

IONIC CONDUCTIVITY AND MICROSTRUCTURE OF CERIA-BASED POWDERS SYNTHESIZED BY GLYCINE COMBUSTION FOR SOFC

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Abstract

Nanocrystalline $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ powders (GDC) have been successfully synthesized using combustion synthesis with metal nitrates as an oxidant and glycine as the fuel. X-ray diffraction patterns of the as-burnt GDC powders showed a single phase cubic fluorite structure. The crystalline size of the GDC powders increased with increasing the calcination temperatures. The densification and grain size of the GDC was found to increase when the sintering temperatures were increased from 1200-1350°C. Grain growth was observed after sintering at 1350°C, while the optimum densification and grain size was obtained after sintering at 1300°C. The grain interior and grain boundary conductivity related to the degree of densification and grain size of the sintered GDC electrolyte is discussed in this study.

Keywords: Ceria-based electrolyte, GDC, combustion, SOFC

Introduction

A solid oxide fuel cell (SOFC) has been recognized as one of the most promising renewable energy production devices, which can convert chemical energy into electrical energy without releasing toxic gases (Singhal and Kendall, 2004). The conventional yttria-stabilized zirconia (YSZ) electrolyte requires a high operating temperature (~1000°C) to obtain sufficient ionic conductivity, so it has problems of a high thermal corrosion rate and the limitation of cell components. Lowering

the operation temperature has a lot of benefits, such as a cheaper and wider choice of cell component materials and lower degradation problems (Zhang *et al.*, 2006). Nowadays, ceria-based ceramics have been widely considered for use as electrolytes at intermediate temperatures (600-800°C) because of their ionic conductivity which is superior to that of YSZ. Various aliovalence cations, such as Ca^{2+} , Y^{3+} , Gd^{3+} , and Sm^{3+} were doped on a ceria structure to improve ionic conductivity

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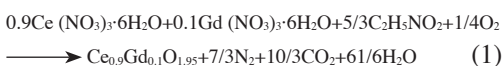
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(Hui *et al.*, 2007). Among them, the Gd^{3+} doped ceria electrolyte exhibited the highest ion conductivity because it had the smallest association enthalpy between the dopant cation and oxygen vacancies in the fluorite lattice (Steele, 2000). It was reported that the highest ionic conductivity was obtained with the Gd content at 10 mol% (Steele, 2000) which was later confirmed by Fuentes and Baker (2008). Thus, the Gd content of 10 mol% was then selected for further study. SOFC solid electrolytes should have high densification to prevent direct mixing between the fuel and oxygen gases. However, CeO_2 -based powders synthesized via the solid state reaction obtained high densification at high sintering temperatures of about 1500-1600°C (Ma *et al.*, 2004). These sintering ranges also gave rise to the transformation of Ce^{4+} to Ce^{3+} (Zhang *et al.*, 2004). This behavior led to high ohmic resistance due to the short circuit. It was suggested that this problem could be avoided by reducing the sintering temperature down to 1300°C. It is well known that a lower particle size could reduce the sintering temperature, so various methods, such as combustion, sol-gel, and co-precipitates, were suggested for synthesis of the nano-sized ceria-based powders. Combustion synthesis is one of the most popular methods for preparation of nanocrystalline powders. The main feature of the combustion is the requirement of a very short time for attaining high combustion temperatures due to the heat released during exothermic reactions. Oxide powders have been synthesized successfully by combustion synthesis using different fuels, such as glycine (Singh *et al.*, 2006), citric acid (Peng and Zhen, 2007), and urea (Chinarro *et al.*, 2007). Especially, glycine combustion synthesis has been known to produce homogeneous, low impurity, and nano-sized powders (Lenka *et al.*, 2008). Therefore, this project reported the synthesis of nano-crystalline GDC powders by glycine combustion. The phase transformation, microstructure, densification, and ionic conductivity of the combustion GDC electrolyte at different sintering

temperatures have been reported.

