High-Performance Ni Nanocomposite Anode Fabricated from Gd-doped Ceria Nanocubes for Low-Temperature Solid-Oxide Fuel Cells

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Abstract

Gadolinium-doped ceria (GDC) nanocubes with highly reactive {001} facets were synthesized as an anode material for solid-oxide fuel cells by organic-ligand-assisted hydrothermal treatment with a water-soluble amino acid, 6-amino hexanoic acid (AHA). An aerosol technique was applied to fabricate a NiO–GDC nanocube composite with water as a green solvent. The NiO–GDC nanocube composite was easily sintered even at a temperature of 1100 °C, while the conventional NiO–GDC composite covered with the most stable {111} facets was sintered at 1300 °C. Sintering at such a low temperature inhibited undesirable coarsening of NiO and GDC particles, resulting in an enlarged, triple-phase boundary (TPB). The NiO–GDC nanocube composite anode with the enlarged TPB exhibited a rather low area specific resistance of $0.14 \Omega \cdot \text{cm}^2$ compared with the conventional NiO–GDC composite anode's resistance of $0.58 \Omega \cdot \text{cm}^2$ when operated at 600 °C.

Keywords: Ceria; SOFCs; Hybrid materials; Nanocrystals; Aero-sol; Microstructures;

Introduction

Solid-oxide fuel cells (SOFCs) have received much attention as a promising next-generation electric power generation systems, because of the former's high generation efficiency with direct conversion of chemical energy into electricity. The latest critical issue regarding SOFCs is the reduction of the operation temperature from 800–1000 °C to 600 °C or lower. Low-temperature operation enables shorter startup time and suppression of the degradation of SOFC components. For operation at lower temperatures, many researchers have reported the development of new SOFC materials,^[1–4] fabrication of a thinned electrolyte film,^[5–8] and microstructural control of the anode and cathode.^[9–13] The sintering temperatures of anode materials such as Ni–GDC and Ni–YSZ cermet typically reach 1300 °C. Sintering at such a high temperature causes significant decrease in the triple-phase boundary (TPB) as a result of coarsening of the controlled size and microstructure of NiO and GDC. Therefore, simple ball milling is applied to fabrication of the anode structure, with grinding and mixing of commercial NiO and GDC powders in many cases.^[14–16] Nanotechnologies using solution processes, especially for control of the crystallographic planes, are thus not employed for the synthesis of anode materials.

Zhang et al. have reported supercritical hydrothermal synthesis of tailor-made ceramic nanocrystals with organic ligands selectively adsorbed on particular crystal planes.^[17–19] In their studies, CeO₂ nanocubes with highly reactive {001} crystal facets were synthesized by supercritical hydrothermal treatment with a carboxylic acid such as decanoic acid and hexanoic acid, and the {001} facets participated in extra-low-temperature oxygen storage capacity.^[19] In our study, we focused on the singular functional material as a novel anode component, which was expected to contribute to the lowering of the working temperature because of the enlarged TPB caused by low-temperature anode fabrication.

We examined the organic-ligand-assisted hydrothermal synthesis of Gd³⁺-doped CeO₂ (GDC) nanocubes with a water-soluble amino acid, 6–amino hexanoic acid (AHA), for the control of crystal facets and the development of hydrophilicity. The NiO–GDC nanocube composite was fabricated by an aerosol process for homogeneous hybridizing of the GDC nanocubes and NiO nanoparticles. Fabrication of high-performance anode or cathode composites, such as NiO–Sm-doped ceria (NiO–SDC) and NiO–Sr- and Mg-doped LaGaO₃ (NiO–LSGM), or Sr-doped LaCoO₃ (LSC) and Sr-doped LaMnO₃–Y-stabilized zirconia (LSM–YSZ), with homogeneous hybridization and ideal fine microstructures using an aerosol process has been

reported.^[20–22] It is also an appropriate procedure for homogeneous hybridizing of highly dispersible GDC nanocubes and NiO.

