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ScienceDirect

Journal of the European Ceramic Society 34 (2014) 1563–1569

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Synthesis and densification of lanthanum silicate apatite electrolyte for intermediate temperature solid oxide fuel cell via co-precipitation method

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Received 30 July 2013; received in revised form 30 November 2013; accepted 3 December 2013
Available online 30 December 2013

Abstract

Lanthanum silicate apatite (LSA, $La_{9.33+x}Si_6O_{26+1.5x}$, $x = 0$–0.67) has been widely investigated as a promising electrolyte material for intermediate temperature solid oxide fuel cell (SOFC). In this work, a facile and low-cost co-precipitation method is used to synthesize LSA precursor powders. The well dispersed nanopowders (*ca.* 70 nm) with pure hexagonal LSA phase are obtained by calcining the precursor at 900 °C. Impurity of La_2SiO_5, caused by the different precipitation productivities of $La(NO_3)_3$ and TEOS, can be eliminated through lowering the La/Si ratio in the starting mixtures. The dispersant (PEG200) plays a crucial role in co-precipitation processes, which can effectively mitigate the agglomeration and therefore significantly improve the sinterability of the nanoparticles. Dense LSA ceramic with relative density of 98% is obtained after sintering at 1550 °C, which exhibits a conductivity of 0.13 mS cm^{-1} at 500 °C.

Keywords: Solid oxide fuel cells; Electrolyte; Apatite; Co-precipitation; Sintering

1. Introduction

As a promising electrochemical energy conversion device, solid oxide fuel cell (SOFC) has been intensively studied for numerous applications from large-scale stationary to portable power generators in both civilian and military aspects. Traditional SOFC is based on yttria-stabilized zirconia (YSZ) electrolyte and typically operated at high temperature (>800 °C) to ensure an acceptable power density. However, high operating temperature causes complex material-related issues, such as chemical and physical compatibility between cell components and material selection restriction of interconnects and seals, thus increasing fabrication costs of the cell system. In this sense, developing alternative electrolytes that can provide sufficient performance in the so-called intermediate temperature range of 500–750 °C (defined by Steele[1]) is one of the key issues for extensive commercialization of SOFC.

Several materials are being investigated for intermediate temperature SOFC, including oxide-ion conductors represented by doped ceria[2] and $LaGaO_3$[3] and proton conductors represented by doped $BaCeO_3$.[4] In addition to these oxides, lanthanum silicate apatite (LSA) with a general formula $La_{9.33+x}Si_6O_{26+1.5x}$ ($x = 0$–0.67) also draws much attention due to its high conductivity in the intermediate temperature range and high oxygen transference number across a wide range of oxygen partial pressure[5,6] since discovered by Nakayama.[7] A very interesting aspect of LSA is that, rather than vacancy-hopping mechanism in most oxide-ion conductors, the oxygen ion conduction occurring in LSA is via interstitial-type transport mechanism as proved by neutron powder diffraction,[8,9] atomistic computer modeling technique[10–12] and HRTEM observation.[13] The conductivity of LSA increases with La content in $La_{9.33+x}Si_6O_{26+1.5x}$ because excess oxygen ions are introduced into the interstitial position of lattice. $La_{9.92}Si_6O_{26.88}$ shows higher conductivity than YSZ below 650 °C.[14] The conductivity of LSA can be

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http://dx.doi.org/10.1016/j.jeurceramsoc.2013.12.007

further improved through lattice doping. Yoshioka et al.[15] reported that a small amount of Mg substitution in the Si site can enhance the conduction of oxygen ions with a conductivity of 88 mS cm^{-1} at 800 °C, combined with a very low level of activation energy (0.42 eV). Its conductivity is higher than YSZ below 900 °C and even comparable to doped $LaGaO_3$ below 550 °C.

