

Assessment of thermochemically stable apatite $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ as electrolyte for solid oxide fuel cells

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Abstract

Apatite-type lanthanum silicate with a formula of $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ is a potential candidate electrolyte for SOFC system because of its high ionic conductivity and low activation energy. Pure $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ powder was prepared by solid state reaction and using a suitable thermal pretreatment (1000 °C/5 h) of the as-purchased La_2O_3 powder. Materials characterization, thermal behaviors, and electrical properties of $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ samples were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and two-point probe DC conductivity. A pure $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ pellet was prepared at the sintering process of 1600 °C and 2.5 h with a high relative sintered density of 96.91%. The existence of secondary phases in $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ pellet resulted in a lower conductivity than that of pure $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ pellet. Eight-hour reduction-resistant stability tests under reducing atmosphere at the elevated temperature of pure $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ prepared in this study shows a good thermochemical stability as compared to the well-developed 8 mol% Y_2O_3 stabilized ZrO_2 (8YSZ).

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1. Introduction

8YSZ is the most mature material to be an electrolyte in traditional solid oxide fuel cells (SOFCs). Owing to its low ionic conductivity, however, SOFC systems usually operated at elevated temperatures (800–1000 °C) for a higher efficiency of power generators. Thus, several issues such as thermal mismatch between ceramic components and coking problems etc. should be considered carefully due to its high operation temperature [1]. In order to reduce the operation temperature of SOFCs from 800 °C to 500 °C while maintaining the higher power generation efficiency, the main current researches have been focused on the developments of preparing a thin-film electrolyte (<10 μm) [2–4] and new electrolyte materials with higher conductivity [5–8] to decrease the resistance of cells.

Rare earth silicates with an apatite-type structure were discovered as a novel oxide-ion conductor for its exceptional ionic conductivity of oxygen ions, lower activation energy and

excellent stability [8–10]. Rather than the electrolytes with fluorite (e.g. doped ZrO_2 , CeO_2) and perovskite (e.g. doped LaGaO_3) related structures with high symmetric structures, the apatite silicates with a high ionic conduction are believed to migrate via an interstitial pathway mechanism. Excess oxide ions in the apatite silicates can be introduced in the structure and enhance the oxide-ion migration in the conduction channel along the *c*-axis, which is in contrast to the oxide ion vacancy mechanism in perovskite and fluorite-type oxide ion conductors [8–10].

Nakayama et al. have firstly declared the ionic conductivities of lanthanoid silicate of the $\text{Ln}_{10}(\text{SiO}_4)_6\text{O}_3$ (Ln: La, Nd, Sm, Gd, Dy, Y, Ho, Er and Yb) solid solution series [11,12]. Among these lanthanoid silicate series, doped lanthanum silicate, $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$, is believed to be a good candidate electrolyte for SOFC use, because of its higher ionic conductivity at lower temperatures (500–800 °C). According to their results of the hexagonal structure of the $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ (space group: $\text{P6}_3/\text{rn}$) ceramics determined by the Rietveld method, a three-dimensional (3D) network structure is established by inter-connection of the tetrahedral-site SiO_4 and the octahedral-site LaO. Besides, they also referred that the mobile oxygen ions located at the 2a site are surrounded by lanthanum ions at the 6h positions [11,12].

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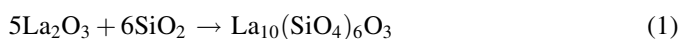
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For the preparation of lanthanum silicate from La_2O_3 and SiO_2 as starting materials by solid state reaction, either La_2SiO_5 or $\text{La}_2\text{Si}_2\text{O}_7$ with lower ionic conductivity is easily formed as secondary phase, which might be due to the inevitable absorption of La_2O_3 by H_2O and CO_2 from the ambient atmosphere. Thus, Béchade et al. proposed a new faster and lower temperature method for preparing pure apatite-type lanthanum silicate from a solid-state method by using an appropriate thermal treatment of the starting mixture [13]. Besides, Nakao et al. have referred a single solid oxide fuel cell with a sandwiched structure of $\text{Pt}/\text{La}_{10}(\text{SiO}_4)_6\text{O}_3/\text{Pt}$ under a presence of CO_2 in a hydrogen fuel gas [14]. In the chemical stability test of their fabricated single-cell system, the cell voltage under a constant current density was stable during the operation for over 100 h.

In this study, the material investigated is strictly focused on preparation and characterization of $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ by solid state reaction and using a suitable thermal pretreatment (1000 °C for 5 h) of the as-purchased La_2O_3 powder. XRD and SEM were used to examine the microstructural morphology, crystal structure, and surface porosity of the sintered pellets. TGA/DTA was used for analyzing the thermal behavior of the calcination process for different $\text{La}_2\text{O}_3/\text{SiO}_2$ powder under nitrogen atmosphere. Archimedes method was applied to measure the relative densities of the samples. The thermochemical stability of $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ powder at temperatures of 500–800 °C under reducing atmosphere was carried out by TGA as compared to the common electrolytes 8YSZ, Bi_2O_3 and GDC10 (Gadolinium Doped Ceria, $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$).

