EDS spectrum selection area. In the electrolyte region close to the anode, there is a Ni peak of 11.08%. Meanwhile, other peaks such as La, Sr, Ga, Mg and O are the constituent elements of the LSGM electrolyte. The presence of Ni peaks that appear in the EDS spectrum, indicates the presence of NiO located in the electrolyte region. This can occur as a result of the selection of the electrolyte area close to the anode region, so it could be read and appears in the EDS spectrum.

Triple Phase Boundary Microstructure on LSGM/LCM:
The microstructure of the TPB between the cathode and the electrolyte is shown in the micrograph on the SEM cross-section presented in figure 4. In this study, the boundaries of the electrolyte-cathode region are still relatively clear between each other. The LSGM electrolyte has a fairly dense density and vice versa at the cathode. It is more porous than the electrolyte in accordance with the criteria for electrolytes and cathodes that can be used in SOFC single cells.

In this interfacial region, gaps were found indicating that the adhesion of the cathode to the electrolyte face was uneven along the boundary. This is generally expected to have an effect on increasing the electrolyte-electrode interface resistance which needs to be further confirmed through the results of the EIS analysis. The average pore size of the LCM cathode is 1.9161 m which is larger than that of the electrolyte which is 0.6584 m. The porous cathode is expected to be able to carry out rapid diffusion of O₂ gas to the TPB so that the reduction reaction is expected to increase when O₂ species are adsorbed on the cathode surface of the LCM and migrate along the cathode surface to the TPB. This process is followed by a reduction process to oxygen ions and transfer of ions to the LSGM electrolyte phase. The electrolyte which is relatively dense compared to the cathode, can prevent the migration of O₂ gas from the air into the electrolyte phase which can interfere with electrochemical reactions.

To see the chemical reactivity at the cathode-electrolyte boundary, an analysis of the constituent elements of the electrolyte component was carried out. The EDS spectrum in figure 5 shows the peaks of the components in the EDS selection area. The peaks of the constituent components, namely La, Sr, Ga, Mg, Ca, Mn and O and the absence of other elements besides the cathode and electrolyte constituent elements in the EDS selection area are in accordance with the morphology that clearly separates the boundary between LCM and LSGM.

Fig. 4: Micrograph on SEM cross section of cathode and electrolyte in the form of LCM/LSGM with 3000 times magnification

Fig. 5: The EDS spectrum in the selected area of the LSGM electrolyte layer in the LCM/LSGM cross section
Table 3 shows the percentage of elements present in the selection area of the EDS spectrum. In the electrolyte area adjacent to the cathode, there is a peak of 6.84% Ca and 9.28% Mn. Meanwhile, other peaks such as La, Sr, Ga, Mg and O which are the constituent elements of the LSGM electrolyte can indicate that the selected area is an electrolyte region adjacent to the LCM cathode. The presence of Ca and Mn elements that appear in the EDS spectrum indicates the presence of LCM which is located within the boundary of the electrolyte region, so that it can be read and appears in the EDS spectrum.

**Table 3**

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass/ %</th>
<th>Atom/ %</th>
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</thead>
<tbody>
<tr>
<td>O</td>
<td>19.45</td>
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<tr>
<td>La</td>
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<tr>
<td>Sr</td>
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<td>1.06</td>
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<tr>
<td>Mg</td>
<td>0.33</td>
<td>0.65</td>
</tr>
</tbody>
</table>

**Conclusion**

The crystallinity of cell components above 80% allows cells to produce high conductivity with microstructures at the triple phase boundary of porous electrodes compared to relatively dense electrolytes which can increase the probability of meeting gases, ions and electrons in TPB in NiO/LSGM/LCM cells.

**Acknowledgement**

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