Materials and Methods

The reagent grades of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\text{C}_2\text{H}_5\text{NO}_2$ (glycine) were used as starting materials (Sigma-Aldrich Inc., St. Louis, MO, USA, 99% purity). The nitrates were weighed according to their compositions and dissolved into water to form a solution. The amount of 5/3 mol% glycine fuel was calculated based on the valence of the oxidizing and reducing element, according to the following equation:



Cerium nitrate and gadolinium nitrate were taken in the required ratio, according to the formula $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ or GDC, and dissolved in water with glycine. The homogeneous solution was stirred and heated on a hot plate at 80°C until auto-ignition and self-sustaining combustion occurred. The ash was subsequently ground for 20 min using a vibration mill with zirconia balls. After the GDC ash was sieved, the as-synthesized powders were calcined at 300-800°C for 1 h. The calcined powders were uniaxially pressed into disks (10 mm in diameter) under a pressure of 100 MPa, followed by sintering at 1250°C, 1300°C, 1350°C, and 1400°C for 1 h in air. Phase transformations of the GDC electrolytes were studied by the X-ray diffraction (XRD) technique using PANalyticalX' Pert PRO MPD (PANalytical B.V., Almelo, Netherlands). The crystallite sizes of these GDC powders were calculated by the Scherrer formula (Singh *et al.*, 2011), as follows;

$$D = \frac{0.89 \lambda}{B \cos \theta} \quad (2)$$

where λ is the wavelength of the X-ray, θ is the diffraction angle, $B = \sqrt{B_m^2 - B_s^2}$ is the corrected half-width, B_m is the observed half

width of the (111) reflection of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$, and B_s is the (111) reflection of the standard CeO_2 . Densities of the sintered samples were measured based on the Archimedes principles. The microstructure was observed under a scanning electron microscope (SEM). In the AC impedance spectra process, silver paste (SPI Supplies division of Structure Probe, Inc., West Chester, PA, USA) was painted onto both sides of the pellets as an electrode and it was then measured for ionic conductivity between 250-600°C by an impedance spectroscopy (Solartron, SI1260, Solartron Group Ltd., Cambridge, UK) in the range of 10^{-10} to 10^7 Hz.

Results and Discussion

The SEM micrograph of the as-burnt GDC powders is presented in Figure 1. The loose and porous structure of the as-burnt powders

was due to the evolution of large amounts of the volatile gases (N_2 , CO_2 , and H_2O) during the combustion reaction (Kashinath *et al.*, 2002).

Figure 2 shows the XRD patterns of the as-burnt GDC powders and the calcined GDC powders at different temperatures. It was indicated that the as-burnt GDC powders showed the single phase of a cubic fluorite structure. It could be explained that the Ce^{4+} ions were completely substituted by Gd^{3+} ions after the self-sustaining combustion. When the as-burnt GDC powders were calcined at different temperatures, the XRD patterns indicated a similar structure of a cubic fluorite. Table 1 shows the crystalline size of the as-burnt GDC powders and the different calcinations of the GDC powders. In order to produce the smallest crystallite size of the GDC powders, it was required to reduce the sintering temperature and there was obtained

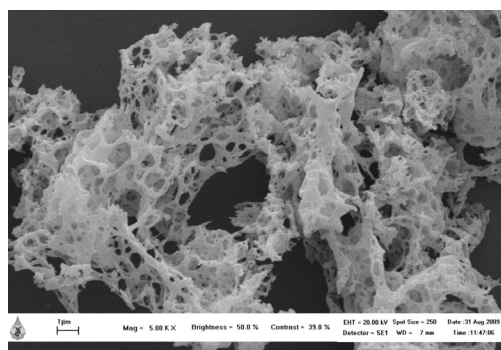


Figure 1. SEM micrograph of as-burnt GDC powders

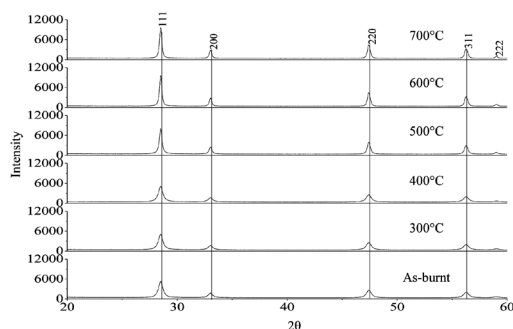


Figure 2. XRD patterns of as-burnt GDC powders and calcined GDC powders at different temperatures

Table 1. Crystallite size of as-burnt GDC powders and calcined GDC powders at different temperatures

GDC powders	Crystallite size (nm)
As-burnt	17.12
Calcined at 300°C	18.71
Calcined at 400°C	19.56
Calcined at 500°C	30.60
Calcined at 600°C	33.07
Calcined at 700°C	34.17

the as-burnt GDC powders (17.12 nm). The crystallite size was slightly larger when the GDC powders were calcined at 300-400°C. However, it rapidly increased after calcinations at 500-800°C. It is well known that a larger crystallite size has an adverse effect on the difficult densification and grain growth. Thus, the as-burnt GDC powders were selected.

