

Syntheses and Characterization of CeO₂ Based Oxide Prepared by Precipitation Methods for SOFCs

by

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Abstract

Cerium oxides and Gadolinia doped ceria (GDC) were prepared by a homogeneous precipitation, a pH adjusted precipitation and a solid state reaction method. The GDC prepared by the pH adjusted precipitation was nanosized crystallite with mesopore. The maximum power density for the pH adjusted GDC of 0.295 W cm⁻² was observed at 900 °C on 0.700 mA cm⁻², which is higher than that of the GDC by the solid state reaction.

Keywords: SOFCs, Cermet anode, GDC, homogeneous precipitation, pH adjusted precipitation

1. Introduction

If solid oxide fuel cells (SOFCs) would utilize hydrocarbons by direct reforming on the anode, the system can be compact because of the unnecessary reformer. If petrol or town gas can be utilized as a fuel, a fuel cell vehicle or a distributed generator for domestic use can be appeared and commercialized because of its well-organized infrastructure.¹⁾ Ceramic-metal (cermet) with porous structure has been used for an anode of SOFCs. Triple phase boundaries (TPBs) consisting of gas/nickel/oxide are important for an electrochemical reaction area for the cermet anode, therefore, size, porosity and morphology of an oxide in the cermet are important for the electrochemical property. If hydrocarbons fed into the cermet anode directly, carbon deposition becomes problems because of an obstruction of the porous microstructure of the cermet.²⁻⁴⁾

Reforming reaction of hydrocarbon is encouraged more in the anode than conventionally used Ni-YSZ cermet anode by replace the ZrO₂ based oxide for rare earth doped ceria (RDC) in the nickel-oxide cermet because of its high oxide-ion and electronic conductivity.^{5,6)} Ni-samarium doped ceria (SDC) cermet shows a higher electrode activation than Ni-scandia stabilized zirconia (ScSZ) for n-dodecane (C₁₂H₂₆) fuel at S/C of 2.⁷⁾ In our previous study, carbon distribution and carbon bonding state were successfully visualized for model electrodes of Ni/YSZ, Ni/ScSZ and

Ni/Gadolinia doped ceria (GDC) systems by micro-Raman spectroscopy.^{8,9)} No carbon was observed on nickel of the Ni/GDC system at 600 °C under dry 4.9% CH₄/Ar for 20 min in contrast to the Ni/YSZ and the Ni/ScSZ.⁸⁾ However, RDC was generally difficult to obtain by the solid state reaction method because of its sintering resistance, which is required over 50 h and 1400 °C. In this study, a homogeneous precipitation and a pH adjusted precipitation were selected to synthesis the cerium oxides due to save the energy and shorten the time. The solid state reaction method was also carried out as a reference. Electrochemical measurements were carried out for SOFC cells with prepared GDC cermet anodes.

2. Experimental

2.1. Syntheses of the GDC powders

Fig. 1 shows the Flow chart for preparing CeO₂ particles. The cerium oxides were prepared by the homogeneous precipitation, the precipitation of pH adjusted, and the solid state reaction methods. For the homogeneous precipitation, as shown in Fig. 1a, Ce(NO₃)₃·6H₂O (98%, Wako Pure Chemical Industries, Ltd.) and PEG (Polyethylene Glycol 200, Wako Pure Chemical Industries, Ltd.) were mixed at 60 °C in a 1 : 2 weight ratio and then the mixture was kept at 110 °C for 3 h. The cerium oxide was separated by centrifugation 2 times at 3000 rpm for 30 min with distilled water from the obtained white solution and then drying at 150 °C for 3 h. The specimen of the pH adjusted

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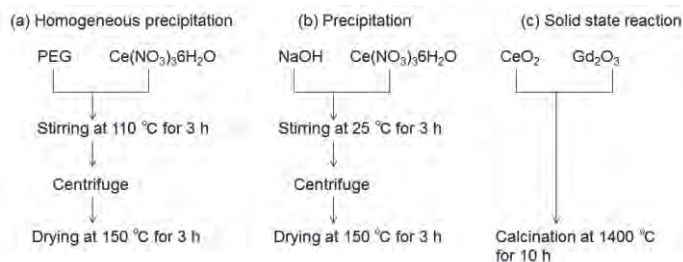


