Study of Gadolinium-doped Cerium Oxide by XRD, TG-DTA, impedance analysis, and positron lifetime spectroscopy

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Abstract. X-ray diffraction, thermogravimetry differential thermal analysis, impedance analysis, and positron lifetime spectroscopy were conducted for Gadolinium-doped cerium oxides (GDC) prepared using oxalate coprecipitation method. XRD revealed the fluorite structure indicating that gadolinium is successfully doped into cerium oxide. Prior to sintering, the vacancy-sized free volume and nanovoid were observed at grain boundaries. The vacancy-sized free volumes shrank with increasing sintering temperatures and finally got dominant.

1. Introduction

Solid oxide fuel cells have been intensively studied due to their high power conversion efficiency. There has been a long-standing problem of extremely high operating temperature for solid oxide fuel cells. Gadolinium-doped cerium oxides are one of the most promising candidates as the electrolytes operated at intermediate temperature [1-3]. The total ionic conductivity of GDC is governed by the local atomic structure of transgranular [4], which is expected to be correlated with sintering. Song et al. [5] reported that the points defect is an important factor which influences the evolution of structure and chemical changes in hydrogen irradiated CeO₂. Zhang et al. [6] investigated the effect of transition metal oxide loading on sintering behaviour and ion conductivity of GDC. It is thus of significance to investigate the local structural change induced by sintering. In this paper, we investigated GDC prepared using oxalate coprecipitation method by XRD, TG-DTA, impedance analysis, and positron lifetime spectroscopy.

2. Experimental

Gadolinium-doped cerium oxides (GDC) were prepared using oxalate coprecipitation method [7]. The cerium and gadolinium nitrate mixed solution at a molar ratio of Ce³⁺/ Gd³⁺ = 4/1 was dropped into a stirred oxalate acid solution to produce the oxalate precipitate. The precipitates were calcined at 873K for 1 h in the air to form oxides. They were compacted into a pellet by uniaxial pressing (20MPa) and sintered in the wide temperature range (873 - 1473K) for 6 h in air. The lattice constant of GDC was determined by XRD using NaCl as internal standard. The relative density was measured by Archimedes method. The Pt electrodes were formed on the both side of GDC pellet by heating at 1473 K using Pt paste (Tanaka Kikinzoku TR-7070). The ionic conductivity of the pellet was measured.
from 673K to 973K conducted by AC impedance analyzer (Princeton applied research corp. VersaSTAT3) in the frequency range from 100 μHz to 1MHz. Positron lifetime spectroscopy was conducted using ²²Na positron source at room temperature. The positron lifetime spectra were numerically analyzed using the POSITRONFIT code [8].

3. Results and discussion

Figure 1 shows the XRD patterns of GDC and CeO₂ sintered at 1073K for 6h in air. The XRD pattern indicates that GDC has a fluorite type structure without any other phases. All peaks of GDC are shifted to low angle region against to the corresponded ones of CeO₂ indicating the expansion of interplanar spacing for GDC by Gd doping. The lattice constants calculated for GDC and CeO₂ are 0.5429 nm and 0.5415 nm, respectively. This implies that it is partially substituted Ce⁴⁺ with Gd³⁺ and formed of an oxygen vacancy successfully.

The results of TG-DTA analysis for Ce and coprecipitated oxalate are shown in Figure 2. They lost chemically adsorbed water at 473K and began to decompose to oxides with the producing CO, CO₂ and O₂ gases at 573K. The exothermic peak in DTA curves was detected at a higher temperature for coprecipitated than for Ce oxalate.

![Figure 1. XRD patterns of GDC and CeO₂.](image1)

![Figure 2. TG-DTA curves of Ce and coprecipitated oxalate.](image2)

Figure 3 shows the temperature dependence of the total ionic conductivity for GDC. The data was fitted with least-square method. Samehishima et al. reported that CeO₂ sintered at 1873K for 4 h in dried air shows the total ionic conductivity of 4.9×10⁻⁵ S / cm at 773 K lower by 20 times than the value for GDC sintered at 1473 K in the present study. The activation energy of GDC (81kJ / mol) is higher than that of CeO₂ (61.7kJ / mol) measured by Samehishima et al [9]. This indicates that the substitution of Ce⁴⁺ with Gd³⁺ with larger ionic radius than that of Ce⁴⁺ is caused to form the high potential energy barrier. The total ionic conductivity is explained by oxygen ion diffusion and is influenced by the number of oxygen vacancies existed in the samples.
Figure 4 shows the results of positron lifetime spectroscopy for GDC. Prior to sintering, two components $\tau_1$ ($\sim 260$ ps) and $\tau_2$ ($\sim 500$ ps) corresponding to a vacancy-sized free volume and a nanovoid were obtained with their relative intensities $I_1$ ($\sim 80\%$) and $I_2$ ($\sim 20\%$). The average size of GDC crystallite evaluated from 311 peak broadening using Scherrer's equation is $12.8$ nm before sintering, which is by far smaller than the typical positron diffusion length in solids of $\sim 300$ nm [10]. Positrons implanted in GDC crystallite can thus efficiently diffuse out and annihilate at grain boundaries. We therefore conclude that the vacancy-sized free volumes and nanovoids detected by the present positron lifetime spectroscopy are present at grain boundaries. Similar observation was reported for yttria-stabilized zirconia by Cizek et al. [11].

Upon increasing temperatures the positron lifetime $\tau_1$ decreases and its relative intensity $I_1$ increased, signifying shrinkage of vacancy-sized free volumes together with sintering. The lifetime $\tau_2$ and its relative intensity $I_2$ exhibit the opposite tendency to those of vacancy-sized free volume (see right hand in Figure 4). The vacancy-sized free volumes got dominant at the sintering temperature of 1473 K, while the nanovoids almost disappear. The results suggest that a substantial increase of local electron density at grain boundaries occurs as a result of sintering and the process of sintering follows the kinetics of vacancy-sized free volumes and nanovoids at grain boundaries.

Figure 3. Arrhenius plots of total conductivity of GDC and CeO$_2$. Solid lines are results of the least-square fit.

Figure 4. Plot of positron lifetimes against sintering temperature for GDC.
4. Conclusions

We prepared gadolinium-doped cerium oxide using oxalate coprecipitation method. XRD revealed the fluorite structure indicating that gadolinium is successfully doped into cerium oxide. The total ionic conductivity of GDC is $9.8 \times 10^{-4}$ S/cm at 773K, which is 20 times higher than that of CeO$_2$ sintered at 1873K in air. This result indicated that the oxygen vacancies have an influence on the total ionic conductivity effectively. Positron lifetime spectroscopy revealed the presence of vacancy-sized free volumes and nanovoids, of which the kinetics is associated with sintering.

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