SEM micrographs of the GDC pellets after sintering at 1200°C, 1250°C, 1300°C, and 1350°C are presented in Figure 3(a-d), respectively. It was observed that the neck formation just started at 1200°C, so the microstructure was full of pores with a small average grain size about 0.18 μm . With increasing the sintering temperature to 1250-1300°C, the necks between the GDC particles were highly formed, while the grain boundaries were clearly observed, as shown in Figure 3(b) and 3(c). However, the sintered GDC electrolyte at 1350°C (Figure 3(d)) showed the grain growth behavior. To confirm the densification of the as-burnt GDC powders better, the relative densities and the average grain sizes of the GDC electrolyte at different sintering temperatures are shown in

Figure 4. The lowest relative density of the sintered GDC electrolyte was observed at 1200°C. It was found that the relative density was rapidly improved after sintering at 1250-1300°C due to the neck growth. Therefore, the highest shrinkage was obtained in this stage, while the average grain size was significantly increased in the range of 0.2-0.5 μm at 1250-1300°C. After being sintered at 1350°C, densification of the GDC electrolyte was still increased slightly, but the grain growth (1.24 μm) was observed.

Figure 5 shows the semi-circle features according to the response of the grain boundary and grain interior resistivity of the sintered GDC electrolyte at different sintering temperatures. It was seen that both the grain boundary and grain interior conductivity values were improved with higher sintering depending on the lower porosity. It was known that the movement of ions could be obstructed by porosity (Christie and Berkel, 1996). Figure 6(a) shows the model which simulated the movement of the oxygen ion (O^{2-}) at the grain interior and grain boundary regions. This model illustrated how oxygen

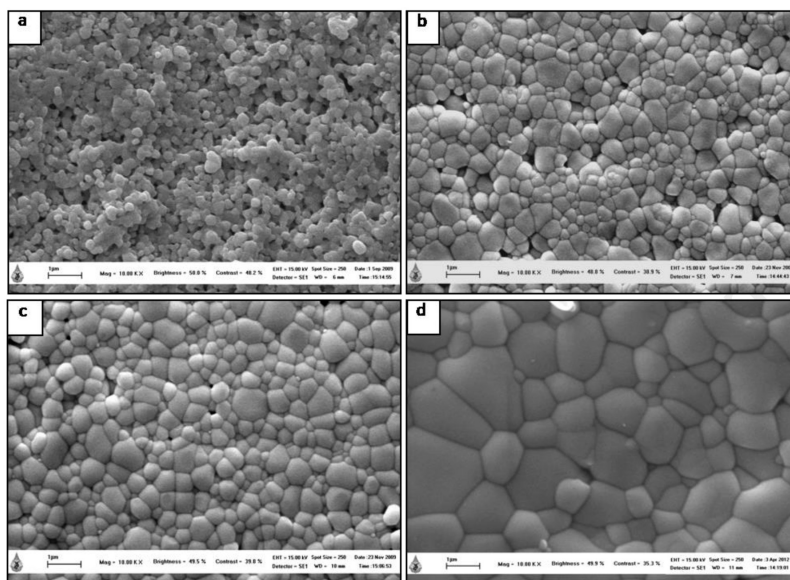


Figure 3. SEM micrograph of GDC compacted powders after being sintered at (a) 1200°C, (b) 1250°C, (c) 1300°C, and (d) 1350°C

ions were blocked by pores located at different locations giving rise to suppression of the grain interior and grain boundary conductivity. In general in polycrystalline materials, mass transportation in the grain boundaries is higher than in the grain interior region. In

contrast, with this GDC electrolyte it was found that the grain boundary had a higher resistivity than the lattice because almost all the pores remained at the grain boundary. Although the grain boundary resistivity tended to decrease with higher

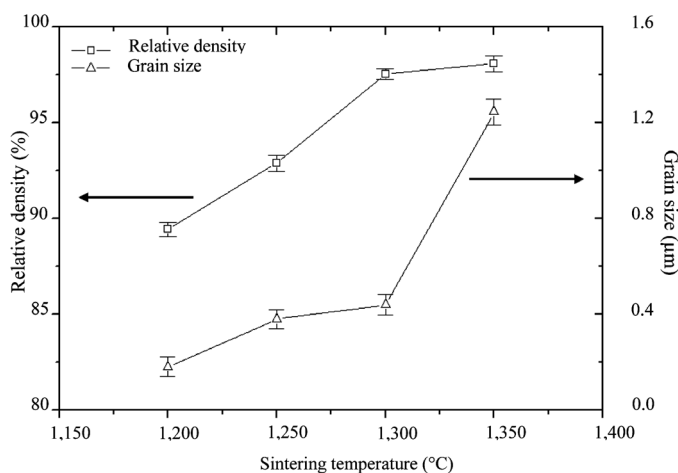


Figure 4. Relative density and grain size of GDC compacted powders with different sintering temperatures

