

Sonochemical synthesis of highly sinterable/nanocrystalline CeO₂-based electrolyte powders for intermediate-temperature solid oxide fuel cells

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Sonochemical processing was used to synthesize highly sinterable nanocrystalline cerium oxide-based materials (i.e., Gd₂O₃-doped and Sm₂O₃-doped CeO₂ electrolytes). The crystallinity and grain size was investigated using X-ray diffraction and transmission electron microscopy, confirming that the nanocrystals were approximately 5 nm to 7 nm in size. The feature of nanocrystalline particles resulted in a 200 °C lower sintering temperature than the conventional 1,550 °C sintering temperature used for commercial microcrystalline CeO₂-based materials. This significant improvement in sintering temperature was confirmed by microstructural and sintering characterization.

Key words: Sonochemical processing, Nanocrystalline electrolytes, Solid oxide fuel cells, Cerium oxide.

Introduction

Solid oxide fuel cells (SOFCs) have been receiving extensive academic and industrial attention due to their unique environment-friendly features, such as highly efficient clean energy sources with less pollution and compatibility with recyclable fuels and auxiliary subsystems [1, 2]. Most of the current SOFC research focuses on ZrO₂-based electrolytes operating at high temperatures of 800 °C to 1000 °C [3]. However, high-temperature operation places undesired limitations on the selection of materials for cathodes, electrolytes, anodes, and interconnects as well as gas-impermeable sealing materials. In particular, the interconnect materials are extremely costly and difficult to machine. In order to overcome limitations imposed by high-temperature operation, a new electrolyte is necessary for use below 800 °C, more specifically for operation from 600 °C to 650 °C. To this end, CeO₂-based electrolytes have been proposed as promising candidates since they have the highest conductivity among the fluorite-based electrolytes [4]. However, CeO₂-based electrolytes are difficult to sinter and are unstable under a reducing atmosphere, although they do satisfy the high conductivity in oxygen ions prerequisite of intermediate-temperature solid oxide fuel cells [5, 6].

The sintering characteristics can be enhanced by

incorporating appropriate additives and/or particle sizes, including nanocrystalline powders, which can be formed through a variety of fabrication routes [7-9]. Although solid state reactions can be used to synthesize the desired materials, the resulting powder is limited by low sinterability due to the inherent micrometer-scale features of the particles. Therefore, chemically-driven procedures are preferred in terms of purity, homogeneity, and particle size. Specifically, high-frequency sonication in combination with dispersing agents stabilized in a nitrate-based chemical solution is expected to yield high dispersion between particles and nano-scale features in the particle-forming stage. Yin et al. synthesized cerium oxide via a sonochemical approach, but the materials were limited to cerium oxide only and no attempt was made to prepare electrolytes containing dopants [10].

A novel approach for synthesizing nanocrystalline CeO₂-based materials with improved sinterability for use in intermediate-temperature solid oxide fuel cells is proposed in this paper. Nanocrystalline CeO₂ powders were synthesized using co-precipitation assisted by high-frequency sonication in order to obtain a high homogeneity and small grain sizes in Gd₂O₃-doped CeO₂ (GDC) and Sm₂O₃-doped CeO₂ (SDC). The crystallinity, grain size, microstructure, and composition of the synthesized materials were investigated using X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and energy-dispersive X-ray spectrometry, respectively. The implications of these synthesized materials in the context of intermediate-temperature solid oxide fuel cells are also discussed.

