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Evaluation of Li_2O as an efficient sintering aid for gadolinia-doped ceria electrolyte for solid oxide fuel cells

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HIGHLIGHTS

- Using Li_2O as sintering aid, gadolinia-doped ceria (GDC) be densified at 900 °C.
- Surface and bulk morphology of the sintered GDC samples was evaluated.
- Li-containing residues in the sintered GDC samples were examined.
- Bulk conductivity of 0.059 S cm^{-1} at 600 °C was achieved for GDC sintered at 1000 °C.

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ABSTRACT

Li_2O has been evaluated as a sintering aid for $Gd_{0.1}Ce_{0.9}O_{2-\delta}$ (GDC). Using 2.5 mol% ratio of Li_2O to GDC (5LiGDC), dense samples with relative density of 99.3% were achieved at sintering temperature as low as 900 °C. A high total conductivity of 0.059 S cm^{-1} at 600 °C was obtained for the 5LiGDC samples sintered at 1000 °C (5LiGDC1000), while 5LiGDC samples sintered at 1400 °C showed a lower conductivity of 0.017 S cm^{-1} at 600 °C. It has been found that Li_2O has the tendency to accumulate in the grain boundary region to form Li–Gd–Ce–O phases when the 5LiGDC sintering temperature is at 1000 °C or below, leading to an increase in the grain boundary conductivity. Increasing the 5LiGDC sintering temperature above 1000 °C will accelerate the vaporization of Li_2O, association of the oxygen vacancy and formation of additional pores in the bulk, resulting in a decrease of both the grain boundary and grain interior conductivity. Secondary ion mass spectrometry (SIMS) results have confirmed the existence of Li ions for the 5LiGDC samples sintered at or below 1000 °C, while most of Li species has vaporized for the 5LiGDC samples sintered above 1000 °C.

1. Introduction

Solid oxide fuel cell (SOFC) is an energy conversion device that can convert the chemical energy of the fuel directly to electricity with high efficiency, low emissions and fuel flexibility, and has recently attracted significant attentions worldwide due to the limited fossil fuel resources and the increasing environmental concerns [1]. Electrolytes for SOFCs are mainly based on the yttrium doped zirconia (YSZ) and gadolinium doped ceria (GDC), of which GDC possesses much higher conductivity at lower operating temperatures [2–4]. Consequently, GDC has been expected to be an ideal electrolyte operating at low operating temperatures of 400–600 °C [5–8]. However, high sintering temperatures such as 1550 °C are typically needed to densify GDC electrolyte [9], increasing cost and difficulty in the cell fabrication process. Consequently, lowering the sintering temperature to achieve relatively high density of sintered GDC samples has become an active research area. Two main approaches have been extensively explored to enhance the sinterability of GDC. The first one is to use different powder preparation methods such as co-precipitation and hydrothermal method to synthesize active nano-sized GDC powders with high sintering ability [10–12]. However, the complex powder synthesis process and low yield make it difficult for cost

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effective and scalable practical applications. Another strategy is to apply sintering aid to reduce the sintering temperature. Jud et al. [13] successfully lowered the sintering temperature by 200 °C using 1 mol % ratio of cobalt oxide as the sintering aid to GDC, while Perez-Coll and co-workers [14] found that the addition of Co_3O_4 lowered the grain and grain boundary activation energy, and at the same time increased the grain and grain boundary conductivity in lower temperature zone.

In our previous study [15], 2.5 mol % Li_2O was applied as the sintering aid for GDC (5LiGDC) and dense GDC samples has been obtained at a low sintering temperature of 800 °C. For application of GDC as the electrolyte in SOFCs, the conductivity value of GDC is one of the most important metrics that should be evaluated. The total conductivity could be further separated into the grain interior conductivity and grain boundary conductivity, and both of them could be influenced when using Li_2O as the sintering aid. On the other hand, easy vaporization of Li_2O at high temperatures makes it even more complicated for the sintering processes [16]. The objective of this study is to examine the conductivity of 5LiGDC samples sintered at different temperatures, to characterize the composition and microstructure of the sintered samples, to study the shrinkage behavior of the samples during sintering, and to elucidate possible sintering mechanisms.

2. Experimental

$Gd_{0.1}Ce_{0.9}O_{2-\delta}$ (GDC) raw powder was synthesized from a sol–gel method [17]. Specifically, $Ce(NO_3)_3 \cdot 6H_2O$ and Gd_2O_3 were mixed in stoichiometric ratio and ball milled for 48 h. 5 wt% of $(NH_4)_2SO_4$ was then added as initiator and 2 wt% of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine as the catalyst. The mixture was stirred until a sol–gel was formed. The sol–gel was then dried and calcined at 800 °C for 2 h to obtain the GDC powder. 5 mol% ratio of $LiNO_3$ was added into GDC (5LiGDC) (equals to 2.5 mol% Li_2O doped GDC since $LiNO_3$ will decompose to Li_2O at 600 °C) with ethanol as dispersant and ball milled for 24 h. The slurry containing $LiNO_3$ and GDC was dried at 65 °C and the mixture obtained was further calcined at 600 °C for 2 h. The 5LiGDC powder was then die-pressed (220 MPa) to pellets with diameter of 20 mm and thickness of 0.8 mm. The 5LiGDC pellets were firstly heated up at a heating rate of 3 °C min^{-1} to 600 °C for 2 h, then further sintered at 900, 1000, 1100, 1250 and 1400 °C for 6 h with a heating rate of 1 °C min^{-1}, and finally cooled down to room temperature. The sintered pellets were noted as 5LiGDC900, 5LiGDC1000, 5LiGDC1100, 5LiGDC1250 and 5LiGDC1400, respectively. Relative densities were all above 95% for the sintered pellets tested by the Archimedes drainage method. For comparison, GDC pellets without adding Li_2O were also sintered at 1400 °C (denoted as GDC1400). The surface of all the pellets was polished using 600 grid sand paper prior to the conductivity tests.

