Materials Research Bulletin 46 (2011) 130–135

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Effect of the sintering temperature on the properties of $Ce_{0.85}La_{0.10}Ca_{0.05}O_{2-\delta}$ electrolyte material

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ARTICLE INFO

Article history:
Received 12 August 2010
Received in revised form 1 September 2010
Accepted 16 September 2010
Available online 8 October 2010

Keywords:
A. Ceramics
C. Impedance spectroscopy
D. Ionic conductivity
D. Microstructure
D. Thermal expansion

ABSTRACT

Rare earth and alkaline earth co-doped $Ce_{0.85}La_{0.10}Ca_{0.05}O_{2-\delta}$ electrolyte material with the powder obtained by solid-state reaction method was sintered at 1300, 1400, 1500 and 1600 °C respectively. The results showed that the ionic conductivity of the sample sintered at 1400 °C was slightly lower compared to that sintered at 1500 °C in the temperature range of 300–550 °C, while the sample sintered at 1400 °C showed the highest ionic conductivity in all the samples above 550 °C. The ionic conductivity of ~0.021 S/cm at 600 °C and the relative density of 98.2% were observed for the sample sintered at 1400 °C. In addition, the highest flexural strength with 145 MPa was also obtained for the sample sintered at 1400 °C. It suggested that the sintering temperature for $Ce_{0.85}La_{0.10}Ca_{0.05}O_{2-\delta}$ electrolyte may be reduced to as low as 1400 °C with desired properties.

1. Introduction

Ceria-based electrolytes are of current interest for application in intermediate- and low-temperature solid oxide fuel cells (IT- and LT-SOFCs) because of their high ionic conductivity [1–4]. Pure cerium oxide is basically not a fast oxygen ion conductor unless it is doped with aliovalent cations (Sm^{3+}, Y^{3+}, Gd^{3+}, La^{3+}, Ca^{2+}, etc.). The introduction of those cations into the host lattice gives rise to oxygen vacancies as charge compensating defects thereby enhancing the ionic conductivity of ceria-based materials [5]. In the recent past, co-doping method has been extensively conducted and proved to be more effective compared with those of singly doped ceria. Some well-known examples for co-doped ceria-based electrolytes are: $Ce_{0.8}Sm_{0.2-x}Mg_xO_{2-\delta}$ [4], $Ce_{1-a}Gd_{a-y}Sm_yO_{2-0.5a}$ [6], $Ce_{1-x-y}La_xSr_yO_{2-z}$ [7], $Ce_{0.8}Sm_{0.2-x}Y_xO_{1.9}$ [8], $Ce_{0.8+x}Y_{0.2-2x}Ca_xO_{1.9}$ [9] and so on. In our previous work, the properties of La and Ca co-doped $Ce_{1-x}La_{x-y}Ca_yO_{2-\delta}$ ($x = 0.15$ and 0.20, $0 \leq y \leq x$) were studied [10]. The results revealed that the co-doping electrolyte, when $x = 0.15$ and $y = 0.05$, appeared higher ionic conductivity and lower activation energy than those of singly doped ones in the temperature range of 500–800 °C. It suggested that $Ce_{0.85}La_{0.10}Ca_{0.05}O_{2-\delta}$ might be the better electrolyte material for SOFCs.

Solid-state reaction, a simple and cost-effective method, is often adopted to prepare polycrystalline bulk electrolyte samples [11,12]. However, on preparing ceria-based oxides, a sintering temperature higher than 1600 °C is necessary to obtain ceramics from oxides powder with densities high enough for use as electrolytes of SOFCs [13,14]. Obtaining a dense ceria-based electrolyte at lower temperatures on common solid-state reaction methods can make electrolyte and electrode be co-sintered without chemical reactions between them, which simplifies the fabrication process and reduces the cost. Preparation condition, especially sintering temperature and time is a crucial parameter, which can affect the electrical and mechanical properties of electrolyte markedly.