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Experimental Procedure

Nanocrystalline GDC and SDC powders were prepared using $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich, 99.99%), $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich, 99.99%), and $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich, 99.99%) as starting materials. Predetermined mole fractions of these starting materials were obtained, as shown in Fig. 1, and subsequently dissolved in distilled water along with PEG 400 (poly-ethylene glycol, average $M_w = 400$ g). The CeO_2 -based nanoparticles were synthesized through co-precipitation with NaOH (0.02 g/ml), which was added drop-wise up to pH 10 at a temperature of 70 to 80 °C, and high-frequency sonication. The final solution was purified/filtered using non-hydrous ethanol and centrifugation to eliminate the undesired impurities, followed by drying at 80 °C for 12 h then at 120 °C for 2 h. The dried powders (GDC and SDC) were milled using a mortar and pestle to eliminate any particle agglomeration. The final powders were pressed into disk-shaped specimens with diameters of 9 mm and thicknesses of approximately 1 mm using a unidirectional dry press. Specimens were then cold-isostatically pressed at 235 MPa for 2 minutes. The pressed specimens were heated at a rate of 3 °C/minute up to 400 °C, where they were held for 1 hr, and finally up to 1350 °C, where they were held for 6 h. After the high-temperature sintering, the specimens were furnace-cooled slowly to ambient temperature.

The crystallinity and grain size of the synthesized powders were characterized using X-ray diffraction (MAX Ultima III, Rigaku, Japan) and transmission electron microscopy (Techni, FEI Co., USA). Scanning electron microscopy (JSM-6700F, JEOL, Japan) was employed to observe the microstructure and degree of

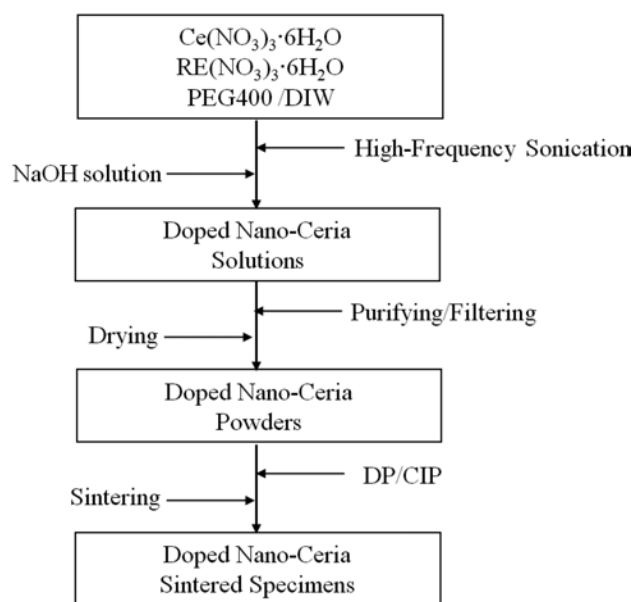


Fig. 1. Schematic of the processing steps employed in the synthesis of CeO_2 -based materials. (RE: Rare Earth, DIW: Deionized Water, DP: Dry Pressing, CIP: Cold Isostatic Pressing)

densification in the sintered specimens. The sintering behavior was confirmed using a high-resolution dilatometer (Netsch Dil 402C/3/G, Germany).

Results and Discussion

Fig. 2 compares the powder X-ray diffraction information for microcrystalline (commercial) CeO_2 and the nanocrystalline CeO_2 powders synthesized in this work. A comparison of the primary peaks indicates that both materials have a fluorite structure. As expected given the nanocrystallinity of the synthesized powder, the full-width-at-half-maximum of the diffraction peaks widened with decreasing grain size. Fig. 3 shows the diffraction patterns of nanocrystalline CeO_2 , Gd_2O_3 -doped CeO_2 and Sm_2O_3 -doped CeO_2 . Comparison of these XRD data (Fig. 4) suggests that the additive Gd_2O_3 and Sm_2O_3 materials will form corresponding solid solutions that are ionically-conducting. The high-resolution transmission electron microscopy images revealed that the size of the GDC particles ranged from 5 nm to 7 nm, without significant agglomeration (Fig. 5). The chemical compositions of the synthesized CeO_2 -based materials were analyzed using energy-

