Bi$_2$O$_3$ and La$_{10}$Si$_6$O$_{27}$ composite electrolyte for enhanced performance in solid oxide fuel cells

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Abstract. Adding suitable metal oxide into lanthanum silicate apatite can produce a composite with a good oxygen ion-conducting electrolyte that enhances the performance of solid oxide fuel cells (SOFCs). In this paper we present the synthesis and characterisation of Bi$_2$O$_3$ and La$_{10}$Si$_6$O$_{27}$ composite prepared by a solid state reaction. The sintering temperature of the composite was 1500°C for 10 hours with the heating and cooling rates of 10°C per minute. The properties of the resulting composite have been characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM), and ionic conductivity measured by an a.c. impedance spectroscopy (IS). Rietveld refinement of XRD data shows that the composition is purely the mixture of Bi$_2$O$_3$ and La$_{10}$Si$_6$O$_{27}$ with the unit cell parameters of the main phase as $a = 9.9810$ Å and $c = 7.3239$ Å. The room temperature crystal structure was hexagonal with space group P6$_3$/m. The highest ionic conductivity of $1.76 \times 10^{-2}$ S cm$^{-1}$ with a corresponding activation energy of 0.39 eV was obtained at 750°C. SEM images show the material is dense enough to use as an electrolyte for SOFCs.

1. Introduction

Solid oxide fuel cell (SOFC) is a type of electrochemical device that receives much research attention over the years due to its sustainable energy systems, highly efficient conversion of chemical energy into electrical energy, fuel flexibility and environmentally clean power generation [1-3]. SOFC systems consist of a dense electrolyte that separates the anode and the cathode in a unit SOFC. Low to intermediate operating temperatures SOFC (400 to 800°C) give significant advantages such as wider range of material selection, longer life and lower manufacturing costs. Many intensive researches have been done to produce solid oxide electrolytes that exhibit high oxide ion conductivity even at the intermediate temperatures (600 to 800°C) to replace yttria-stabilized zirconia (YSZ) that operates at temperatures as high as 900 to 1000°C [4-8].

Doped ceria and lanthanum gallate perovskite are among the solid oxide electrolytes that exhibit higher oxide ion conductivity at the intermediate operating temperatures. However, chemical instability and degradation of GDC10, LSGM and Y$_2$O$_3$-Bi$_2$O$_3$ electrolytes have led to several research efforts for alternative, low cost and stable solid oxide electrolytes that can produce high oxide ion conductivity at relatively low to intermediate operating temperatures [9].
Recently some new high oxide ion conductivity solid oxide electrolytes at intermediate operating temperature have been produced to overcome these problems. Among the list was the apatite based on rare-earth silicates with a chemical formula $\text{RE}_{10}\text{Si}_6\text{O}_{27}$ (RE = La, Pr, Nd, Sm, Gd and Dy) [10]. $\text{La}_{10}\text{Si}_6\text{O}_{27}$ apatite has been reported as having the highest oxide ion conductivity compared to other apatite type rare earth silicates [11-16]. Thus $\text{La}_{10}\text{Si}_6\text{O}_{27}$ apatite attracts most of the attention. Other advantages of $\text{La}_{10}\text{Si}_6\text{O}_{27}$ apatite are purely ionic conductivity with oxygen transference numbers near unity over a wide oxygen partial pressure range and stable electrochemical performance under various gases feed stocks [11, 17-20].

In recent years, many low cost production methods have been applied to eliminate secondary products of $\text{La}_{10}\text{Si}_6\text{O}_{27}$ apatite ($\text{La}_2\text{SiO}_5$ and $\text{La}_2\text{O}_3$) reduce the complete formation temperature of $\text{La}_{10}\text{Si}_6\text{O}_{27}$ apatite and produce dense $\text{La}_{10}\text{Si}_6\text{O}_{27}$ apatite with high oxide ion conduction [21-25]. Benefits of various dopants have also been studied to improve the ionic conductivity of $\text{La}_{10}\text{Si}_6\text{O}_{27}$ apatite that increases the interstitial oxide ions concentration in the electrolytes. Two potential atomic sites for doping $\text{La}_{10}\text{Si}_6\text{O}_{27}$ apatite are the La and Si sites. Si site doping has shown to increase the overall ionic conductivity of $\text{La}_{10}\text{Si}_6\text{O}_{27}$ apatite than the La site [11, 26]. Most recent research has shown that doping metal oxide into $\text{La}_{10}\text{Si}_6\text{O}_{27}$ apatite resulted in a dense solid oxide electrolyte at low sintering temperature and high oxide ion conductivity at the intermediate operating temperature [27]. This indicates that doping $\text{La}_{10}\text{Si}_6\text{O}_{27}$ apatite with metal oxide can improve the performance of the $\text{La}_{10}\text{Si}_6\text{O}_{27}$ apatite.