Experimental Section

Synthesis of GDC nanocubes and fabrication of NiO–GDC nanocube composite:

Ce_{0.9}Gd_{0.1}O_{1.95} (GDC) nanocubes were synthesized by organic-ligand-assisted hydrothermal treatment. Ce(NO₃)₃·6H₂O (2.7 mmol, Wako Pure Chemical), Gd(NO₃)₃·6H₂O (0.3 mmol, Kanto Chemical), and AHA (18 mmol, Tokyo Chemical Industry) were dissolved in distilled water (29.5 mL). In addition, *tert*-butylamine (0.5 mL) was quickly added to the mixed solution with vigorous stirring. After 5 min of stirring, the GDC nanocube sol precursor was placed in a Teflon-lined stainless steel autoclave (total volume was 50 mL), where it was then heated at 180 °C for 24 h for the growth of {001} facets with coordination of AHA. The GDC nanocube precipitate was isolated by centrifuging and then washed three times with distilled water.

Fabrication of NiO–GDC nanocube composite by aerosol process: Fabrication of the

NiO–GDC nanocube composite was carried out by a simple aerosol process.^[20–22]

The undried GDC nanocube specimen was dispersed in an aqueous solution of $\text{Ni}(\text{CH}_3\text{COO})_2$ (0.05 M, 300 mL; molar ratio Ni/GDC = 3.63:1), and the pH value was adjusted to 8 with aqueous NH_3 . After 10 min of sonication, the suspension was atomized with an ultrasonic vibrator that was operated at 1.7 MHz. The atomized water droplets were transported to the reaction furnace using air as a carrier gas at a fixed flow rate of 1 L min^{-1} . The three reaction furnace temperatures were set at 200, 400, and 600 °C, respectively. The sample powders from the furnace outlet were collected on a membrane filter. For comparison, a NiO–GDC composite was prepared by a conventional aerosol process from an aqueous solution of Ni, Ce, and Gd nitrates.

Cell fabrication and cell performance tests: A NiO–GDC nanocube composite powder prepared by the aerosol process was mixed with PEG #400 that served as a binder. The paste was deposited by screen printing onto dense GDC electrolyte pellets (thickness: 400 μm , AGC Seimi Chemical) prepared by sintering at 1500 °C for 4 h. The NiO–GDC nanocube composite anode was prepared by sintering at various heating temperatures. After that, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) powder was prepared by the aerosol process as the cathode was prepared on the flip side by

sintering at 900 °C for 2 h. The effective anode and cathode areas were both 0.282 cm² (6 mm in diameter). Pt wires were used as the reference electrode, and they were wound around the electrolyte pellets and fixed with Pt paste. Pt meshes were attached on top of each electrode to serve as the current collectors. The anode and cathode compartments were separated by a Pyrex glass ring gasket. The single-cell performance tests were carried out at 600 °C by supplying 3% moisturized hydrogen gas (H₂ + 3% H₂O) and air to the sides of the anode and cathode, respectively. The flow rates at both sides were adjusted to 50 cm³ min⁻¹. Current–voltage (*I*–*V*) measurements and electrochemical impedance spectroscopy (EIS) measurements were performed using an Electrochemie Autolab PGSTAT302N analyzer, with a frequency range of 0.01–10⁵ Hz and an amplitude of less than 30 mV. All measurements within this study were performed under open-circuit conditions.

