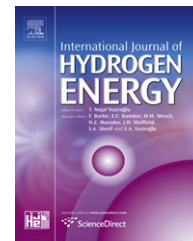




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# Effect of titania concentration on the grain boundary conductivity of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ electrolyte

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## ABSTRACT

The effect of titania ( $\text{TiO}_2$ ) addition on the densification, crystal structure and electrical property of  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  (GDC) are examined.  $\text{TiO}_2$  addition reduces GDC sintering temperature by  $\sim 200$  °C and considerably improves grain boundary conduction. The minimum grain boundary resistivity is obtained at 0.8 mol%  $\text{TiO}_2$  concentration. XRD analysis suggests that the solubility limit of  $\text{TiO}_2$  in GDC is  $\sim 0.6$  mol%. The optimum doping level (0.8 mol%) is slightly higher than the solubility limit (0.6 mol%), which implies that a small amounts of  $\text{TiO}_2$  ( $\sim 0.2$  mol%) at the grain boundaries benefits the grain–boundary conduction.

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## 1. Introduction

Fluorite structure oxides such as zirconia and ceria have been extensively studied as electrolyte materials for solid oxide fuel cells (SOFCs) [1,2]. Yttria–stabilized zirconia (YSZ) is the most commonly used electrolyte for SOFCs. Nevertheless, the necessity for its high operating temperature ( $\sim 1000$  °C) results in extreme requirements for other SOFC components [3,4]. In recent years, significant efforts have been exerted in developing alternative electrolytes with low operating temperatures [5,6]. Doped ceria is one of the most promising electrolyte candidates for intermediate temperature (IT) SOFCs given its high ionic conductivity within 500–700 °C [7,8].

However, the refractory nature of doped ceria leads to significant challenges in its implementation in SOFCs [9,10]. Several transition metal oxides, such as  $\text{Fe}_2\text{O}_3$  [11],  $\text{SrO}$  [12]

and  $\text{ZnO}$  [13,14], reportedly improve the sinterability of doped ceria effectively. Chen and Chen [15] found that  $\text{TiO}_2$  addition enhances grain boundary mobility at 0.1 mol% levels. Culter et al. [16] showed that  $\text{TiO}_2$  addition (1 mol%) increases the sintering activity of  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$  electrolyte. However, studies on the influence of  $\text{TiO}_2$  doping on the electrical properties of doped ceria are limited. The electrical properties of  $(1-x)\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9} + x\text{TiO}_2$  ( $x = 0.01\text{--}0.06$ ) have been investigated both in air and hydrogen atmosphere [17]. However, the separation of grain and grain boundary contributions to the total electrical conductivity has not been carried out; thus, the exact role of  $\text{TiO}_2$  remains uncertain.

In this work,  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  (GDC) electrolyte is studied as a function of the  $\text{TiO}_2$  concentration. The sintering behavior and grain–boundary conduction are analyzed.

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## 2. Experimental

### 2.1. Sample preparation

The starting materials used for  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  (GDC) added with 0 mol%–1 mol%  $\text{TiO}_2$  (denoted as “GDCxT”;  $x = 0, 0.2, 0.4, 0.6, 0.8$  and  $1.0$ ) solid solutions were stoichiometric quantities of  $\text{CeO}_2$  (99.5%; Yixing Xinwei Leeshing Rare Earth Co., China),  $\text{Gd}_2\text{O}_3$  (99.99%; Beijing Founde Star Science and Technology Co., China) and  $\text{TiO}_2$  (99.95%; Shanghai Chemical Reagent Plant, China) powders. The  $\text{CeO}_2$ ,  $\text{Gd}_2\text{O}_3$  and  $\text{TiO}_2$  powders were thoroughly mixed by wet-ball-milling for 8 h using zirconia balls in polyethylene jars. After drying and grinding, the powders were annealed in air at  $1200^\circ\text{C}$  for 2 h. The calcined powders were ground again in an agate mortar and formed into 14 mm-diameter pellets under a pressure of 100 MPa. The pellets were subsequently sintered in air at  $1200$ – $1600^\circ\text{C}$  for 10 h.

### 2.2. Characterization

The density of the each sintered sample was measured by Archimedes' principle and expressed as the relative density. The X-ray diffraction (XRD) data of the solid specimens (ground into powders) were obtained using an ARL-X'TRA (Thermo, USA) diffractometer with  $\text{Cu K}\alpha$  radiation over the range of  $2\theta = 20^\circ$ – $80^\circ$  at room temperature. The microstructures of the as-prepared samples were characterized using JSM-5900 and JSM-6360 (JEOL, Japan) scanning electron microscopy (SEM) systems. For SEM observation, the fractured cross-sections and surfaces of the samples were sputter-coated with gold after etching at  $1200^\circ\text{C}$ . The average grain sizes of the specimens were observed on the SEM graphs using the JEOL Smile View software (version 2.1).