In this study, solid-state reaction was used to obtain $\text{Bi}_2\text{O}_3$-$\text{La}_{10}\text{Si}_6\text{O}_{27}$ composite electrolyte. The objectives of this study are to obtain pure $\text{Bi}_2\text{O}_3$-$\text{La}_{10}\text{Si}_6\text{O}_{27}$ composite electrolyte under low sintering temperature and investigate the oxide ion conductivity at low to intermediate operating temperatures.

2. Experimental

2.1. Sample preparation and characterisation

The metal oxide powders of 5 weight % $\text{Bi}_2\text{O}_3$ (China) and 95 weight % $\text{La}_{10}\text{Si}_6\text{O}_{27}$ (77.8 weight % $\text{La}_2\text{O}_3$ (Merck) and 17.2 weight % $\text{SiO}_2$ (Fluka Analytical Sigma-Aldrich)) were used as an initial materials. Appropriate amounts of the powders were mixed with distilled water. Two drops of polyvinyl alcohol was added to the mixture as a binder. The ceramic slurry was then milled with alumina balls using ABBE Jar Rolling Mills (model: 202241) for 24 hours and dried completely in an oven at a temperature of 100°C. The ceramic powder obtained after drying the slurry was ground and 1 g of the powder was pressed uniaxially using a hydraulic pressing device in a 1.3 cm diameter mold at a constant pressure of 4 bars and a hold up time of 3 minutes. The prepared pellets were sintered at 1500°C for 10 hours in the presence of air with the heating and cooling rates of 10°C/min to obtain dense ceramic composites. Room temperature X-ray diffraction pattern of the ceramic composite was obtained on SHIMADZU XRD-6000/7000 (version: 5.21) using Cu-Kα1 radiation (wavelength $\lambda = 1.5406$ Å) at 40 kV and 30 mA. A sampling pitch of 0.02 degree and a scan speed of 2 degree per minute were used to determine the purity and crystal parameters. Microstructural analysis was carried out on a JEOL JSM-7610F scanning electron microscopy. The pellet densities $\rho$ were measured using the relation

$$\rho = \frac{\text{mass of pellet}}{\text{volume of pellet}} \quad (1)$$
The pellet densities were compared with the theoretical density \( \rho_{th} \) obtained using the relation

\[
\rho_{th} = \frac{\text{molecular weight of compound}}{N_A \sqrt[3]{a^2 c}}
\]

where \( N_A \) is the Avogadro constant (6.022 x 10^{23} \text{ mol}^{-1}), \( a \), and \( c \) are the lattice parameters of the ceramic composite (cm).

2.2. Conductivity Measurements
Conductivity measurements were performed using an in-house designed furnace with two platinum wires used as current collectors. A symmetrical cell with silver paste coating on each side of the pellet was made. The coated pellet was heated at 700°C for 2 hours to burn any organic additives used in the paste. A.C. impedance measurements were collected in 50°C steps in air between 400 and 750°C using a Solartron impedance analyzer system (Solartron™ SI 1260, UK) combined with electrochemical interface (Solartron™ SI 1287, UK) controlled by Zplot electrochemical impedance software. An excitation voltage of 50 mV was used between 0.1 and 1 MHz. Total resistance (sum of bulk and grain boundary resistances) was obtained from fitting the impedance plot. The total conductivity \( \sigma_{total} \) at different temperatures was evaluated using the following equation:

\[
\sigma_{total} = \frac{t}{SR}
\]

where \( t \) is the thickness of the pellet, \( S \) is the surface area of the pellet and \( R \) is the total resistance.