Fig. 1 Flow chart for the preparing CeO_2 specimens.

precipitation was shown in Fig. 1b. 20 cm^3 of 1 mol dm^{-3} NaOH (93%, Wako Pure Chemical Industries, Ltd.) and 100 cm^3 of 0.2 mol dm^{-3} $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solutions added to a glass beaker and mixed with stirring at $25 \text{ }^\circ\text{C}$ for 3 h. The obtained solution was centrifuged and then drying at the same condition of the homogeneous precipitation. The solid state reaction was carried out at $1400 \text{ }^\circ\text{C}$ for 10 h as shown in Fig. 1c. Powders of 20 mol% Gadolinia doped ceria were prepared as same as cerium oxides.

2.2. Characteristic analyses

Scanning electron microscopy (SEM) images of all of the specimens were taken with a Field-emission scanning electron microscope (FE-SEM), which was conducted on a HITACHI S-4800 instrument, at an accelerating voltage of 3.0 kV. XRD patterns were obtained on a Bruker D8 DISCOVER diffractometer with $\text{CuK}\alpha$ radiation. Nitrogen adsorption-desorption isotherms were obtained on a BEL Japan BELSORP-mini II apparatus. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The pore size and its distribution of the samples with meso and/or macro pores can be analyzed from the adsorption isotherm with the BJH method.¹⁰⁾

2.3. Fabrication of the SOFC cell

Electrolyte disks (2.0 mm thick) were prepared from 8 mol% Y_2O_3 -92 mol% ZrO_2 (YSZ, Tosoh, TZ-8YS). The

powder was pressed into disks uniaxially, and sintered at $1400 \text{ }^\circ\text{C}$ for 5 h in air. The sintered disks were polished with $0.3 \text{ }\mu\text{m}$ alumina particles.

A Ni-GDC cermet anode with 50 vol% of Ni was prepared from NiO (Wako) and the prepared GDC powders. The resulting powders mixed with 2-propanol were applied on the electrolyte disks and fired at $1200 \text{ }^\circ\text{C}$ for 1 h in air. Platinum paste was applied on the opposite side of the electrolyte as a cathode electrode and fired at 1273 K for 1 h in air. The electrode area was 0.785 cm^2 for all samples. A platinum wire as the reference electrode was attached on side edge of electrolyte.

2.4 Electrochemical measurement

The NiO-GDC cermet was reduced in a H_2 gas at $900 \text{ }^\circ\text{C}$ for 1 h. Cell tests were started at $900 \text{ }^\circ\text{C}$. Current-voltage and current-power characteristics were performed at 900, 800 and $700 \text{ }^\circ\text{C}$. The fuel composition was $\text{H}_2 : \text{H}_2\text{O} = 97 : 3$ (S/C = 0.03). Dry O_2 was fed into the cathode. Both the fuel and the oxygen were flowed at the rate of 30 ml/min.

3. Results and discussion

3.1. SEM observation of the specimens

The cerium oxides were prepared by the homogeneous precipitation, the precipitation of pH adjusted and the solid state reaction methods. The GDC could be also prepared by the pH adjusted precipitation and the solid state reaction methods. In contrast, no precipitation was obtained by the homogeneous precipitation. Fig. 2 depicts SEM images of the CeO_2 and GDC specimens. Fig. 2a and e show the CeO_2 particles by the homogeneous precipitation. Primary particles agglomerated and its diameter was around 150 nm. Fig. 2b, f, c, and g present the CeO_2 and the GDC by the pH adjusted method. Primary particles in diameter of around 20 nm

