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Synthesis and characterization of calcium and iron co-doped lanthanum silicate oxyapatites by sol–gel process for solid oxide fuel cells

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HIGHLIGHTS

- Oxyapatite co-doped with Ca and Fe is synthesized by a sol–gel process (SGP).
- The ion conductivity of LCSFO(SGP) is significantly higher than that of LCSFO(SSP).
- Ca and Fe Co-doping for oxyapatite could improve the sinterability and ion conductivity.

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ABSTRACT

Lanthanum silicate oxyapatites with and without calcium (Ca) and iron (Fe) doping, $La_{10}Si_5FeO_{26.5}$ (LSFO) and $La_{9.5}Ca_{0.5}Si_{5.5}Fe_{0.5}O_{26.5}$ (LCSFO), are synthesized by sol–gel process (SGP) and solid state reaction process (SSP). The phase formation, microstructure and conductivities of LSFO and LCSFO oxyapatites are characterized by X-ray diffraction (XRD), scanning electron spectroscopy (SEM) and complex impedance analysis. The morphologies of LCSFO oxyapatite nanoparticles synthesized by SGP were characterized by transmission electron microscope (TEM). The thermal and decomposition properties of the LCSFO gel were analyzed by simultaneous differential scanning calorimetry and thermal gravimetric analysis (DSC–TGA). The results show that the phase formation of LCSFO synthesized by SGP occurs at temperatures as low as 750 °C, significantly lower than ~1500 °C required for LCSFO synthesized by SSP. Co-doping of Ca and Fe significantly improves the densification, sinterability and oxide-ion conductivity of lanthanum silicate oxyapatites. The best results were obtained on LCSFO synthesized by SGP, achieving oxide-ion conductivity of 2.08×10^{-2} S cm^{-1} at 800 °C, which is higher than 5.68×10^{-3} S cm^{-1} and 1.04×10^{-2} S cm^{-1} for LSFO and LCSFO synthesized by SSP, respectively, under the identical test conditions.

1. Introduction

Oxide-ion conductors are important in their application to sensors, solid oxide fuel cells (SOFCs) and oxygen pumps. A number of oxide-ion conductors, such as the doped lanthanum gallate, doped ceria, yttria-stabilized zirconia (YSZ) have being developed for applications as the electrolytes in SOFCs [1–4]. Apatite-type oxides with a general formula $RE_{9.33+x}Si_6O_{26+3x/2}$ (RE = rare-earth elements) are attracting considerable attention as a new class of electrolyte materials for SOFCs [5–16]. The oxyapatite lattice consists of covalent SiO_4 tetrahedra and ionic-like RE/O channels [12,17]. The RE-site cations occupy cavities created by SiO_4 units with four distinct oxygen positions, additional oxygen sites form channels through the lattice. The open structure of oxyapatite suggests that this material should be appropriate for the electrolyte applications for intermediate temperature SOFCs [18,19]. Mineshige et al. [16] studied the ionic and electronic conductivity of lanthanum silicate ($La_{9.333+x}Si_6O_{26+1.5x}$ with and without Al doping and showed that the electronic conductivities are in the range of 10^{-5}–10^{-4} S cm^{-1} at temperatures of 800–1000 °C, orders of magnitudes lower than ~10^{-1} S cm^{-1} for ionic conductivities. The ionic transfer number is very close to one and independent of

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oxygen partial pressure. The lanthanum silicate electrolyte has basically ionic conducting characteristics regardless of Al doping. This shows that lanthanum silicate apatite materials are pure oxygen ion conductors with negligible electronic conductivity, showing the promising potential as alternative electrolytes for next generation of SOFCs.

Direct evidences for the importance of the silicate units were obtained from the solid state ^{29}Si NMR studies, which shows a close correlation between the silicon environment and the observed oxide-ion conductivity [20]. The computer modeling studies also indicated the importance of the silicate substructure in aiding the motion of the oxide ions down the channels in the oxyapatites. Detailed studies of the Fe-doped lanthanum silicate oxyapatite systems, $La_{10}Si_{6-x}Fe_xO_{27-x/2}$, by Kharton et al. [21–23] showed that the ionic conductivity increases with the Fe doping level, reaching a maximum value for $x = 1.0$. Further Fe incorporation resulted in a decrease in the conductivity up to the fully stoichiometric composition, $La_{10}Si_4Fe_2O_{26}$. La-site vacancies, particularly in positions enveloping oxygen channels, obviously affect the ionic transport in the apatite lattice. The La-site deficiency influences the SiO_4 tetrahedra relaxation and may cause displacement of the anions from channels into new interstitial sites, thus creating vacancies at fixed oxygen content [12,24–26]. Studies of doping alkaline earth elements on La site show that the doped oxyapatites containing oxygen excess, e.g. $La_9MSi_6O_{26.5}$ (M = Ca, Sr, Ba), exhibit high oxide-ion conductivities [25–27]. The results of doping lower valent ions on the La or Si sites as shown above indicate clearly that the formation of either cation vacancies or oxygen excess can improve the oxide-ion conductivity of the oxyapatites.