For electrical characterization, Ag pastes were coated on both faces of the sintered specimens and cured at  $750^\circ\text{C}$  (10 min hold). The electrical properties were measured using a PARSTAT 2273 impedance analyzer from  $300^\circ\text{C}$  to  $750^\circ\text{C}$ . The AC impedance spectra were measured in air over 0.1 Hz–100 kHz frequency range with 10 mV of AC signal amplitude. Curve fitting analyses were carried out using ZSimpWin (EChem Software).

## 3. Results and discussion

### 3.1. Shrinkage and densification

Fig. 1 shows the variation of relative densities with sintering temperatures for GDCxT samples. For the specimens with  $\geq 0.4$  mol%  $\text{TiO}_2$ , the relative densities all reach 94% after sintering at  $1400^\circ\text{C}$  for 10 h; meanwhile the relative density for GDC is only 73%. To achieve a similar value (94%), GDC should be sintered at  $1600^\circ\text{C}$  for 10 h. This reduced sintering temperature ( $1400^\circ\text{C}$ ) is lower than a previously reported sintering temperature of around  $1500^\circ\text{C}$  [16,17]. The discrepancy may be attributed to the difference in impurity levels and initial particle sizes of the raw materials.

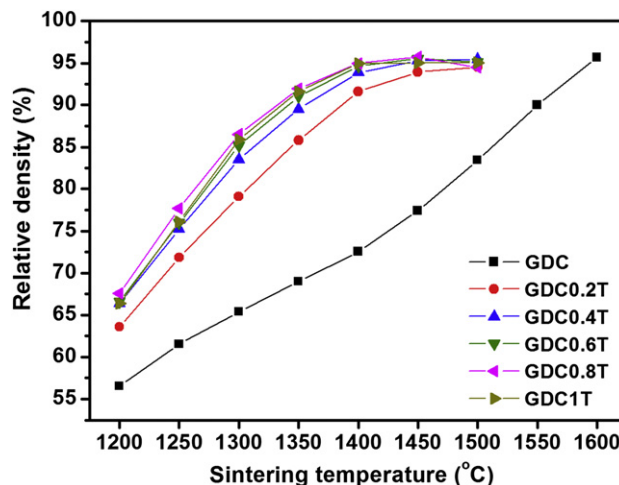


Fig. 1 – Relative density versus sintering temperature for GDC with different  $\text{TiO}_2$  contents.

### 3.2. Crystal structure and phase composition

The XRD patterns of GDCxT samples sintered at  $1400^\circ\text{C}$  (GDC at  $1600^\circ\text{C}$ ) for 10 h are shown in Fig. 2. All samples are confirmed to be single phase and have a cubic fluorite structure. No significant second phase is identified in the XRD patterns, or the concentration of the second phase is below the detection limit.

The lattice parameters are calculated by full curve fitting using the Jade software. The effect of the  $\text{TiO}_2$  content on the lattice parameters is shown in Fig. 3. The lattice parameters linearly decrease with increased  $\text{TiO}_2$  concentration when the content is less than 0.6 mol%, and then linearly increase with further  $\text{TiO}_2$  addition. The ionic radius decreases in the order  $\text{Gd}^{3+}$  (1.053 Å) >  $\text{Ce}^{4+}$  (0.97 Å) >  $\text{Ti}^{4+}$  (0.74 Å)/ $\text{Ti}^{3+}$  (0.67 Å) [18]; thus,  $\text{Ce}^{4+}$  may be replaced by the smaller  $\text{Ti}^{4+}/\text{Ti}^{3+}$  cation. The variation in lattice parameters indicates that the solid solubility limit of  $\text{TiO}_2$  in ceria is around 0.6 mol%. Notably, when the  $\text{TiO}_2$  content exceeds the solubility limit, the lattice parameters, increase with the addition of  $\text{TiO}_2$ . Gd segregation at grain boundary has been reported for  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  samples

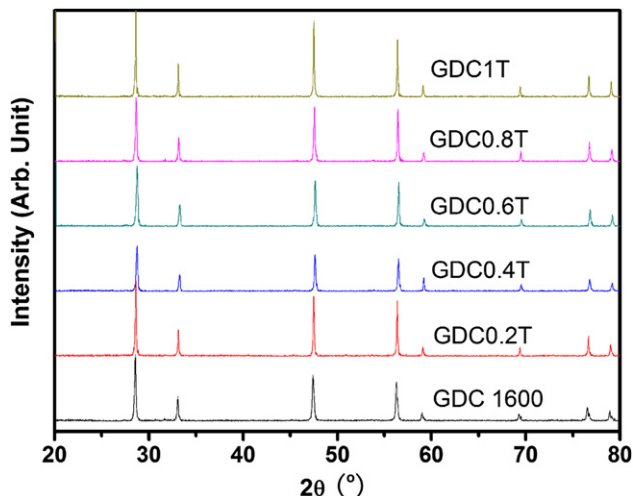


Fig. 2 – XRD patterns of GDC with different  $\text{TiO}_2$  contents.

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