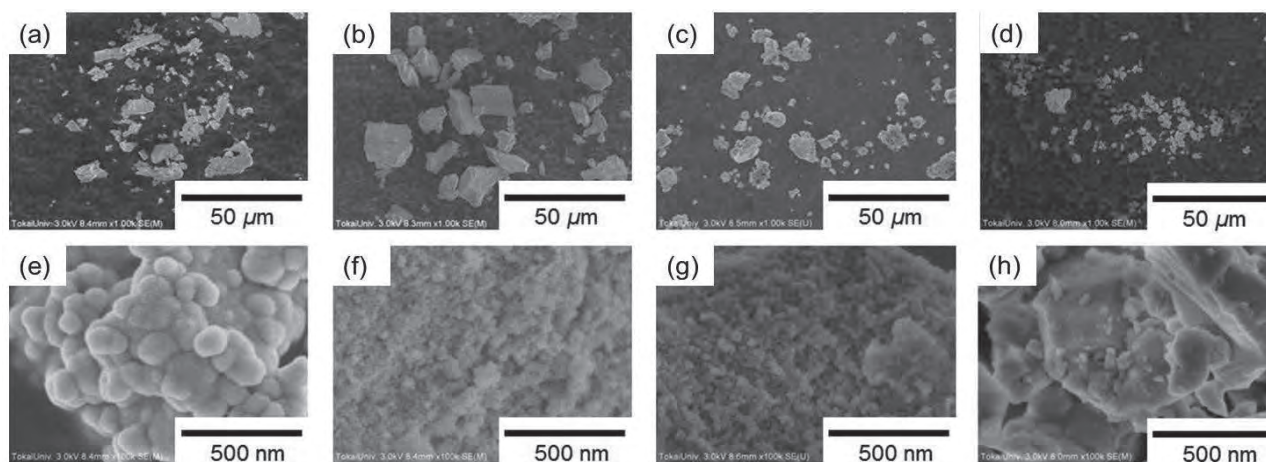


Fig. 2 SEM images of the CeO_2 and GDC specimens of (a) cerium oxide prepared by the homogeneous precipitation (its magnified area e), (b) cerium oxide prepared by the pH adjusted precipitation (its magnified area f), (c) GDC prepared by the pH adjusted precipitation (its magnified area g), and (d) GDC prepared by the solid state reaction (its magnified area

agglomerated. For comparison, a GDC specimen of which primary particles size was over 500 nm was synthesized by the solid state reaction. Whole primary particles agglomerated, and created secondary particles in diameter from several microns to several ten microns without the methods. The sizes of primary particles were different among the preparing methods as followed; $P_{\text{pH adjusted method}} < P_{\text{homogeneous}} < P_{\text{solid state reaction}}$. The primary particle sizes were depending on the processes of the preparation methods and also the heat treatment conditions.

3.2. XRD patterns of the synthesized powders

Fig. 3a shows an XRD pattern of the CeO₂ powder by the homogeneous precipitation. The diffraction peaks were significantly broadened because of the small crystallite size. The XRD pattern was consistent with that of the fluorite-type CeO₂ as shown in Fig. 3e.¹¹⁾ Fig. 3b and c show XRD patterns of the CeO₂ and the GDC by the pH adjusted method, respectively. The peaks were broadened as same as that of the homogeneous precipitation CeO₂. Nanocrystalline CeO₂ and GDC could be obtained by the pH adjusted method with heat treatment at 150 °C for 3 h, whereas the reaction process is not elucidated. Fig. 3d presents an XRD pattern of the GDC by the solid state reaction. The pattern confirmed that single-phase of the fluorite-type structure.¹¹⁾ The crystallite size of the CeO₂ and the GDC by the homogeneous precipitation and the pH adjusted precipitation was estimated to be about 10 nm from Scherrer's Formula that can be written as followed:

$$\tau = K\lambda / \beta \cos\theta \quad (1)$$

where τ is the size of the crystalline, which is smaller or equal to the grain size of the specimens. K is the shape factor that has about 0.9 in this case for the diffraction peaks from Miller indices of $\{h00\}$. λ is the wavelength of the X-ray, β is the peak broadening at half the maximum intensity (FWHM), and θ is Bragg angle. The crystallite size of the pH adjusted GDC is in reasonable agreement with the primary particle size of the SEM observations (Fig. 2g). On the other hand, the crystallite size of the GDC by solid state reaction was calculated to be about 60 nm, which was smaller than its primary particle size by the SEM observations (Fig. 2g).

