FABRICATION OF NiO-SDC AND CuO-GDC CERMET MATERIALS FOR SOFC ANODE BY CITRATE METHOD

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ABSTRACT

New NiO-SDC cermet powders consisting of NiO and fluorite SDC mixture with homogeneous nano-composite structure have been studied. The citrate process has been used to produce the cermet powder by co-precipitation from a mixture of Ni$_2$CO$_3$, Ce$_2$(CO$_3$)$_3$ and Sni$_2$(CO$_3$)$_3$ aqueous solutions. The precipitates are fired at 1000°C for 10 h. The resulting powder is a mixture of NiO and fluorite SDC phase as confirmed by X-Ray Diffraction (XRD) analysis. The microstructures of cermet powders have been evaluated by SEM and EDX, and the crystallite sizes calculated from the XRD line broadening. A powder having homogeneous elements distributions in the whole sample, with crystallite size of 76 nm for NiO and 48 nm for SDC is obtained. The citrate process is also applied to CuO-GDC cermet powders synthesis. The CuO-GDC powder fired at 1000°C, resulted in significant grain growth of CuO up to 10 μm. Decreasing the firing temperature to 800°C, we successively obtained CuO-GDC cermet material with nano-ordered homogeneous distributions of CuO and GDC in the whole sample which had crystallite sizes of 53 nm for CuO and 46 nm for GDC.

INTRODUCTION

Solid oxide fuel cells (SOFCs) have attracted a growing interest for their high energy conversion efficiency, wide flexibility of the fuel (hydrogen, hydrocarbons), negligible production of pollutants (NOx, carbon particulates), good durability, and lower manufacturing cost than PEFCs (1). Ceria based cermet materials are state-of-the-art materials for SOFC anode, and consist of nickel and electrolyte material such as stabilized zirconia and doped ceria. The oxidation reactions of fuel species take place at the metal - electrolyte - fuel gas interface, the so called three phase boundary (TPB). Electrolyte particles in anode supply the oxygen ionic path and also hinder the coarsening of Ni particles under SOFC operation to avoid degradation of electrochemical properties (2). Optimization of the anode microstructure by decreasing particle size of NiO would increase the length of Ni-SDC-gas triple phase boundaries, and thus improve the anodic performance. The anode microstructure strongly affects the anode electrochemistry.

The conventional anode cermets are usually prepared by mechanical mixing of NiO and SDC powders prepared separately. The particle sizes, distributions and homogeneity of the cermet are strongly affected by the powder milling process. There is, however, a limit to downsizing the particle size by physical milling process; and it is desired to use a new...
process that can produce a mixture of NiO and SDC fine particles without aggregation.

Generally, a liquid phase process such as sol-gel method or Pechini method has been used to produce composite oxide materials with high chemical homogeneity and small particle size under 1 μm (3, 4). Most of these processes use metal nitrates as starting material; however, nitrogen oxides (NOx) are generated during the powder synthesis process. NOx is a pollutant and also introduces risk of explosion in the fabrication process. A solution to these problems will have a positive impact on environment, as well as enable mass production of SOFCs.

Recently, we have developed a new process to fabricate fine and homogeneous powder of Sm doped ceria material (SDC), with our original citrate method by using carbonates and hydroxides as starting materials instead of nitrates. This citrate process is quite attractive being clean and not generating any pollutant gas, and allows low cost synthesis from the industrial viewpoint. This SDC powder can lower the sintering temperature to 1200°C, which is otherwise usually about 1600°C, because of its homogeneous and fine powder characteristics.

One of the merits of a SOFC is the applicability of hydrocarbons as fuel. Recently, Park et al. showed that CuO-ceria cermet anode has a promising tolerance for using hydrocarbon fuel directly, and can suppress carbon precipitation (5, 6). However, problem arises in the preparation of CuO-ceria anode because CuO has relatively low melting point, 1026°C compared to 1960°C for NiO, which is lower than the ceria phase formation temperature. They impregnated aqueous Cu(NO3)2 to YSZ anode substrate to overcome this melting problem.

In this paper, we investigate the applicability of the citrate method to the production of the NiO-SDC cermet materials. Also, we applied this process to CuO-Gd doped ceria (GDC) cermet material, which is the new anode material for direct-hydrocarbon-fuel SOFCs. In order to analyze the homogeneity of the cermet materials, XRD and analytical electron microscopy were used.

**EXPERIMENTAL**

**Sample Preparation**

A series of NiO-SDC (60 wt% NiO + 40 wt% Sm0.2Ce0.8Ox) and CuO-GDC (70 wt% + 30 wt% Gd0.2Ce0.8Ox) was prepared by the citrate method. NiCO3, Ce2(CO3)3, Sm2(CO3)3, CuCO3 and Gd2(CO3)3 were used as starting materials. Concentration of the aqueous solutions was confirmed by chelatometric titration. These starting materials were mixed and citric acid was added to the solution in 3 equivalent molar proportion to the amount of metal cations present. Also 6 equivalent molar of ammonium bicarbonate was added to the solution to accelerate dissolution of ceria carboxide. The powders were then fired at 800°C or 1000°C for 6 hours to remove any remaining organic materials.

For comparison, NiO-SDC cermet powder was also prepared by mechanical mixing of NiO and SDC prepared separately. The NiO powder was prepared by thermal decomposition of Ni(OH)2 at 1000°C for 10 hours in air. The Sm0.2Ce0.8Ox powder was...
prepared by the same citrate method described previously without adding NiCO₃. After firing at 1000°C for 6 h, these powders were milled and mixed using zirconia balls adjusting the particle diameter to about 1 μm.

