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Electrochemical properties of \( \text{La}_{9.33}\text{Si}_{6}\text{O}_{26}(\text{LSO})-\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.55}(\text{LSGM}) \) electrolyte over NiO and \( \text{La}_{0.1}\text{Ca}_{0.9}\text{MnO}_{3}(\text{LCM}) \) electrodes

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Abstract

The electrochemical properties of \( \text{La}_{9.33}\text{Si}_{6}\text{O}_{26}(\text{LSO})-\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.55}(\text{LSGM}) \) electrolyte composites have been evaluated over NiO and \( \text{La}_{0.1}\text{Ca}_{0.9}\text{MnO}_{3}(\text{LCM}) \) electrodes using symmetric and asymmetrical cells of NiO/LSO–LSGM/LiO and NiO/LSO–LSGM/LCM, respectively. The Nyquist plot obtained from this study suggested that the new electrolyte system exhibits excellent performance over the NiO and LCM electrodes and shows an ideal Randel cell electrical circuit characteristic in both NiO/LSO–LSGM/LiO and NiO/LSO–LSGM/LCM cells. The area-specific resistance (ASR) and the activation energy \( (E_a) \) of NiO/LSO–LSGM/LiO from the Arrhenius plot are lower than the NiO/LSO–LSGM/LCM, which is 0.30 \( \Omega \) cm\(^{-2}\) and of 0.74 eV vs 0.40 \( \Omega \) cm\(^{-2}\) with \( E_a \) of 0.76 eV, respectively.

1. Introduction

The electrolyte in Solid Oxide Fuel Cell (SOFC) plays an essential role in determining the operating temperature of the system. The high operating temperature SOFC (up to 1400 K) contains many pitfalls; in terms of materials stability, thermo–mechanical mismatch, thermal management, and efficiency [1–5]. An ideal electrolyte should provide chemical stability at high temperatures and high electrical performance at low temperatures [6–8]. Yttrium–stabilized zirconia (YSZ) is the well–known electrolyte for SOFC [9]. However, it has lacked chemical stability when being used at high operating temperatures, even though it possesses a high conductivity property. On the other hand, lanthanum silicate oxides apatite electrolyte (LSO) can be a potential electrolyte to substitute the YSZ due to its lower activation energy \( (E_a) \), namely up to 0.32 eV [10–13].

LSO can provide better chemical compatibility on the lanthanum calcium manganese (LCM) perovskite cathodes, the result of its less reactivity toward the cathodes [14, 15]. LSO also demonstrates excellent thermo–mechanical compatibility due to its lower thermal expansion coefficient (TEC) compared to YSZ, lanthanum strontium gallium magnesium oxide (LSGM), and cerium–gadolinium oxide (CGO) [16, 17]. However, LSO has not provided an excellent high ionic conductivity due to its ionic hexagonal conduction path, which is lower mobility if compared with the one in cubic fluorite of YSZ, or other cubic forms of CGO and LSGM. This is because, during the ionic diffusion, the interstitial mechanism in LSO is likely to occur instead of the direct diffusion mechanism [18]. The low conductivity of LSO tends to contribute to a lower power density. To manage this issue, LSO is preferable to combine with another SOFC electrolyte such as LSGM the one we discussed in our earlier study [15].

Here we evaluated the electrochemical properties of composite electrolyte of LSO–LSGM in both symmetrical and unsymmetrical cells. We found that the composite electrolyte of LSO–LSGM showed a low area resistance, high chemical stability, thermomechanical compatibility over the LCM cathode[15]. However, the interaction of LSO–LSGM composite to NiO anode in the symmetrical cell NiO/LSO–LSGM/NiO and to both...
LCM and NiO electrodes in the complete cell of NiO/LSO–LSGM/LCM has not been studied. The preparation of the electrolytes and the electrochemical performance analysis will be discussed in detail.

2. Experimental method

LSO was synthesized using our previously reported hydrothermal method [19], [20–22]. Briefly, this method is carried out at a relatively low temperature in a closed system using autoclaves by obtaining LSO with high crystallinity. The LSO–LSGM electrolyte composite was prepared using the conventional solid-state method, as reported elsewhere [15]. The LSO–LSGM electrolyte composite was then divided into two button cells by pressing uniaxially using Grasby specac hydraulic pressor with the area (A) and thickness (t) of 1.7679 cm$^2$ and 0.15 cm$^2$, respectively. These button cells were then sintered at 1473 K to obtain a dense-solid and well-built pellet. For NiO symmetrical cells, the NiO paste was applied on both sides while heated at 1373 K for 3 h to eliminate the organic solvent and to enhance the adhesion properties to the electrolyte. For the case of the complete cell of NiO/LSO–LSGM/LCM, the NiO paste was applied first on one side of the button. After that, the LCM was applied onto another side by a heating process at 1123 K for 2 h. The electrochemical performance of NiO/LSO–LSGM/NiO and NiO/LSO–LSGM/LCM was analyzed by electrochemical impedance spectroscopy (EIS) using LCR Meter GW instek 8105 G at ambient with AC signal of 1.00 V and the frequency range of 20 Hz – 5 MHz. The measurement was conducted under a temperature range of 1173 K to 973 K for NiO symmetrical cell and 1173 K to 923 K for the complete cell, with 50 K increments. The impedance was then plotted in a Nyquist diagram and interpreted by ZView®. Scanning Electron Microscopy (SEM) and EDS analysis were also carried out on the electrolyte-electrode interface to understand the probability of the electrode ionic migration into the bulk of electrolytes and vice versa.