3.3. BET surface areas of the specimens

Fig. 4 shows nitrogen adsorption isotherms of the homogeneous precipitation CeO₂ and the pH adjusted GDC. The BET surface areas, S_{BET} , were 28.4 m² g⁻¹ for the GDC by the pH adjusted method and 10.6 m² g⁻¹ for the CeO₂ by the homogeneous precipitation. Assuming spherical particles, the particle diameter, d_{surface} , was evaluated using the formula,

$$D_{\text{surface}} = 6000 / (\rho \times S_{\text{BET}}) \quad (2)$$

where ρ is the theoretical density (about 7 g cm⁻³).

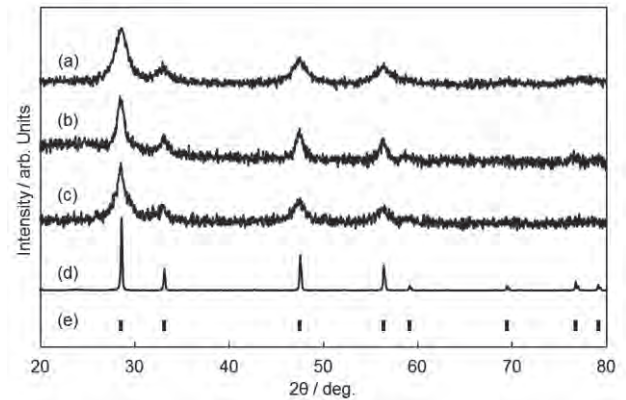


Fig. 3 XRD pattern of the CeO₂ powder by the homogeneous precipitation of (a) cerium oxide prepared by the homogeneous precipitation, (b) cerium oxide prepared by the pH adjusted precipitation, (c) GDC prepared by the pH adjusted precipitation, (d) GDC prepared by the solid state reaction, and (e) Cubic cerium oxide, JCPDS ICDD, #00-034-0394.

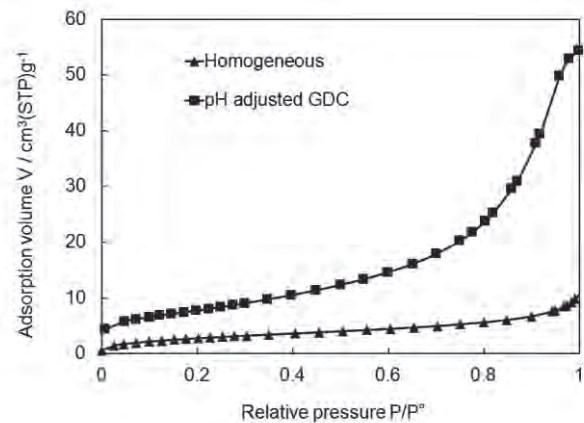


Fig. 4 Nitrogen adsorption isotherms of the homogeneous precipitation CeO₂ and the pH adjusted GDC.

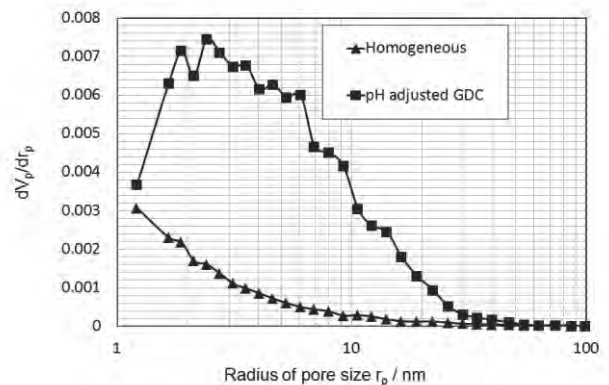


Fig. 5 Area distribution of pore size of for the homogeneous and the pH adjusted GDC.