Characterization

Sample powders were analyzed by powder X-ray diffraction (XRD) technique (RINT 2100, Rigaku Co., Ltd., Japan, CuKα). The microstructures of the samples were investigated using scanning electron microscope (SEM, S-4700, Hitachi Co., Ltd., Japan). The element distributions were observed using energy dispersive spectrometry (EDX, EMAX-7000, Horiba Co., Ltd., Japan). Surface-area measurements of the powder samples were carried out by an isothermal nitrogen adsorption/desorption method (GEMINI 2375, Shimadzu Co., Ltd., Japan). The particle size distributions were evaluated by particle size analyzer (LA-920, Horiba Co., Ltd., Japan).

RESULTS AND DISCUSSION

NiO-SDC

Figure 1 shows the XRD patterns of NiO-SDC cermet (a) prepared by the citrate method and (b) prepared by mechanical mixing of NiO and SDC. All peaks for both samples are confirmed as a mixture of NiO and fluorite ceria phase. No other peaks for the inter-binary phases of these metal oxides are detected. The cermet powder composed of NiO and SDC phase is successively obtained by co-precipitation from the citrates using carbonates as raw materials. This result agrees well with those reported by Fang et al. (3) and Yin et al. (4) who applied co-precipitation Pechini method to NiO-SDC cermet materials. The surface areas were evaluated as 4.4 m²/g for the citrate co-precipitation sample and 2.9 m²/g for the mechanical mixing sample by BET measurement. The mean particle size, D₅₀ for the citrate and mechanical mixing samples were 0.97 μm and 1.45 μm, respectively. The specific surface area for the homogeneous sample was larger than that for mechanical mixing.

SEM micrographs with EDX analyses are shown in Fig. 2. From the SEM micrographs, both NiO-SDC powders consisted of very fine primary particles under 0.1 μm, with secondary agglomerated particles. As can be seen from EDX results, the sample prepared by mechanical mixing of NiO and SDC that was fired separately is made up of agglomerations of original fired particles of about 1 μm size. On the other hand, the citrate co-precipitation powder has homogeneous distributions of Ce, Sm, Ni elements and there is no aggregation and extra grain growth of the component particles.

Next, we calculated the crystallite sizes of the samples from the XRD results. The broadening of the X-ray diffraction peak was used to calculate crystallite size in the <101> direction for NiO and <111> direction for SDC using the Debye-Scherrer equation. The crystallite sizes are calculated as 48 nm for SDC and 76 nm for NiO in the citrate sample, whereas 41 nm for SDC and over 100 nm for NiO in mechanical mixing sample. The crystallite sizes of SDC are almost equal for both samples; however the NiO size for mechanical mixing sample is larger than that of the citrate sample. The suppression of NiO grain growth may be caused by the homogeneous distribution of NiO and SDC.
elements dissolved from the precursor during the process. Furthermore, it may be stated that homogeneous cermet powder made by the citrate co-precipitation method is suitable to avoid grain growth and aggregation of NiO, that reduce cell operating performance.

![XRD patterns of NiO-SDC powders fired at 1000°C prepared by (a) citrate co-precipitation method and (b) mechanical mixture of NiO and SDC powders by ball milling.](image)

Figure 1. XRD patterns of NiO-SDC powders fired at 1000°C prepared by (a) citrate co-precipitation method and (b) mechanical mixture of NiO and SDC powders by ball milling.

![SEM and EDX images of NiO-SDC powders fired at 1000°C prepared by (a) citrate co-precipitation method and (b) mechanical mixture of NiO and SDC powders by ball milling.](image)

Figure 2. SEM and EDX images of NiO-SDC powders fired at 1000°C prepared by (a) citrate co-precipitation method and (b) mechanical mixture of NiO and SDC powders by ball milling.
CuO has a low melting point of 1026°C. Also the formation of Gd<sub>2</sub>CuO<sub>4</sub> phase at 980°C is reported by R. Horyn et al. (7) To investigate the firing temperature of CuO-GDC, we prepared one powder at 1000°C and the other at 800°C to prevent the CuO reaction.

The X-ray diffraction patterns for CuO-GDC fired at (a) 1000°C and (b) 800°C are shown in Fig. 3. The data indicate that both of the fired powders are mixtures of CuO and GDC phases. The SEM images and EPMA mapping images of CuO-GDC fired at (a) 1000°C and (b) 800°C are provided in Fig. 4. In the SEM image of Fig. 4(b), two kinds of particles can be observed for the 1000°C fired powder, very fine particles (~0.1 μm) covering the smooth surface of large particles. From the EDX results, the large particle is attributed to the Cu rich phase, mainly CuO, and fine particles to the GDC phase. It is considered to be a result of CuO grain growth and/or partial melting of CuO. The crystallite sizes, calculated from the Debye Scherrer equation, using <11-1> direction for CuO and <111> direction for SDC of XRD line broadening, also show that both CuO and GDC particles became too large over the Scherrer equation application limit (>100 nm). On the other hand, the microstructure of the sample fired at 800°C shows very uniform and fine particle agglomeration without observable large grain formation. The crystallite sizes for the CuO and GDC are 53 nm and 46 nm, respectively. It is thought that the CuO crystal growth is fairly suppressed by the homogeneous mixture of CuO and ceria particles obtained during the co-precipitation method. The surface area is evaluated as 5.8 m<sup>2</sup>/g and D<sub>50</sub> is 1.36 μm for the powder fired at 800°C.
NiO-SDC cermet powders that consist of a mixture of NiO phase and SDC-fluorite phase are obtained by the citrate method using carbonates as starting materials. The NiO and SDC particles, which have crystallite sizes of 76 nm and 48 nm, respectively, are homogeneously dispersed in the sample. By lowering the firing temperature down to 800°C, it is confirmed that the citrate method is also applicable to CuO-GDC cermet fabrication, which is a promising anode material for direct hydrocarbon SOFCs.

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