The phases of the sintered samples were characterized using X-ray diffractometer (XRD, PANalytical, X'PertPRO, the Netherlands) with CuKα radiation, a scanning step of 0.02°, a scanning speed of 3° min^{-1}, and 2θ range of 10–90°. Netzsch Dil402C dilatometer was used to study the sintering behavior of the 5LiGDC and GDC samples in air, with a heating rate of 10 °C min^{-1} up to 1400 °C. In order to exclude the surface adsorption impurity elements influence, the sintered samples were polished and thermally etched for surface microstructure study using scanning electron microscope (SEM, JEOL JSM 6700F and Zeiss Ultraplus). The cross section images were taken from samples without thermal etching as to keep the origin status. transmission electron microscopy (TEM) samples were prepared by classic dimpling method using the Gatan dimpler 626, and the final sample thickness was down to <10 nm by ion milling (Fischione Model 1010) .The local elemental distributions are characterized by the scanning transmission electron microscope with energy-dispersive X-ray spectroscopy (STEM-EDX) method using a Cs-corrected Hitachi HD-2700C equipped with a Cold-FEG, operated at 200 kV. Secondary ion mass spectrometry (SIMS, Hiden Analytical Ltd.) is also utilized as a complementary surface analytical method to XRD and SEM. For SIMS tests, Ar^+ primary ions accelerated in the range of 5 keV are bombarded to the surfaces of the samples. A small fraction of the samples is evaporated from the outer surface layer, producing various different kinds of ionized molecular fragments. The ionized molecular fragments are counted using a quadrupole mass spectrometer. The mass of the fragments provides information on the chemical species formed on the samples uppermost surface layers.

Ag electrodes (with diameter of ~0.8 cm) were coated on both sides of the dense pellets and fired at 700 °C for 0.5 h. Electrochemical impedance spectroscopy measurements were performed using a Zahner IM6 Electrochemical Workstation under dry air in a temperature range between 150 and 700 °C over the frequency range of 0.1 Hz to 4 MHz.

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the XRD of 5LiGDC pellets sintered at different temperatures (900, 1000, 1100, 1250 and 1400 °C, respectively) and GDC pellets sintered at 1400 °C, respectively. The same sample

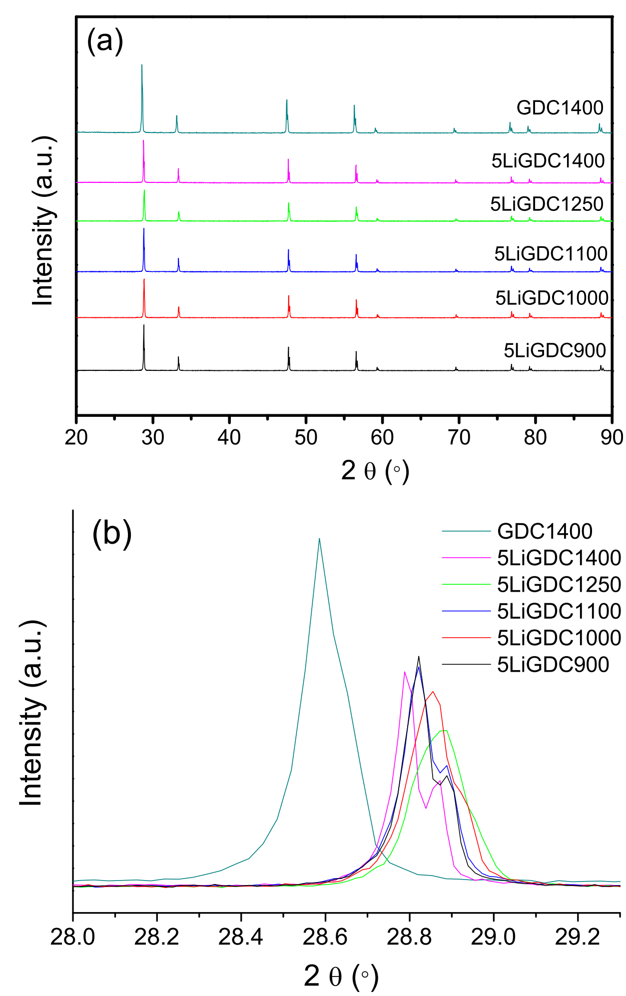

Fig. 1. The XRD of GDC1400 and 5LiGDC samples sintered at different temperatures.