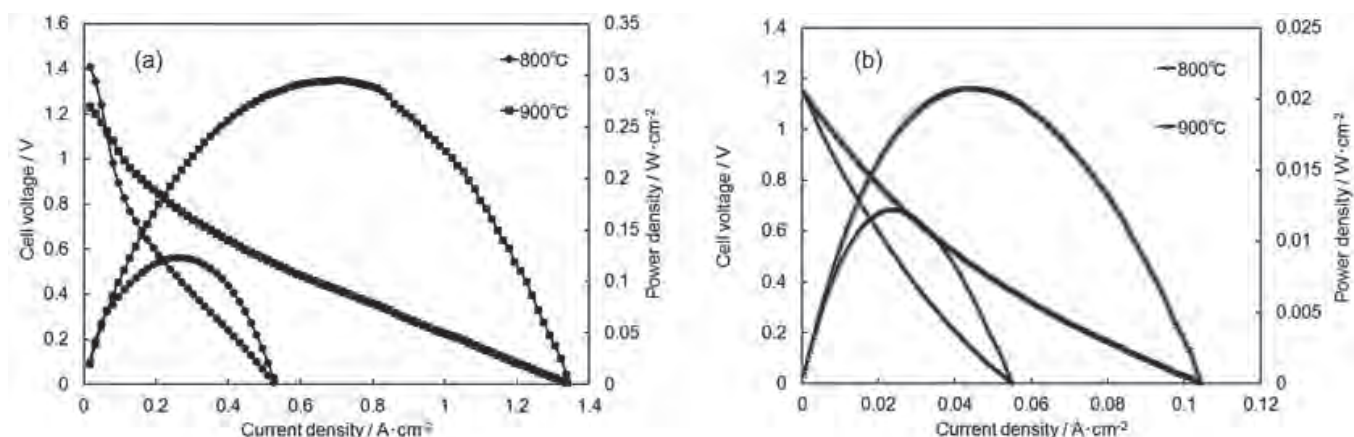


Fig. 6 Voltage and power density versus current density curves at various cell temperatures ranged between 800 and 900 °C under 100% H₂ gas of (a) the Ni-ph adjusted GDC/YSZ/Pt cell and (b) the Ni-solid state reaction GDC/YSZ/Pt cell.

The d_{surface} were calculated to be about 30 nm for the pH adjusted GDC and about 100 nm for the homogeneous precipitation CeO₂ which is consistent with the SEM observations. Fig. 5 presents area distribution of pore size of for the homogeneous precipitation CeO₂ and the pH adjusted GDC by the BJH method. For the pH adjusted GDC, a peak was observed around 2.4 nm. In contrast, peaks were not observed for the homogeneous precipitation CeO₂. This pH adjusted GDC specimen seems to be a high activation ceramics as a cermet anode material due to its surface area and the mesopore.

3.4. Electrochemical measurements

Fig. 6a depicts the voltage and power density versus current density curves of the Ni-ph adjusted GDC/YSZ/Pt cell at various temperatures ranged between 800 and 900 °C under 100% H₂ gas at 50 cc/min. The Ni-ph adjusted GDC/YSZ/Pt cell exhibited an open circuit voltage (OCV) of approximately 1.00 V depending on cell temperature. I-V curves for the pH adjusted GDC show a clear linear dependence of cell voltage on current density. The maximum power density of 0.295 W cm⁻² was observed at 900 °C on 0.700 mA cm⁻², which is clearly higher than that of the GDC by the solid state reaction. The pH adjusted GDC shows high cell performance as 15 times as that of the solid state reaction GDC. The high cell performance could be generated from good electrode microstructure because its particle size, crystalline size and mesopore could be fabricated long Triple Phase Boundary (TPB). The electrode reaction can proceed on the anode with the pH adjusted GDC more than that that with the solid state reaction GDC.

4. Conclusions

The nanosized crystallite GDC with mesopore was successfully synthesized by the pH adjusted precipitation.

The maximum power density for the pH adjusted GDC of 0.295 W cm⁻² was observed at 900 °C on 0.700 mA cm⁻², which is higher than that of the GDC by the solid state reaction due to the size and the mesopore.

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