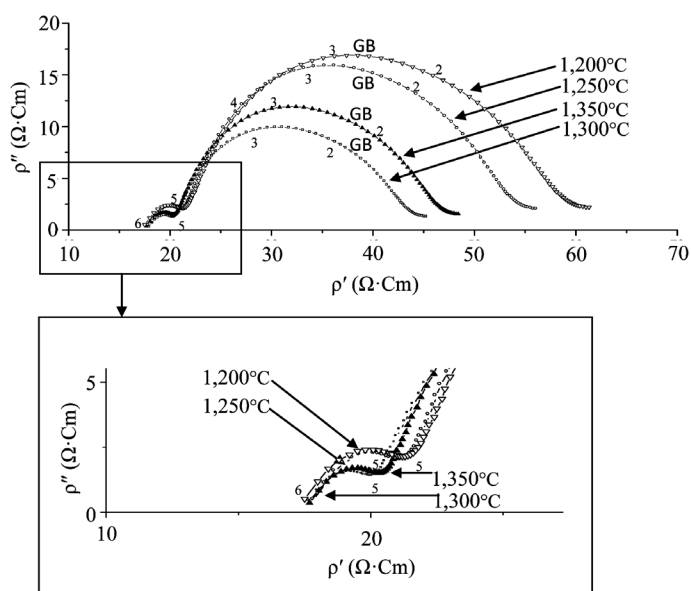


Figure 5. Impedance spectra measured at 500°C for the GDC compacted powders with different sintering temperatures (the given number above the filled symbols are the power of ten of the corresponding frequency)

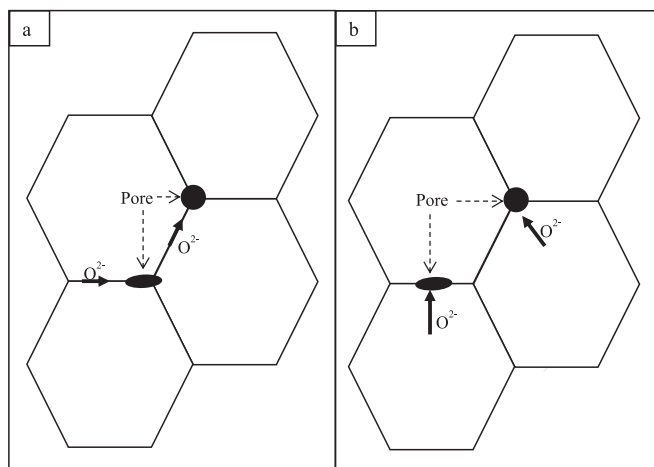


Figure 6. The simulation of oxygen ion movement (a) along grain boundary and (b) across grain boundary

sintering temperatures (1200-1300°C), it increased after being sintered at 1350°C. It was assumed that the transformation of Ce^{4+} to Ce^{3+} had an effect to produce electrons. These electrons must be located in the grain boundaries and formed the space charge effect, so the positive charge carrier or oxygen vacancies at the grain boundaries decreased (Hui *et al.*, 2007). The movement of oxygen vacancies in the grain boundaries was therefore obstructed by the space charge. From the results, it was found that GDC powders synthesized by glycine combustion could be used without calcinations. These GDC powders had a nano-crystalline size so they could have high densification and a small grain size with lower sintering temperatures at about 1250-1300°C, where the transformation of Ce^{4+} to Ce^{3+} could be prevented.

Conclusions

$Ce_{0.9}Gd_{0.1}O_{1.95}$ powders were synthesized by the glycine combustion method. The XRD pattern of the as-burnt and all calcined GDC powders indicated a single phase of a cubic fluorite structure. High densification and a small average grain size were achieved for the GDC electrolyte at 1250-1300°C. The grain

interior and grain boundary conductivity were improved with lower porosity. However, the grain boundary conductivity was slightly decreased with the space charge effect after being sintered at 1350°C.

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