Results and discussion

All samples for the current study were synthesized by organic-ligand-assisted hydrothermal treatment at 180 °C for 24 h with AHA. X-ray diffraction results confirmed that they had a fluorite structure irrespective of the amount of Gd-doping, and the diffraction peaks were also observed to shift to higher angles with increasing

Gd concentration (**Supporting information Figure S1**). The morphologies of the CeO₂ nanocube and GDC nanocube particles were characterized by transmission electron microscope (TEM) analysis. As shown in **Figure 1a**, the CeO₂ nanocubes exhibited a highly dispersed cubic shape with an average size of approximately 15 nm. High-resolution TEM (HR-TEM) observations of a 0.27-nm lattice fringe corresponding to the (002) facet (Figure 1b) indicated that the CeO₂ nanocubes were covered with {001} crystal facets. Furthermore, the inset's fast Fourier transform (FFT) image shows {002} diffractions, which also supported the results. Similarly, GDC nanocubes were also confirmed to have cubic morphology with {001} facets (Figure 1c and d). However, their average size was decreased to 10 nm with Gd doping. AHA coordination on the {001} crystal facets of CeO₂ nanocubes and GDC nanocubes was confirmed by Fourier-transform infrared (FT-IR) spectroscopy measurements (**Supporting information Figure S2**).

Figure 2 shows a comparison of the XRD patterns of the NiO–GDC nanocube composite and the conventional NiO–GDC composite prepared by an aerosol process. Each diffraction pattern contained characteristic diffraction peaks corresponding to NiO and CeO₂ (CaF₂ structure). Thus, it was confirmed that a secondary phase was not formed in the samples. The atomic ratios of the GDC nanocube and NiO–GDC

nanocube composite were determined by electron probe microanalysis and wavelength-dispersive X-ray analysis (EPMA-WDX). The analytical results were in good agreement with the initial ratios; the atomic ratios were Ce/Gd = 89.76:10.24 for the GDC nanocubes, which had an initial ratio of Ce/Gd = 90:10, and Ni/Ce/Gd = 78.39:19.40:2.21 for the NiO–GDC nanocube composite, which had initial ratios of Ni/Ce/Gd = 78.40:19.44:2.16. Therefore, the weight ratio of NiO/GDC was determined to be 61:39.

Figure 3a and **b** present the I – V and power–current (I – P) curves of the single cells (Ni–GDC/GDC/La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF)) at 600 °C with different sintering temperatures of the NiO–GDC nanocube composite and NiO–GDC composite. In Figure 3a, the maximum power density of the NiO–GDC nanocube composite anode cells obtained by sintering at 900, 1000, 1100, and 1200 °C were 25, 41, 97, and 59 mW·cm⁻², respectively. On the other hand, the maximum power density of the NiO–GDC composite anode cells obtained by sintering at 1100, 1200, 1300, and 1400 °C were 22, 26, 67, and 44 mW·cm⁻², respectively (Figure 3b). Many researchers have reported that the optimal sintering temperature for fabrication of an ideal anode structure is around 1300 °C. ^[1,3,5,6,8–16,21,22] It is important to note that

higher maximum power density was obtained with a lower sintering temperature using a cermet anode material with a reactive crystal surface.

Scanning electron microscope (SEM) images of the NiO–GDC composite prepared by the aerosol process and cross-sectional images of the anode after the power generation test with the composites are shown at **Figure 4**. The NiO–GDC nanocube composite had a spherical morphology that resembled the shape of water vapor droplets (Figure 4a), and the mean diameter was approximately 200–400 nm. After the power generation test, the spherical morphology disappeared, and the GDC nanocubes grew to grains with diameters of 100 nm after sintering at 1100 °C, which were finely deposited on the porous metal Ni framework (Figure 4b). Figure 4c presents the NiO–GDC composite morphology, which was confirmed to have the same shape and mean diameter as those of the NiO–GDC nanocube composite. In the NiO–GDC composite anode, a metal Ni framework was also formed; however, the GDC nanoparticles grew into grains with diameters of 400 nm after sintering at 1300 °C (Figure 4d). Thus, the significantly enlarged TPB was successfully realized by sintering of the NiO–GDC nanocube composite at a lower temperature.