3. Result and Discussion

The interaction between LSO and electrode materials occurring in the triple-phase boundary (TPB) at the electrolyte-electrode interface was analyzed using an SEM micrograph. Both chemical or physical reactivity was found to occur through the distribution of element contents in the electrolyte and/or electrode towards the electrolyte and/or electrode at higher operating temperatures. Our study suggested that a firm boundary exists between electrolyte and electrode interfaces (figure 1 (a) and (b)) even a high operation temperature (1173 K) was applied. The electrolyte area shows to be denser with tiny-lack porous than the electrode. Meanwhile, the cathode area showed smaller particles with a less compact structure than the anode one. The electrolytes area near the boundaries also indicates differences in structure compared with the anode area, which is more porous and perforated.

The EDS analyses were carried out at the electrolyte area near the boundaries with the anode and cathode. Table 1 summarizes the atomic compositions of the composite electrolytes' elements, such as La, Ga, Si, Sr, and O. Based on the EDS analysis (table 1), the atomic composition of the LSO–LSGM electrolyte composite does not comply with the initial stoichiometric of LSO–LSGM which should follow $La_{9.33}Si_{6}O_{26}–La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3}$. This suggests that the element of the electrodes can be possibly migrated across the boundaries to the electrolyte or interfacial reaction between LSO–LSGM and the LCM or NiO occurred which induced a new phase of lanthanum–based species and distorted the stoichiometric of LSO–LSGM.
LSGM. Despite this fact, the Nyquist plot of NiO/LSO–LSGM/LCM did not signify a significant Warburg element change as presented in figure 2(a). This Warburg behavior, which proposes a mass-transfer process, was slightly obvious in NiO/LSO–LSGM/NiO Nyquist plot, even at the lowest temperature (973 K) as illustrated in figure 2(b). From the EDS results, it is also found that the presence of 2.84% Mn in LCM cathode and 4.21% Ni in NiO anode.

Figure 2 shows the Nyquist plot obtained from the composite electrolyte under symmetric and non-symmetrical cells. The Nyquist plot from both systems denoted a pattern that follows ideal Randel’s cell. From the results, we can figure out that the cell’s ASR value decreases as the operating temperature increases. ASR

### Table 1. The mass and atomic composition of the electrolyte area at the LCM side (a) and NiO side (b) were obtained from EDS analysis.

| Element | Mass/% | Atomic Composition/% | Mass/% | Atomic Composition/% |
|---------|--------|----------------------|--------|----------------------|
| O       | 15.68  | 52.61                | 18.64  | 55.69                |
| Mg      | 1.17   | 2.59                 | 2.09   | 4.12                 |
| Si      | 4.33   | 8.27                 | 4.71   | 8.02                 |
| Sr      | 2.59   | 1.59                 | 3.64   | 1.98                 |
| La      | 63.42  | 24.51                | 55.91  | 19.24                |
| Mn      | 2.96   | 2.84                 | —      | —                    |
| Ga      | 9.85   | 7.58                 | —      | —                    |
| Ni      | —      | —                    | 5.17   | 4.21                 |

Figure 3. The Arrhenius plot of NiO/LSO–LSGM/LCM and NiO/LSO–LSGM/NiO cells.

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represents the overall electrochemical properties related to oxygen reduction, oxygen surface/bulk diffusion, and gas-phase oxygen diffusion in TPB and the bulk [23]. The Gerischer and Warburg behaviors were not found in the cell, suggesting good chemical stability between the electrodes and the electrolytes. Gerischer represents the chemical reactivity in the bulk electrolyte solution corresponding to electrons lost from the reaction site at the electrode-electrolyte interface. Meanwhile, the Warburg corresponds to the diffusion process of transferred ionic species from the bulk electrolyte into the electrolyte–electrode interface due to chemical reaction. However, since in our case no chemical reaction in the electrolyte–electrode interface, the Warburg behavior in the low-frequency region did not appear. To compare the electrical performance between the symmetrical and unsymmetrical cells, the ASR values of each cell were listed in table 2.

The Ea value of NiO/LSO–LSGM/LCM is lower than NiO/LSO–LSGM/NiO. The value represents a phenomenon that oxide ions conversion is more active in the NiO symmetrical cell than in the complete cell. The lower Ea profound a condition that the oxidation reaction was assuredly taking place at LCM cathode. Meanwhile, the NiO anode facilitated the reduction reaction. This behavior explained the reason why the NiO/LSO–LSGM/LCM has a lower ASR value than the NiO/LSO–LSGM/NiO cell, which is correlated to the activity of oxide–ion transfer into the anode site through the bulk of LSO-LSGM electrolytes.