2. Experimental

La_2O_3 powder (99.99%, Alfa Aesar, USA) and SiO_2 powder (99.9%, Alfa Aesar, USA) were used to prepare apatite-type $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ samples by solid state reaction process. The flowchart of the experimental steps is shown in Fig. 1. In order to determine the appropriate stoichiometry of $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ powder, the thermal pretreatment of La_2O_3 powder under 1000 °C for 5 h was firstly performed, which could eliminate the lanthanum hydroxide ($\text{La}(\text{OH})_3$) or lanthanum hydroxycarbonates ($\text{La}_2(\text{OH})_{6-2x}(\text{CO}_3)_x$) due to the exposure of La_2O_3 powder to the atmosphere. A stoichiometric ratio (5:6) of thermally pretreated La_2O_3 powder and as-purchased SiO_2 powder were added in ethyl alcohol and then physically mixed and grounded at 380 rpm for 1 h by high energy ball milling in a planetary ball mill (Model PM100, Retsch, GmbH, Germany). The obtained mixture slurry was dried at a vacuum evaporator at 40 °C and subsequently calcined at a heating rate of 10 °C/min using a programmable cube furnace in air at 1200 °C for 10 h to obtain the stoichiometric reaction:



The calcined powder was uniaxially pressed at a pressure of 100 MPa to form a circular pellet of 15 mm in diameter. The pellets were then sintered at 1550–1600 °C for different hours in air at a heating rate of 5 °C/min. A Netzsch STA 449F3

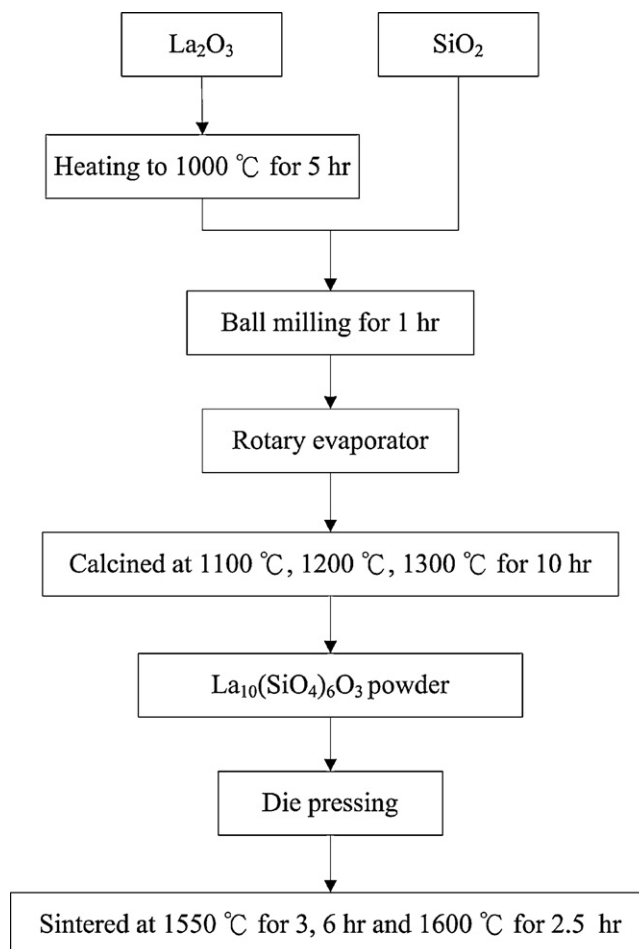


Fig. 1. Experimental flowchart of apatite-type $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ prepared in this study.

thermogravimetric analyzer/differential thermal analysis (TGA/DTA) was used for analyzing the thermal behavior of the calcination process for different $\text{La}_2\text{O}_3/\text{SiO}_2$ powder under nitrogen atmosphere. Then, the calcined powder and sintered pellets were verified by the X-ray diffractometer (XRD, Bruker D2 Phaser, Cu-K α radiation of radiation of $\lambda = 1.5405 \text{ \AA}$), employing a scanning rate of 0.05 deg s^{-1} in the 2θ range from 20 to 60°. Secondary electron images from SEM were used to observe the microstructural morphology and grain size of the sample. The sintered densities of $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ pellets were then derived by the Archimedes relations. Conductivities of the sintered $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ samples were measured at temperatures ranging from 500 °C to 800 °C. Silver electrodes of 0.1 cm diameter were secured via Ag adhesive paste, which were coated on either sides of the sample pellet and held at raised temperature for 1 h. Two-point probe DC conductivity was measured accordingly.

The thermochemical behavior of $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ powder at temperatures of 500–800 °C under reducing atmosphere was carried out by TGA. The ramping process was firstly heating to the fixed temperature under N_2 atmosphere. Then, 20% H_2 reducing gas with a flow rate of 20 sccm was introduced to TGA chamber for the 8-h reduction-resistant stability test.

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