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Synthesis of nickel coated gadolinia doped ceria nanopowders by microwave radiation

Jongmin Lim and Sang Woo Kim*

Center for Energy-Materials Research Center, Korea Institute of Science and Technology, Haweoulgog-dong, Sungbuk-gu, Seoul 136-791, Korea

Nickel coated gadolinium doped ceria (GDC) powders were synthesized by microwave radiation and combustion. For the synthesis, precipitates of gadolinium cerium oxycarbonate hydrate ($Gd_xCe_{2-x}O(CO_3)_2 \cdot H_2O$) were formed by a microwave-radiated reaction between cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$), gadolinium nitrate ($Gd(NO_3)_3 \cdot 6H_2O$) and urea ($CO(NH_2)_2$), then nickel coatings on the gadolinium cerium oxycarbonate hydrate were performed by a further microwave reaction between nickel chloride and urea. The shape and size of the gadolinium cerium oxycarbonate hydrate particles were critically dependent on aging time during the microwave radiation. Irregular particles were transformed to rod-shape particles which were well-crystallized by increasing the aging time to 40 minutes at 70-80 °C because of the gradual decomposition of urea during the microwave radiation. Small nickel precursor particles were homogeneously coated on the gadolinium cerium oxycarbonate hydrate particles with a rod shape with aid of microwave radiation at 80 °C for 40 minutes. As a result, nickel coated GDC nanopowders were successfully produced by the microwave radiation synthesis and further microwave combustion at 450 °C for 20 minutes.

Key words: GDC, CGO, Microwave, Nickel coating, Urea, Nickel chloride, Cerium nitrate, Gadolinium nitrate.

Introduction

Low-temperature (below 650 °C) solid oxide fuel cells (SOFCs) have recently attracted much attention because the cost of materials and fabrication will be dramatically reduced. With high ionic conductivity between 500 and 700 °C, ceria-based materials have been extensively studied as electrolytes for reduced-temperature SOFCs [1-4]. Gadolinia doped ceria (GDC) shows a higher ionic conductivity below 650 °C as compared to the presently-used yttria-stabilized zirconia (YSZ) which has sufficient ionic conductivity only around 1000 °C. Further, ceria-based materials are also being considered to be used as fuel electrodes for SOFCs [5]. Ceria has been used as the ceramic part in Ni- or Ru- cermet anodes [6-9]. Various synthesis and processing methods have been used to prepare doped ceria-based materials, including hydrothermal synthesis [10], homogeneous precipitation, a sol-gel process, and a glycine-nitrate process. Wet chemical synthesis using microwave radiation offers significant advantages over those conventional methods. Previous researches have revealed several advantages from the microwave-assisted wet chemical synthesis in reaction acceleration, yield improvement, enhanced physicochemical properties and the evolvement of new material phases [11-12]. Although there are many advantages, much efforts are still needed to reveal a more comprehensive understanding of the effects of microwaves on the processing operations and resultant materials.

In this study, we report our results on the synthesis of Ni coated GDC nanopowder using urea and metal salts by microwave radiation and combustion. We also describe the structure and morphological change of Ni coated GDC precursor powders, which are prepared from the microwave-radiated reaction in aqueous solution under atmosphere.

Experimental

Gadolinium cerium oxycarbonate hydrate ($Gd_xCe_{2-x}O(CO_3)_2 \cdot H_2O$) was prepared by a co-precipitation method. Urea was dissolved into 250 ml of deionized water to form a solution of 1 mol dm^{-3}. Cerium nitrate hydrate ($Ce(NO_3)_3 \cdot 6H_2O$) and gadolinium nitrate hydrate ($Gd(NO_3)_3 \cdot 6H_2O$) were dissolved into 250 ml of deionized water to form a solution of 0.02 mol $dm^{-3}$and 0.01 mol dm^{-3}, respectively. The molar ratios of Ce/Gd/urea were 2:1:100 in a mixed solution of 500 ml. These two solutions were mixed and then heated to various temperatures by microwave radiation. For the preparation of Ni coated GDC powder, Ni was coated on the precipitates of the gadolinium cerium oxycarbonate hydrate by microwave radiation at temperature ranges from 70 to 100 °C for 20 minutes. Nickel chloride ($NiCl_2 \cdot 6\ H_2O$) was dissolved into 250 ml of deionized water containing the precipitates to form a solution of 0.02 mol dm^{-3}. Urea was dissolved into 250 ml of deionized water to form a solution of

*Corresponding author:
Tel : +82-2-958-5526
Fax: +82-2-958-5529
E-mail: swkim@kist.re.kr