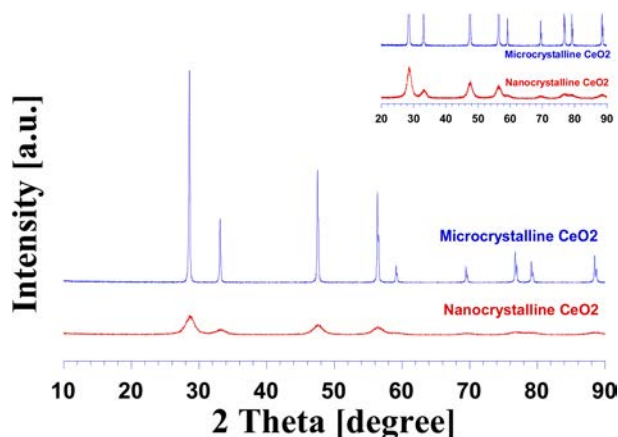


Fig. 2. X-ray diffraction data for microcrystalline and nanocrystalline CeO_2 materials.

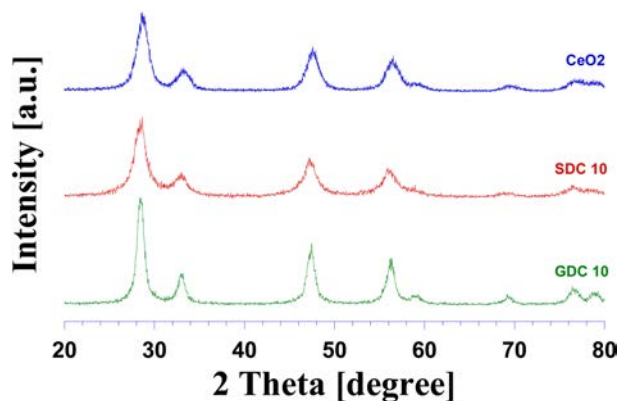


Fig. 3. X-ray diffraction information of sonochemically-synthesized CeO_2 materials (CeO_2 , Gd_2O_3 -doped CeO_2 and Sm_2O_3 -doped CeO_2).

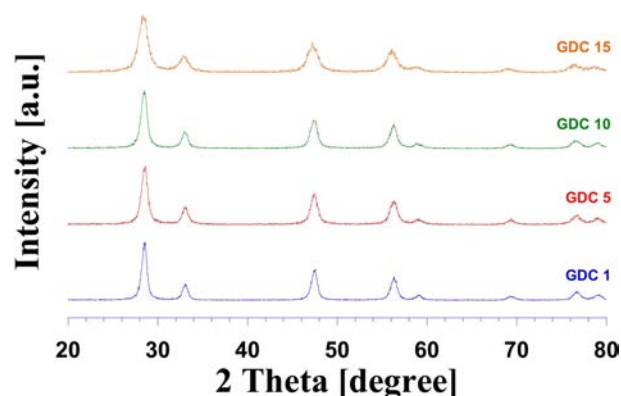


Fig. 4. X-ray diffraction information of sonochemically-synthesized Gd_2O_3 -doped CeO_2 as a function of Gd_2O_3 content (1, 5, 10, and 15 mole % Gd_2O_3).