The ionic conductivity and microstructure of lanthanum silica oxyapatites strongly depends on the synthesis methods and conditions. The traditional method to prepare the lanthanum silicate oxyapatite is the high-temperature solid state reaction process (SSP) [28]. However, lanthanum silica oxyapatites with a high purity level are very difficult to obtain, as the samples are often contaminated with either La_2SiO_5 or $La_2Si_2O_7$ secondary phases [29–31]. In addition, oxyapatite powders synthesized by SSP have to be calcined at high temperatures for a long period, which would result in the significant increase in the manufacturing cost of the cells. To reduce the sintering and phase formation temperatures, other synthesis routes have been developed to synthesize oxyapatite powders, such as freeze-drying [32], gel-casting technique [33,34] and sol–gel process (SGP) [35,36]. Among them, SGP is a low-cost, low temperature, versatile with few steps in the production process for the synthesis of lanthanum silicate oxyapatites [37–39]. The SGP allows the synthesis of compounds in solution, achieving homogeneity on the molecular scale in the final product. After calcining at 800–1000 °C, oxyapatite nanoparticles with pure apatite phase can be obtained.

In this paper, we employed SGP to synthesize the lanthanum silicate oxyapatite co-doped with Ca and Fe, $La_{9.5}Ca_{0.5}Si_{5.5}Fe_{0.5}O_{26.5}$. As shown early [28], doping on the La site of aluminum lanthanum oxyapatites improves the densification, sinterability and oxide-ion conductivity. The effects of SGP and co-doping on the microstructure and oxide-ion conductivity of lanthanum silicate oxyapatites were discussed.

2. Experimental

2.1. Sample preparation

Tetraethyl orthosilicate (TEOS), $La(NO_3)_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Ca(NO_3)_3 \cdot 4H_2O$ and acetic acid were obtained from Sigma–Aldrich and used as received. Lanthanum silicate oxyapatite co-doped with Ca and Fe, $La_{9.5}Ca_{0.5}Si_{5.5}Fe_{0.5}O_{26.5}$ (LCSFO) was synthesized from TEOS, $La(NO_3)_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and $Ca(NO_3)_3 \cdot 4H_2O$, which was weighed in appropriate ratio and dissolved in ethanol and deionized water to form a mixture solution. The pH of the solution was adjusted to 2 by adding slowly acetic acid. TEOS was then slowly added to the solution at room temperature under stirred condition. The stabilized sol was heated to 70 °C, becoming increasingly viscous due to polymerization reaction. Thereafter, the viscous resin was dried at 100 °C for 8 h, followed by calcination at 550 °C for 4 h. The powders were then calcined at different temperatures (700, 750, 800, 900 and 1000 °C) for 10 h in air. The as-calcined powders were dispersed in isopropanol and pulverized in a ball-mill using an Y_2O_3-stabilized zirconia (YSZ) ball medium. The Ca and Fe co-doped lanthanum silicate oxyapatites synthesized by SGP were denoted as LCSFO(SGP).

$La_{10}Si_{5.5}Fe_{0.5}O_{26.5}$ (LSFO) and $La_{9.5}Ca_{0.5}Si_{5.5}Fe_{0.5}O_{26.5}$ (LCSFO) were also prepared from high purity La_2O_3, SiO_2, $Fe(NO_3)_3 \cdot 9H_2O$ and $CaCO_3$ (all from Sigma–Aldrich) by solid state reaction process (SSP). The raw materials were weighed in appropriate ratio and mixed in plastic vessels for 24 h. The details of the procedures for the synthesis of oxyapatite powders by SSP can be found in our previous publications [28]. The obtained products were denoted as LSFO(SSP) and LCSFO(SSP), respectively.

As-synthesized oxyapatite powders by SGP and SSP were pressed uniaxially into pellets under a pressure of 150 MPa and sintered at different temperature from 1500 to 1600 °C for 4 h in air. The sintered pellets were ~9 mm in diameter and 1.5 mm thick.

2.2. Characterizations

Phase formation of the oxyapatite powders synthesized by SGP and SSP were determined by X-ray diffraction (XRD, Philips MPD 1880 – Cu $K_{\alpha 1}$). Simultaneous differential scanning calorimetry and thermal gravimetric analysis (DSC–TGA) of the LCSFO(SGP) gel were carried out using TA STD-2960 V3.0F at a scan rate of 10 °C/min in air. The morphologies of LCSFO oxyapatite nanoparticles synthesized by SGP were characterized by TEM (JEM-2100, JEOL). The microstructure of LSFO(SSP), LCSFO(SSP) and LCSFO(SGP) pellets were examined by scanning electron microscope (SEM, JSM-5600/LV). The bulk densities of the sintered oxyapatite pelletss were obtained from the mass and geometric dimensions of the pellet samples. Silver paste (Ferro Corporation USA) was painted onto both sides of the sintered pellets as the electrodes. Ionic conductivity of the oxyapatites was obtained from the impedance measurement, using a Solartron 1260 frequency response analyzer in conjunction with a 1287 electrochemical interface. The impedance curves were obtained in the frequency range from 0.1 Hz to 10 M Hz in 50 °C interval in air between 300 and 800 °C. The impedance data were analyzed by Zview software.

3. Results and discussion

3.1. Phase and microstructure of the oxyapatites

The phase formation of oxyapatite powders synthesized by SSP and SGP was investigated by XRD. Fig. 1a and b shows the XRD patterns of LSFO(SSP) and LCSFO(SSP) powders calcined at the temperatures of 1000–1400 °C, respectively. The main phase of the powders is primarily apatite, however, a secondary phase, La_2SiO_5, was also found. According to the La_2O_3/SiO_2 phase diagram [40], La_2SiO_5 and $La_2Si_2O_7$ phases are more stable than apatite phase below 1600 °C. As shown previously [28,33,35], La_2SiO_5 is difficult to remove once it is formed during the synthesis process. The reason could be due to the difficulties to obtain a homogeneous mixture of the oxide precursors by the SSP route. With the increase of the calcined temperature, the intensity of the La_2SiO_5 second