Activation energy was then obtained from Arrhenius plot using Arrhenius equation:

\[
\sigma T = \sigma_o \exp \left( \frac{E_a}{kT} \right)
\]

where \( \sigma, \sigma_o, E_a, k, T \) are the conductivity (S cm^{-1}), pre-exponential factor, activation energy (eV), Boltzmann constant (8.62 x 10^{-5} eV/K) and temperature (K), respectively. After a simple arrangement, equation (4) can be written as:

\[
\log(\sigma T) = -\frac{E_a}{k} \cdot \frac{1}{T} + \log(\sigma_o)
\]

3. Results and discussions
Effect of adding bismuth oxide, milling and sintering of the ceramic composite were analysed.

3.1. Phase identification
Room temperature X-ray diffraction pattern of Bi_2O_3-La_{10}Si_6O_{27} composite sintered at 1500°C is shown in figure 1. The main XRD pattern of Bi_2O_3-La_{10}Si_6O_{27} is identical with the standard XRD spectrum of La_{10}Si_6O_{27} (JCPDS File No. 53-0291). Rietveld refinement of XRD data using the Fullprof suite [28] confirmed a purely single phase Bi_2O_3-La_{10}Si_6O_{27} belonging to the hexagonal apatite structure with space group P6_3/m and the lattice parameter of the main phase as \( a = 9.9810 \) (8) and \( c = 7.3239 \) (6) Å. The bulk densities of the pellets after sintering at 1500°C range from 2.8 to 3.4 g cm^{-3} (55.7 to 67.6% of theoretical density). The theoretical density of the pellet is 5.028 g cm^{-3}. 
3.2. Microstructural analysis

Figure 2 presents the microstructure of Bi$_2$O$_3$-La$_{10}$Si$_6$O$_{27}$ composite. SEM micrographs of the ceramic composite show compact hexagonal apatite structure with average particle size from 1 to 10 µm. Bi$_2$O$_3$-La$_{10}$Si$_6$O$_{27}$ composite is also quite dense with a low porosity at the low magnification.

Figure 1. (a) Room temperature XRD of Bi$_2$O$_3$-La$_{10}$Si$_6$O$_{27}$ composite before sintering and (b) Room temperature XRD of Bi$_2$O$_3$-La$_{10}$Si$_6$O$_{27}$ composite after sintering at 1500°C.
3.3. Conductivity measurements

Figure 3 shows the complex impedance plots of sintered Bi$_2$O$_3$-La$_{10}$Si$_6$O$_{27}$ composite at different temperatures from 400 to 750°C. The relative density (measured density over theoretical density) of this pellet is 67.6%. The impedance plots at 400 to 550°C exhibit two semicircles that present grain and grain boundary arcs. However, the grain and grain boundary arcs combine with increasing temperature from 600 to 750°C resulting only one semicircular arc. As a consequence, the total resistance value was used to determine the total conductivity value at different temperatures. The corresponding equivalent circuits for different impedance plots are also shown in figure 3.

![Figure 2. SEM micrographs of Bi$_2$O$_3$-La$_{10}$Si$_6$O$_{27}$ composite sintered at 1500°C.](image)
The corresponding bulk resistance $R_1$, grain boundary resistance $R_2$ and total resistance $R_{total}$ from fitting results are tabulated in table 1. The total conductivity of Bi$_2$O$_3$-La$_{10}$Si$_6$O$_{27}$ composite at different temperatures is calculated using equation (3). The total conductivity $\sigma_{total}$ of the ceramic composite gradually increases with increasing temperature from 400 to 750°C as shown in table 2, which demonstrates that the ionic diffusion process is thermally activated.