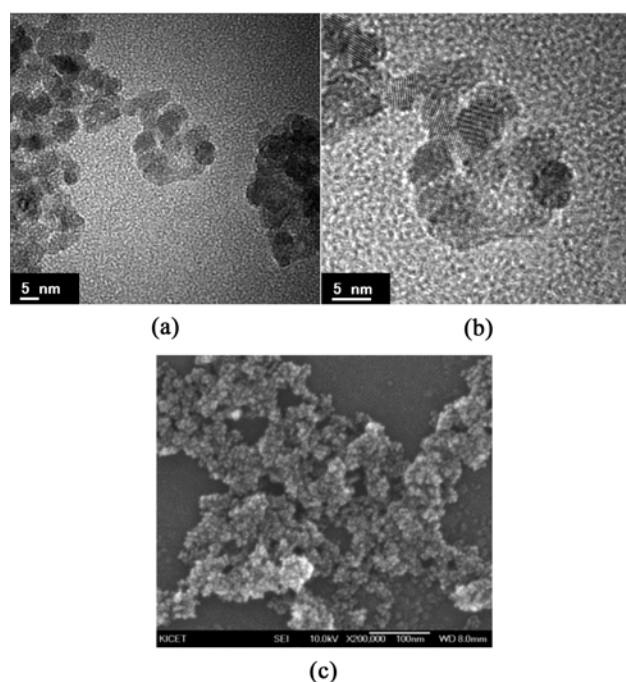


Fig. 5. Transmission electron microscopy images of nanocrystalline GDC particles: (a) Low magnification TEM image, (b) high-magnification TEM image and (c) SEM image.

dispersive X-ray spectrometry (EDX). As demonstrated in Table 1, the calculated compositions were in reasonable agreement with the compositions calculated initially for 10 mole % solid solutions in terms of the corresponding additives, Gd_2O_3 and Sm_2O_3 .

After sintering, the density of the nanocrystalline CeO_2 -based materials increased and no significant pores were evident (Fig. 6). The specimens containing 1 mole % dopant had a higher porosity than the electrolytes containing greater amounts of dopant, and a narrower FWHM than that shown in Figs. 2 and 3 (data not shown). The X-ray diffraction analysis indicated that the resultant materials are of the fluorite structure and the crystal sizes are in the micrometer-scale range. The dilatometry analysis confirmed the accelerated sintering properties of the doped materials

Table 1. Composition analysis of the GDC and SDC nanopowders synthesized through ultrasonication-assisted coprecipitation estimated using energy-dispersive X-ray analysis.

((a) GDC for 10 mole % Gd_2O_3 and (b) SDC for 10 mole % Sm_2O_3)

(a)		
GDC Powder for 10 mole % Gd ₂ O ₃		
Element	wt%	at%
O K	24.79	74.53
Ce L	65.97	22.64
Gd L	9.24	2.83
Calculated Atomic Ratio	88.89% / 11.11%	

(b)		
SDC Powder for 10 mole % Sm ₂ O ₃		
Element	wt%	at%
O K	23.13	72.69
Ce L	65.98	24.06
Sm L	10.89	3.25
Calculated Atomic Ratio	88.10% / 11.90%	

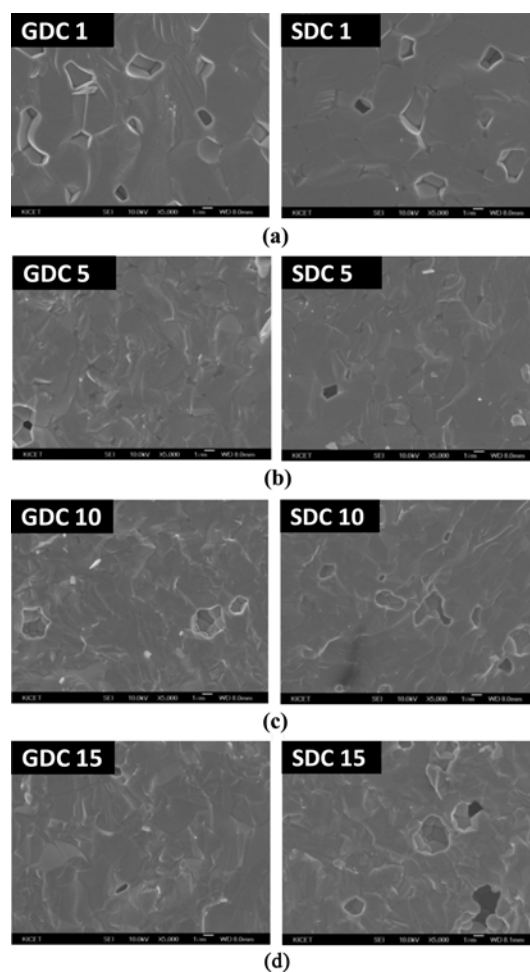


Fig. 6. Microstructure of the sintered GDC and SDC specimens (after sintering at 1350 °C for 6 hrs) as a function of doping concentration. (a) 1 mole% Gd_2O_3 (left) and 1 mole % Sm_2O_3 (right); (b) 5 mole % Gd_2O_3 (left) and 5 mole % Sm_2O_3 (right); (c) 10 mole % Gd_2O_3 (left) and 10 mole % Sm_2O_3 (right); and (d) 15 mole % Gd_2O_3 (left) and 15 mole % Sm_2O_3 (right).