In order to further optimize electrolyte during the preparation, the effect of sintering temperature on the density, crystal structure, thermal expansion, ionic conductivity, microstructure and flexural strength of $Ce_{0.85}La_{0.10}Ca_{0.05}O_{2-\delta}$ was investigated and compared in this study. Special attention is paid to obtain the minimum sintering temperature with desired properties of $Ce_{0.85}La_{0.10}Ca_{0.05}O_{2-\delta}$ electrolyte.

2. Experimental

CeO_2 (99.5%), La_2O_3 (99.9%), and $CaCO_3$ (99%) powders were used in the preparation of $Ce_{0.85}La_{0.10}Ca_{0.05}O_{2-\delta}$. The appropriate amount of raw materials were milled with zirconia balls in distilled water for 8 h and calcined at 1200 °C for 2 h in air. The as-synthesized powder was milled again for 6 h and dried. The obtained powder was ground and pressed into pellets (13 mm in diameter and 1 mm in thickness) followed by cold-isostatic pressing at about 150 MPa. Sintering was performed at 1300,

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doi:10.1016/j.materresbull.2010.09.028

1400, 1500 and 1600 °C in air for 2 h, respectively. The corresponding samples are denoted as CLC13, CLC14, CLC15, and CLC16, respectively. Bars of 62 mm × 5 mm × 5 mm were also pressed at 150 MPa for thermal expansion and flexural strength test. The sintered densities were measured using Archimedean method. The shrinkage was also measured to characterize the sinterability of the samples. The shrinkage was calculated as follows:

$$\text{shrinkage}\,(\%) = \frac{L_0 - L_1}{L_0} \times 100 \qquad (1)$$

where L_0 and L_1 are the length of green samples and sintered samples, respectively.

The crystal structures of the pellets (ground to powder again for measurement) at room temperature were determined by XRD using the ARL X'TRA diffractometer and Cu Kα radiation. The diffractometer was operated at 40 kV and 35 mA in the scanning range of 20–80°, with the step size of 0.02°. Thermal expansion measurements were conducted with a dilatometer (RPZ-01, Luoyang, China), operated from room temperature to 800 °C in air (heating rate 5 °C/min). The cross-section micrographs of samples were characterized by scanning electron microscopy (SEM, Model Jsm-5900, JEP, Tokyo, Japan). The surfaces were gold-coated to prevent electrostatic charging effect. SEM analysis was carried out at 15 kV accelerating voltage.

Flexural strength was measured by the three-point bending test. Edges of the specimens, with the dimension of 50 mm × 3 mm × 4 mm, were chamfered to eliminate machining flaws that could act as fracture origins. The test was conducted with a span of 30 mm at a crosshead speed of 0.5 mm/min by a universal testing machine at the ambient temperature in air. Four specimens of each batch were tested to obtain an average value. The flexural strength was calculated by the following equation:

$$\sigma_f = \frac{3pl}{2bh^2} \qquad (2)$$

where σ_f is the flexural strength, p the load and l, b, h are the span length, width, thickness of the specimen, respectively.

In order to prepare samples for the ionic conductivity measurements, silver paste was painted on both sides of the specimens followed by baking at 600 °C for 30 min. The AC impedance spectra of the samples were measured as a function of temperature (300–800 °C) in air using an impedance analyzer (PARSTAT 2273) with the frequency range from 0.1 Hz to 1 MHz. Curve fitting and resistance calculation were done by ZSimpWin software.

3. Results and discussion

Fig. 1 shows the variation of shrinkage and relative density with sintering temperature for $Ce_{0.85}La_{0.10}Ca_{0.05}O_{2-\delta}$ samples. It can be seen that the shrinkage increases firstly as the sintering temperature increases. When the sintering temperature is higher than 1500 °C, the shrinkage decreases. As can be seen in Fig. 1, the relative density of sintered samples also increases with sintering temperature and reaches a density of 99.0% of the theoretical value when sintered at 1500 °C for 2 h. When the sintering temperature exceeds 1500 °C, the density of samples decreases. That is to say, the maximum density of $Ce_{0.85}La_{0.10}Ca_{0.05}O_{2-\delta}$ samples obtained at 1500 °C. However, the relative density of the sample sintered at 1400 °C can reach as high as 98.2%. It indicates that there is only a slight lower for the sintered density of CLC14 compared with that of CLC15. This suggests that the fine powders synthesized by conventional ceramic technique with the composition of $Ce_{0.85}La_{0.10}Ca_{0.05}O_{2-\delta}$ can be successfully sintered into electrolytes with relatively high density at 1400–1500 °C, whereas $Ce_{0.8}La_{0.2}O_{1.9}$ prepared by the same method required 1600 °C for sintering [15]. Lane et al. [16] reported that the alkaline earth metal addition for $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ acted as a sintering aid, lowering the sintering temperature by approximately 100 °C compared to an untreated specimen of the same material. We also attribute CaO can play a role in a sintering aid in $Ce_{0.85}La_{0.10}Ca_{0.05}O_{2-\delta}$ electrolyte.