Figure 5 shows the EIS results of the NiO–GDC nanocube composite anode and NiO–GDC composite anode, where the ohmic resistance was subtracted from the

total impedance. The area-specific resistances of the two anodes were estimated to be 0.14 and 0.58 $\Omega\cdot\text{cm}^2$, respectively, at a temperature of 600 °C. The lower value of 0.14 $\Omega\cdot\text{cm}^2$ can be clearly attributed to the fine microstructure of the NiO–GDC nanocube composite anode shown in Figure 4. In other words, the smaller GDC particle size and higher porosity of the metal Ni framework obtained by low-temperature sintering led to an enlarged TPB. As shown in Figure 4b, the GDC nanocubes obviously grew, which meant that the cubic morphology disappeared after sintering at 1100 °C, and the GDC nanoparticles contained in both anodes were covered with conventional {111} facets. Therefore, the significantly small ASR can be attributed to the anode's fine microstructure resulting from the difference in surface energy of GDC contained in a composite before sintering.^[23] As NiO has a very high melting point, the NiO diffusion and framework formed were achieved through sintering at temperatures as high as 1300 °C. For the NiO–GDC nanocube composite, the GDC nanocubes were sintered at a lower temperature owing to the high surface energy, which led to diffusion of NiO and fabrication of the framework. Therefore, we conclude that GDC nanocubes with reactive {001} facets are a suitable material for fabricating an ideal anode with fine microstructure via low-temperature sintering.

Conclusions

In summary, GDC nanocubes with highly reactive {001} facets were successfully synthesized by organic-ligand-assisted hydrothermal treatment with AHA. They showed amphipathicity driven by coordination of the carboxylate group in water-soluble amino acid with short methylene chains and hydrophilic amino groups. A NiO–GDC nanocube composite was prepared by an aerosol process with water as a green solvent, followed by sintering at a lower temperature than that for a conventional NiO–GDC composite. The nanocube composite was easily sintered even at 1100 °C, while the conventional NiO–GDC composite covered with the more stable {111} facets was sintered at 1300 °C. A single cell with a NiO–GDC nanocube composite anode showed a higher power density of $97 \text{ mW}\cdot\text{cm}^{-2}$ compared with the value of $67 \text{ mW}\cdot\text{cm}^{-2}$ for a cell with a conventional NiO–GDC composite anode operating at 600 °C. NiO diffusion and fabrication of the framework occurred even at 1100 °C sintering of the reactive GDC nanocubes. Sintering at such a low temperature inhibited undesirable growth of NiO and GDC particles and allowed fine, dispersive deposition of GDC nanoparticles on the porous metal Ni framework, which led to a significantly enlarged TPB. The anode's fine microstructure

drastically decreased the ASR to $0.14 \Omega \cdot \text{cm}^2$ at 600°C , compared with the conventional NiO–GDC composite anode's resistance of $0.58 \Omega \cdot \text{cm}^2$ at the same temperature. These results indicate that the GDC nanocubes with reactive {001} facets are suitable anode material for low-temperature SOFCs.

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Figure 1. TEM and HR-TEM images of a, b) CeO₂ nanocubes and c, d) GDC nanocubes prepared by organic-ligand-assisted hydrothermal treatment at 180 °C for 24 h; the insets show the FFT patterns.

Figure 2. XRD patterns of NiO–GDC composite samples prepared by an aerosol process from GDC nanocubes and a metal nitrate aqueous solution.

Figure 3. *I*–*V* and *I*–*P* curves of SOFC single cells fabricated using various sintering temperatures: a) NiO–GDC nanocube composite anode cell; b) NiO–GDC composite anode cell. Cell performance tests were carried out at 600 °C.

Figure 4. (Left) SEM images of NiO–GDC composites and (Right) cross-sectional images of the NiO–GDC anode after power generation test at 600 °C: a, b) NiO–GDC nanocube composite; c, d) NiO–GDC composite.

Figure 5. EIS spectra of NiO-GDC nanocube composite and NiO-GDC composite measured at 600 °C. Filled circles: NiO-GDC nanocube composite anode; open circles: NiO-GDC composite anode.

Graphical abstract