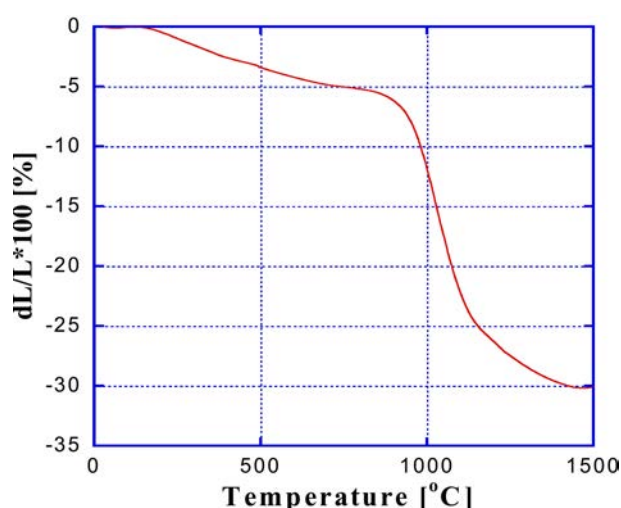


Fig. 7. Dilatometry information for the Gd_2O_3 -doped CeO_2 materials.

at a lower temperature than the conventional temperature of 1550°C (Fig. 7). The highest shrinkage rate occurred at approximately 1025°C , and most of the densification occurred below 1350°C , which was the sintering temperature used in this study. This densification after sintering at 1350°C was consistent with the microstructure observed using scanning electron microscopy (Fig. 6.). Typically, conventional microcrystalline GDC powders are sintered at 1500°C to 1550°C , a much higher temperature than that employed for nanocrystalline CeO_2 -based powders. The highest densification was observed in the 15 mole % Gd_2O_3 - CeO_2 specimen and the 10 mole % Sm_2O_3 - CeO_2 specimen. Furthermore, an intergranular fracture was observed on the electron micrographs, implying superior sinterability between the electrolyte grains.

Although Yin et al. reported the synthesis of nanocrystalline CeO_2 particles, there are no reports of the ultimate sintering behavior of these particles available in the literature [10]. The results of the current study are evidence of the superior sintering features of doped CeO_2 materials and are consistent with the results of the glycine-nitrate method reported by Xia and Liu [11]. The improved sintering features of nanocrystalline CeO_2 -based electrolyte powders can be used to impart the structural modifications required for fabrication of intermediate-temperature solid oxide fuel cells with CeO_2 -based and ZrO_2 -based electrolytes.

Furthermore, a two-phase mixture (e.g., an anode composite) of CeO_2 -based electrolyte and a binary oxide can be fabricated using the proposed approach.

Conclusions

Nanocrystalline CeO_2 -based electrolytes were synthesized using co-precipitation combined with high-frequency sonication. The synthesized GDC and SDC powders were comprised of highly homogenized, equiaxed nanocrystals with grain sizes of 5 nm to 7 nm. EDX analysis revealed that the actual composition of the synthesized powders was consistent with the initially calculated composition. Furthermore, the synthesized powders were highly densified at 1350°C , which is much lower than the temperature required for densification of microcrystalline CeO_2 -based electrolytes. The highest densities were found in the 15 mole % Gd_2O_3 - CeO_2 system and the 10 mole % Sm_2O_3 - CeO_2 system. The improved sinterability of these electrolytes can be exploited to create the structural modifications required in the basic unit cells of intermediate-temperature solid oxide fuel cells.

Acknowledgement

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