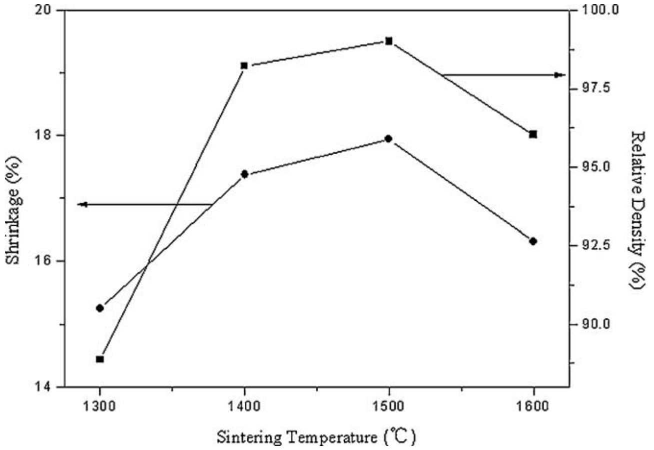

Fig. 1. Shrinkage and relative density of $Ce_{0.85}La_{0.10}Ca_{0.05}O_{2-\delta}$ samples as a function of sintering temperature.

To ensure the complete dissolution of dopant in CeO_2, phase analysis was performed using X-ray diffraction technique. The XRD patterns of $Ce_{0.85}La_{0.10}Ca_{0.05}O_{2-\delta}$ sample sintered at 1300, 1400, 1500, and 1600 °C are shown in Fig. 2. It can be observed that all the samples studied are single phase with a cubic fluorite structure like pure CeO_2.

The electrolyte materials for SOFC must have matched thermal expansion coefficients (TECs) for cathode and anode materials to avoid a microcrack between the anode and electrolyte or between the cathode and electrolyte at the operation temperature. Consequently, thermal expansion is an important property, which governs the performance of high-temperature devices. Fig. 3 shows the thermal expansion characteristic (dL/L_0) of samples obtained during the heating from room temperature (RT) to 800 °C in air, all the samples showed linear temperature dependence. The TECs for all the samples, obtained from the slope of the line

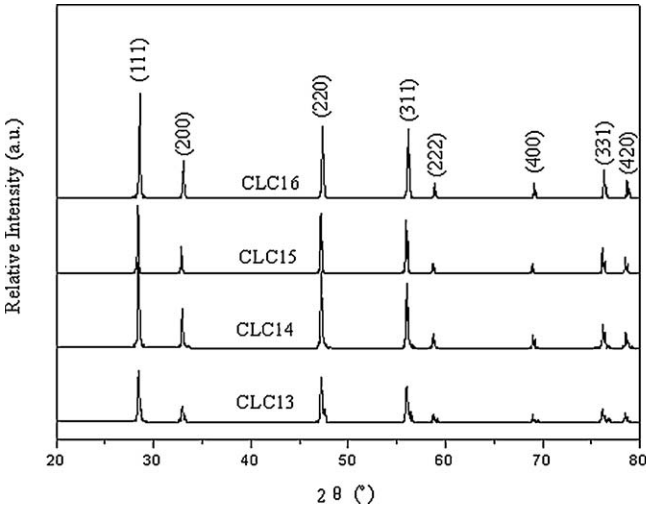

Fig. 2. XRD patterns for $Ce_{0.85}La_{0.10}Ca_{0.05}O_{2-\delta}$ samples sintered at different temperatures.