**Figure 3.** A.C. impedance plots of Bi$_2$O$_3$-La$_{10}$Si$_6$O$_{27}$ composite and equivalent circuits at (a) 750°C and (b) 550°C.
Table 1. Resistance of bismuth oxide-lanthanum silicate composite from fitting results.

| Temperature (°C) | $R_1$ (Ω) | $R_2$ (Ω) | $R_{\text{total}}$ (Ω) |
|------------------|-----------|-----------|----------------------|
| 400              | 1565      | 725       | 2290                 |
| 450              | 450       | 287       | 737                  |
| 500              | 115       | 150       | 265                  |
| 550              | 30        | 77        | 107                  |
| 600              | 51.5      | -         | 51.5                 |
| 650              | 34.2      | -         | 34.2                 |
| 700              | 34        | -         | 34                   |
| 750              | 16        | -         | 16                   |

Table 2. Conductivity of bismuth oxide-lanthanum silicate composite.

| Temperature (°C) | $\sigma_{\text{bulk}}$ (Scm$^{-1}$) | $\sigma_{\text{grain boundary}}$ (Scm$^{-1}$) | $\sigma_{\text{total}}$ (Scm$^{-1}$) |
|------------------|-------------------------------------|-----------------------------------------------|-------------------------------------|
| 400              | 1.80 x 10$^{-4}$                    | 3.89 x 10$^{-4}$                              | 1.23 x 10$^{-4}$                    |
| 450              | 6.27 x 10$^{-4}$                    | 9.84 x 10$^{-4}$                              | 3.83 x 10$^{-4}$                    |
| 500              | 2.46 x 10$^{-3}$                    | 1.88 x 10$^{-3}$                              | 1.07 x 10$^{-3}$                    |
| 550              | 9.41 x 10$^{-3}$                    | 3.67 x 10$^{-3}$                              | 2.64 x 10$^{-3}$                    |
| 600              | -                                   | -                                             | 5.48 x 10$^{-3}$                    |
| 650              | -                                   | -                                             | 8.26 x 10$^{-3}$                    |
| 700              | -                                   | -                                             | 8.3 x 10$^{-3}$                     |
| 750              | -                                   | -                                             | 1.76 x 10$^{-2}$                    |

From Table 2, the bulk conductivity $\sigma_{\text{bulk}}$ and grain boundary conductivity $\sigma_{\text{grain boundary}}$ increase from 400 to 550°C. Figure 4 presents the Arrhenius plot of the ceramic composite. Straight line can be drawn from the Arrhenius plot that is well fitted to the Arrhenius equation. The fitted line also indicates that the diffusion process of oxide ions is thermally activated. From the slope and the intercept of the linear fits in the Arrhenius plot, the activation energy $E_a$ and pre-exponential factor $\sigma_0$ of the ceramic composite can be obtained using equation (5). The values of activation energy $E_a$ and pre-exponential factor $\sigma_0$ are 0.39 eV and 5.21 x 10$^5$ SKcm$^{-1}$ respectively. From Table 2, the highest total conductivity of Bi$_2$O$_3$-La$_{10}$Si$_6$O$_{27}$ composite is 1.76 x 10$^{-2}$ Scm$^{-1}$ at 750°C. The addition of 5 weight % Bi$_2$O$_3$ into 95 weight % La$_{10}$Si$_6$O$_{27}$ resulted in a good conductivity achieved at 750°C for sintering at 1500°C in the presence of air. Unfortunately, dense Bi$_2$O$_3$-La$_{10}$Si$_6$O$_{27}$ pellets could not be obtained for conductivity measurements because the pellets are not fully sintered even after heating at the maximum operating temperature (1500°C) of the furnace. Bi$_2$O$_3$-La$_{10}$Si$_6$O$_{27}$ composite exhibits a significant enhancement on the total conductivity at 750°C for sintering at 1500°C in air. This makes the composite electrolyte suitable for intermediate temperature solid oxide fuel cell.
4. Conclusion

Pure apatite-type Bi$_2$O$_3$-La$_{10}$Si$_6$O$_{27}$ composite electrolyte has been successfully prepared by the solid-state reaction. The room temperature structure of the ceramic composite is hexagonal, space group P6$_3$/m, with $a = 9.9810$ (8) and $c = 7.3239$ (6) Å. The total conductivity obeys the Arrhenius relation, and gradually increases with increasing temperature from 400 to 750°C. The highest total conductivity is $1.76 \times 10^{-2}$ S cm$^{-1}$ at 750°C. This experiment concludes that Bi$_2$O$_3$ has a potential to produce pure Bi$_2$O$_3$-La$_{10}$Si$_6$O$_{27}$ ceramic composite electrolyte at low sintering temperature and improve the conductivity of La$_{10}$Si$_6$O$_{27}$ at low to intermediate operating temperatures.

5. References

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