The Arrhenius plot of both symmetrical and asymmetrical systems was given in figure 3. The plots follow the Arrhenius equation (1):

$$\ln \left( \frac{1}{ASR} \right) = \ln A - \frac{E_a}{RT}$$  \hspace{1cm} (1)

$E_a$ showed the energy required to convert oxygen species ($O_2$) in the ambient air to oxide ion ($O^{2-}$) following the reaction:

$$O_2 + 4e^- \rightarrow 2O^{2-}$$  \hspace{1cm} (2)

When the $E_a$’s value equals 0, the reaction does not occur in the triple-phase boundary [24] which suggested that the conversion of oxygen species to oxide ion does not occur which suggests a manifestation of ‘pure resistance’ in the bulk of the electrolytes and electrodes.

From equation (1), we can calculate the value of (ASR) at this condition ($E_a = 0$) by from the intercept ($lnA$). At this condition, the NiO/LSO–LSGM/NiO cell resulted in a larger value of ASR, i.e., $1.59 \times 10^{-4}$ ohm cm$^2$, compared to the NiO/LSO–LSGM/LCM cell ($1.28 \times 10^{-4}$ ohm cm$^2$). The result indicated that the LCM cathode might contribute to lowering the resistance and increasing the conductivity by supplying some more pathways for oxide ion conduction at the initial condition at which the occurrence of $O^{2-}$ ions transport was not initialized.

However, as the $O^{2-}$ ions transport occurred, our symmetrical cell of NiO/LSO–LSGM/NiO denotes much lower ASR at all the operating temperatures (See table 2) comparing its full cell of NiO/LSO–LSGM/LCM which suggested more facilitated $O^{2-}$ transport indicated by the lowered Ea. This is probably due to the natural characteristics of LCM which acts as a cathode in the SOFC full cell. LCM will reduce more $O_2$ and create abundant $O^{2-}$ ions in the TPB which furthermore hindered the incoming conversion of $O_2$ into $O^{2-}$, thus slowing the ion transport due to saturated ions in the conduction pathways. While in the symmetrical cell of NiO/LSO–LSGM/NiO, even if the conduction pathways might be limited (higher ASR of $1.59 \times 10^{-4}$ ohm cm$^2$ at $E_a = 0$), the conversion of $O_2$ into $O^{2-}$ may rarely occur since the nature of NiO acts as an anode at which no saturated ions hindered the conduction pathways.

| NiO/LSO-LSGM/LCM (a) | NiO/LSO-LSGM/NiO (b) |
|----------------------|----------------------|
| 1000/T (10$^3$K$^{-1}$) | 1000/T (10$^3$K$^{-1}$) |
| ASR/Ω cm$^2$ | ASR/Ω cm$^2$ |
| 1/ASR (Ω$^{-1}$ cm$^{-2}$) (1/ASR) | 1/ASR (Ω$^{-1}$ cm$^{-2}$) (1/ASR) |
| ln $E_a$/eV | ln $E_a$/eV |
| 0.85 | 0.85 |
| 0.40 | 0.30 |
| 2.52 | 3.29 |
| 0.92 | 1.19 |
| 0.89 | 0.89 |
| 0.53 | 0.46 |
| 1.87 | 2.18 |
| 0.63 | 0.78 |
| 0.93 | 0.93 |
| 0.58 | 0.50 |
| 1.73 | 2.02 |
| 0.55 | 0.70 |
| 0.76 | 0.74 |
| 0.98 | 0.98 |
| 0.90 | 0.60 |
| 1.11 | 1.67 |
| 0.11 | 0.51 |
| 1.03 | 1.03 |
| 1.94 | 1.77 |
| 0.52 | 0.57 |
| −0.66 | −0.57 |
| 1.08 | 3.22 |
| 0.31 | −1.17 |
4. Conclusions

NiO/LSO–LSGM/NiO and NiO/LSO–LSGM/LCM cells have been successfully fabricated. Both systems exhibit excellent single-cell electrochemical performances with a low ASR value. The NiO/LSO–LSGM/NiO cell demonstrated a lower ASR value of 0.30 ohm cm$^{-2}$ at 1173 K with $E_a$ of 0.74 eV than the NiO/LSO–LSGM/LCM cell, of which it ASR and $E_a$ values of 0.4 ohm cm$^{-2}$ and 0.76 eV, respectively. The SEM and EDS analysis indicated that ionic migration of electrode elements to the electrolyte areas is low. Even though the LSO and LSGM are widely used respectively as a single electrolyte, the chemically and electrochemically compatibility of LSO–LSGM composite on the commercial SOFC electrodes has not been studied before. Our study can pave the way for the possibility of the chemical and electrochemical compatibility of newly LSO–LSGM composite electrolyte on the commercial NiO and LCM cathode.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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