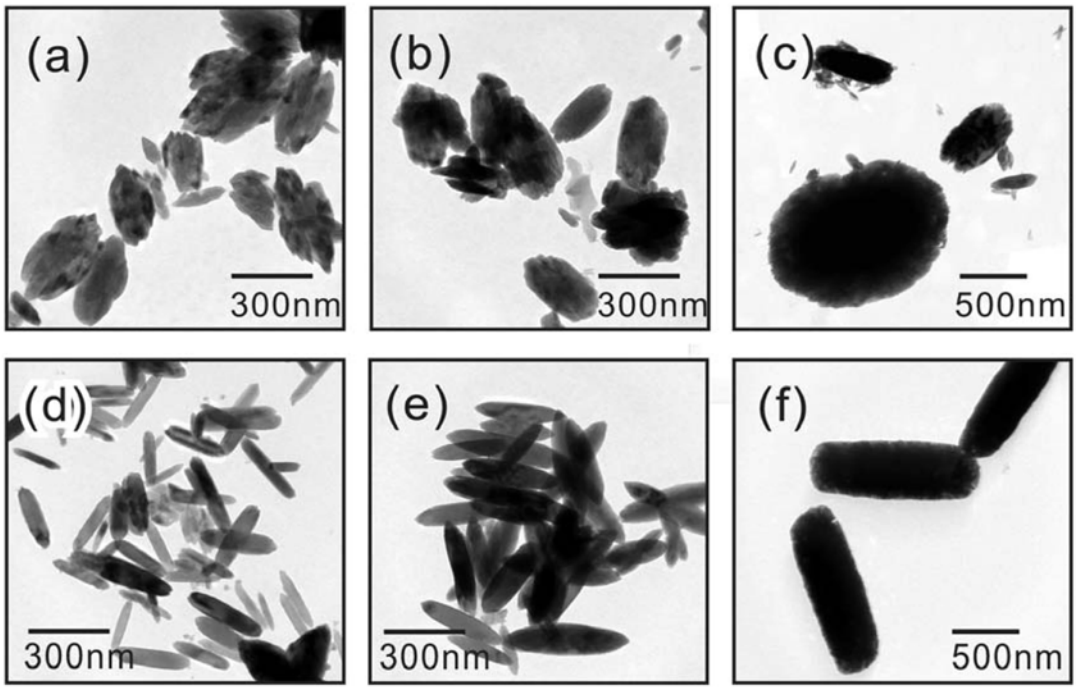

Fig. 1. TEM images of the gadolinium cerium oxycarbonate hydrate particles prepared by microwave radiation: (a,b,c) for 20 minutes; (d,e,f) for 40 minutes; (a,d) at 70 °C; (b,c) at 80 °C; (c, f) at 90 °C.

1 mol dm^{-3}. The two solutions were mixed and then heated to various temperatures by microwave radiation. The heating rate of solution was about 5 $K \cdot minute^{-1}$ and the synthesis temperature was held for 20 minutes. The precipitates were washed with deionized water three times and dried at 60 °C After being oven-dried, the precipitates were calcined in a microwave furnace for 20 minutes at 450 °C in a mixed atmosphere of hydrogen and nitrogen with flow rates of 200, 1000 sccm, respectively. The structures of the solids were determined by X-ray diffraction with CuKα Radiation. The chemical compositions were determined by energy-dispersive X-ray spectroscopy (EDX). The particle shape and size were elucidated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Differential scanning calorimetry(DSC) measurements were performed for thermal analysis.

Results and Discussion

TEM images of the gadolinium cerium oxycarbonate hydrate particles prepared by microwave radiation at different temperatures and times are shown in Fig. 1. Particles with an irregular shape were synthesized at 70 and 80 °C, and grew to large spherical particles by increasing the temperature to 90 °C. With increasing aging time, the irregular particles were transformed to rod-shape particles which were well-crystallized. The figure reveals that the gadolinium cerium oxycarbonate hydrate was gradually synthesized with the decomposition of urea to CO_3^{2-} ions in the solution. A SEM image and EDX result of the nickel oxycarbonate hydrate coated on the gadolinium cerium oxycarbonate hydrate particles prepared

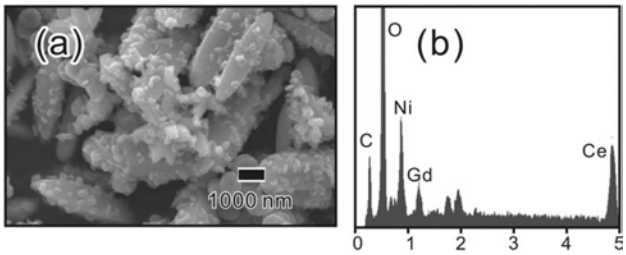

Fig. 2. A SEM image (a) and EDX result (b) of the nickel oxycarbonate hydrate coated on the gadolinium cerium oxycarbonate hydrate particles prepared by microwave radiation at 80 °C for 40 minutes.