Nevertheless, the main limitation of the practical application of LSA remains in the difficulty to prepare dense ceramics. A sintering temperature higher than 1650 °C is typically required to obtain a relative density of 90% for LSA prepared by traditional powder ceramic route.[15,16] Many efforts have been made to synthesize powders with higher sinterability via wet-chemical routes, including sol–gel,[17–19] citric–nitric (modified sol–gel)[20,21] and freeze-drying[22] methods. The sol–gel method was firstly reported by Tao et al.[17] with acetic acid as a catalyst. However, the resultant relative densities were still lower than 80% after sintering at 1400 °C for 3 days and 1500 °C for 22 h. Following this report, Celerier et al.[18] investigated the influence of several processing parameters in this acetic acid-catalyzed sol–gel method. The results showed that pure apatite phase can be obtained under very narrow synthesis conditions and the relative densities could be improved from 69% to 92% by an additional attrition step for the precursor powder before sintering at 1450 °C. A better result was then reported by the same research group that they could prepare ceramics with relative densities of 90–95% at 1400 °C via epoxide-driven sol–gel method, while the preparation periods of dense samples were as long as 14–18 days.[19] Citric–nitric method is also available for obtaining fine LSA powders to reduce the sintering temperature. Jothinathan et al.[20] and Zhou et al.[21] both prepared dense disks of Al-doped LSA at 1500–1550 °C by the citric–nitric method. The best result reported in the literature come from the combination of wet-chemical method with new sintering technique, such as spark plasma sintering (SPS)[22] and pulsed electric current sintering (PECS).[23] Fully dense and transparent ceramics were prepared by SPS at 1200 °C for only 3 min with powders obtained via freeze-drying method.[22] However, these techniques are usually based on advanced equipment, which leads to high preparation costs. Recently, Li et al.[24] reported a facile co-precipitation method to synthesize nano-sized LSA powders, with which dense ceramic with relative density higher than 95% was achieved after pressing under cold isostatic condition and sintering at a rather low temperature of 1300 °C for 10 h. In this process, however, the second phase of La_2SiO_5 emerged, which was eliminated by acid-washing the LSA powders before sintering.

In this study, we develop a modified co-precipitation method to synthesize pure LSA fine powders, with which the densification of LSA can be achieved at low temperature via the conventional ceramic method. We find that the La/Si ratio in the synthesis process plays an important role in the synthesis of pure apatite LSA without second phase La_2SiO_5 and the dispersing agent has strong impacts on the particle morphology and sintering activity of the LSA powders.

2. Experimental

2.1. Sample preparation

$La_{9.33+x}Si_6O_{26+1.5x}$ powders were synthesized by co-precipitation method with ammonia as precipitant. La_2O_3 (AR) and tetraethyl orthosilicate (TEOS, AR) were used as raw materials. La_2O_3 were annealed at 1000 °C for 4 h to remove the absorbed water and carbon dioxide before dissolving in diluted nitric acid (1 M). The appropriate amount of TEOS was firstly dissolved in ethanol to form a solution, which was then added into the diluted nitric acid solution of La_2O_3 under continuous magnetic stirring. The volume ratio of La_2O_3 containing nitric acid solution to the TEOS solution was 1:4 and the final concentration of total metal ions (La^{3+} and Si^{4+}) was 0.1 M. Ammonia (∼28 vol.%, AR) with a certain amount of polyethylene glycol (PEG200, CP) was diluted with the mixture of de-ionized water and ethanol. The pH value of diluted ammonia was adjusted to be 9–10. The amount of PEG200 was five times the volume of TEOS. Then the solution containing metal ions was added into diluted ammonia dropwise with fierce stirring. After that, the obtained suspension of precipitation precursor was centrifuged and washed with ethanol for three times and then dried at 80 °C for 12 h in air. Subsequently, the precursor was ground in a mortar and calcined at 900 °C for 9 h. The obtained powders were uniaxially pressed into pellets under a pressure of 150 MPa with 1 wt.% polyvinyl alcohol (PVA), followed by sintering at 1350, 1450 and 1550 °C for 10 h. For comparison, the LSA powder was synthesized at the identical condition but without dispersant PEG200.

2.2. Characterization

The phase purity of the samples were assessed by X-ray diffraction (XRD) in a Rigaku TTRIII X-ray diffractometer using Cu-Ka radiation, $\lambda = 1.54178$ Å. The particle morphology and lattice structure of the powders calcined at 900 °C were observed by field emission scanning electron microscope (FESEM, SUPRA55), transmission electron microscope (TEM, JEM-2010), and high resolution transmission electron microscope (HRTEM, JEM-2010). The specific surface area of the powders was determined by N_2 adsorption–desorption isotherms at 77 K with surface analyzer equipment (BET, QuadraSorb SI). The powders were degassed at 300 °C before measurement. Assuming particles were spherical, the theoretical average particle size was calculated from the specific surface area according to Eq. (1):

$$D_{BET} = \left(\frac{6000}{\rho \times S}\right) \tag{1}$$

where D_{BET} is the average particle diameter in nanometer, ρ represents the theoretical density of the material in g cm^{-3} and S stands for the specific surface area in m^2 g^{-1}.

The microstructure of sintered pellets were examined by scanning electron microscopy (SEM, LEO-1450) and the relative densities of the pellets were determined by Archimedean method using de-ionized water as the liquid medium for the