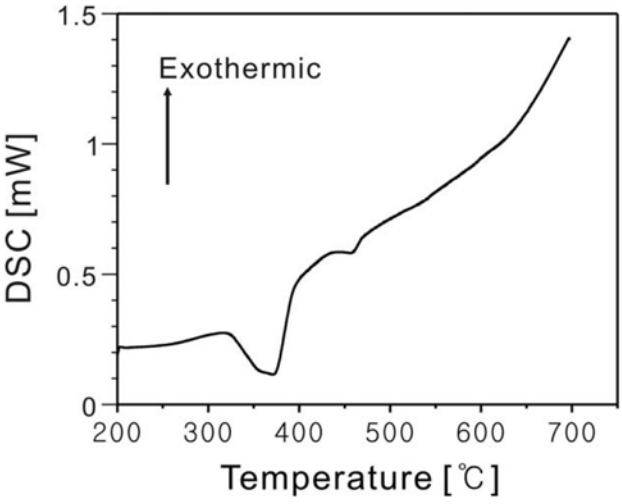

Fig. 3. DSC curve for the nickel oxycarbonate hydrate coated on the gadolinium cerium oxycarbonate hydrate particles prepared by microwave radiation at 80 °C for 40 minutes.

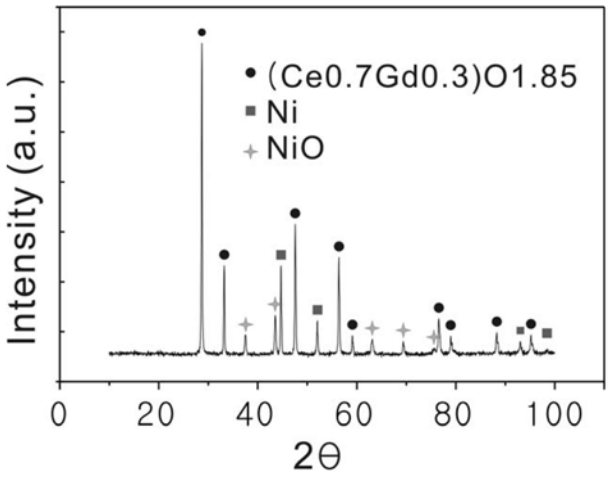

Fig. 4. X-ray diffraction pattern of the Ni coated GDC particles calcined at 450 °C for 20 minutes in a mixed atmosphere of H_2 and N_2.

by microwave radiated at 80 °C for 40 minutes are shown in Fig. 2 (a) and (b). Small nickel precursor particles were homogeneously coated on the gadolinium cerium oxycarbonate hydrate particles with a rod shape. The coated nickel content was confirmed to be 10.5 wt% from the EDX analysis. DSC peaks appeared at 373 and 458 °C, and were assigned to an endothermal reaction due to the decomposition of the oxycarbonate hydrate particles and organic residue, as shown in Fig. 3. The exothermal peaks due to the crystallization of GDC and Ni were not observed because of overapping of temperature of the reactions. The Ni coated GDC powders were produced after the nickel oxycarbonate hydrate coated on the gadolinium cerium oxycarbonate hydrate particles were microwave heated at 450 °C for 20 minutes in a mixed atmosphere of hydrogen and nitrogen. As shown in Fig. 4, the XRD peaks of the macrowave heated powder were identified to be $(Ce_{0.7}Gd_{0.3})O_{1.85}$, Ni, and NiO.

Consequently, the nickel coated GDC nanopowder has been shown to be produced by microwave radiation synthesis and combustion.

Conclusions

The shape and size of the gadolinium cerium oxycarbonate hydrate particles were critically dependent on aging time during microwave radiation. The irregular particles were transformed to rod shape particles which were well-crystallized by increasing the aging time to 40 minutes at 70-80 °C because of the gradual decomposition of urea during microwave radiation. Small nickel precursor particles were homogeneously coated on the gadolinium cerium oxycarbonate hydrate particles with a rod shape with the aid of microwave radiation at 80 °C for 40 minutes. As a result, nickel coated GDC nanopowders were sucessfully produced by the microwave radiation synthesis and further microwave combustion at 450 °C for 20 minutes.

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