Effects of Gallia Addition on Sintering Behavior and Electrical Conductivity of Yttria-Doped Ceria

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The densification behavior and electrical conductivity of Ce0.8Y0.2O2.9 ceramics with gallia concentrations ranging from 0 to 5 mol. % were investigated. The sintered density was found to increase with increasing Ga2O3 content up to 1 mol. % and then to decrease upon further Ga2O3 addition. Dense Ce0.8Y0.2O2.9 ceramics with 94% of the theoretical density could be obtained by sintering the milled mixture with 1 mol. % Ga2O3 addition at 1400°C for 5 h. The conductivity of the 1 mol. % Ga2O3-added specimen showed a maximum value of 1.37 × 10−9 Ω−1·cm−1 at 700°C. Pure Ce0.8Y0.2O2.9 ceramics needed to be sintered at 1550°C in order to obtain an equivalent theoretical density and conductivity. The introduction of Ga2O3 doping had a good effect on the sintering properties and electrical conductivities of Y2O3-doped CeO2.

Keywords: yttria-doped ceria, Ga2O3 addition, sintering, electrical conductivity

1. INTRODUCTION

Oxygen ionic conductors have a wide variety of applications in the field of electrochemistry. They can be used as solid electrolyte membranes in oxygen sensors, fuel cells, and oxygen pumps. Among the oxygen ionic conductors, Y2O3-stabilized ZrO2 (YSZ) has been the most extensively investigated and practically used. However, especially for solid oxide fuel cell (SOFC) applications, a considerable research effort has been devoted to developing alternative solid electrolytes for YSZ, which should possess higher electrical conductivity than YSZ and be operable at lower temperatures of around 800°C.

Ceria-based electrolytes have received much attention as an alternative to YSZ.[1] Among ceria-based electrolytes, yttria-doped ceria is of particular interest because of its comparatively high electrical conductivity and the relative abundance and low cost of the yttrium element.

However, yttria-doped ceria ceramics are difficult to densify below 1550°C.[2] This makes them difficult for manufacturing ceria-based electrolytes which can be used for SOFC systems, because the ceria-based electrolytes and other components such as cathode and anode cannot be cofired at high temperatures.

In order to lower the sintering temperature, other methods utilizing fine starting powders and additives as sintering aids have been explored. The preparation of ultra fine yttria-doped ceria powders has been studied by many investigators.[2-7] Most of the investigators have studied the preparation of ultra fine yttria-doped ceria powders via chemical routes such as coprecipitation,[2-4] combustion synthesis[5,6] and hydrothermal synthesis.[7]

In contrast, only a limited number of reports on the densification of yttria-doped ceria with sintering additives are available.[8,9] The effects of zinc oxide addition on the sintering characteristics and electrical properties of yttria-doped ceria were investigated by Gao et al.[8] They reported that the addition of a small amount of ZnO strongly enhanced the densification kinetics. A ZnO addition of over 0.4 mol. % led to a sintered density of 96% for sintering at 1375°C, which is about 200°C lower than the sintering temperature required without ZnO.

In the present work, the effects of Ga2O3 addition on the Y2O3-doped CeO2 system are studied systematically. We prepared Ce0.8Y0.2O2.9 ceramics with different Ga2O3 contents. Emphasis is especially placed on variations in the sintered density, microstructure and electrical conductivity.

2. EXPERIMENTAL PROCEDURE

Figure 1 shows a schematic flow diagram of the experimental procedures used in this study. Mixtures having a composition corresponding to (Ce0.8Y0.2O1.9)x(Ga2O3)y, (x = 0 ~ 0.05) were prepared using the conventional mixed-oxide method. High purity commercial CeO2 (Aldrich Chemical Co., 99.9%), Y2O3 (Aldrich Chemical Co., 99.99%), and Ga2O3 (Aldrich Chemical Co., 99.99%) powders were

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used as the starting materials.

These mixtures were then ball-milled in ethanol using a plastic jar and zirconia balls for 24 h. After milling the mixtures, the powders were dried. The dried powder mixtures were screened to −325 mesh.

The sieved powders of −325 mesh size fraction were uniaxially dry-pressed at 196 MPa into pellets having a diameter of 12 mm and a thickness of 4 mm. The resulting compacts were then sintered at 1400°C for 5 h using a fixed heating rate of 10°C/min.

The sintered densities were measured using the Archimedes method with water and/or calculated from the weights and dimensions of the specimens. It was found that both methods provided almost the same density values. The average value obtained from five specimens was used.

The fracture surface of the sintered specimens was observed using a field emission scanning electron microscope (FESEM) (Model JSM-6700F, JEOL). The x-ray diffraction (XRD) technique was employed to identify the phases. XRD was performed on milled powders of specimens using a Rigaku D/MAX IIIA diffractometer with Ni-filtered Cu Kα radiation.

The electrical conductivities were measured using the conventional dc four-probe method. The measurement was performed in air over the temperature range of 450°C to 700°C at 50°C intervals.

3. RESULTS AND DISCUSSION

Figure 2 shows the relative density as a function of Ga$_2$O$_3$ content. It can be seen that the sintered density increases with increasing Ga$_2$O$_3$ content up to 1 mol. % and then decreases somewhat upon further addition of Ga$_2$O$_3$. However, the sintered density of the Ga$_2$O$_3$-added specimens was higher than that of the pure specimen.

By applying the measured lattice parameter into the oxygen vacancy model, the theoretical density of Ce$_{0.8}$Y$_{0.2}$O$_{1.9}$ ceramics was calculated and found to be 6.716 g/cm$^3$. From this density, the relative density of the pure Ce$_{0.8}$Y$_{0.2}$O$_{1.9}$ specimens was calculated and found to be 86%, while the specimen containing 1 mol. % Ga$_2$O$_3$ had a higher density of 94%. Furthermore, high densities of over 90% were obtained with the addition of up to 3 mol. % Ga$_2$O$_3$.

In the case of pure Ce$_{0.8}$Y$_{0.2}$O$_{1.9}$ ceramics, a relative density of 95% is usually attained at sintering temperatures above 1550°C,[2] whereas for the 1 mol. % Ga$_2$O$_3$-added specimen 94% of the theoretical density was achieved at just 1400°C. This result suggests that the addition of Ga$_2$O$_3$ can reduce the sintering temperature by about 150°C.

The enhanced sinterability of the Ga$_2$O$_3$-added specimens was also verified by microstructural observations of the sintered specimens. The SEM micrographs of the fracture surface of pure Ce$_{0.8}$Y$_{0.2}$O$_{1.9}$ and 1 mol. % Ga$_2$O$_3$-added Ce$_{0.8}$Y$_{0.2}$O$_{1.9}$ are shown in Fig. 3. There is an obvious difference in the microstructures of the specimens. Higher densification is observed in the Ga$_2$O$_3$-added specimens. The specimen containing 1 mol. % Ga$_2$O$_3$ exhibits a morphology corresponding to a high value of 94% in relative density.

Yoshida et al.[10] reported that sintering of samaria-doped ceria was significantly promoted by the addition of a small amount of gallia. They reported that the samples sintered at 1450°C with the addition of 1% gallium had almost the same average grain size and electrical conductivity as the samples sintered at 1600°C without Ga$_2$O$_3$ addition.

We previously studied the effects of Ga$_2$O$_3$ addition on the sintering behavior of Ce$_{0.8}$Gd$_{0.2}$O$_{1.8}$ ceramics prepared by coprecipitated powders.[11] The results are described as follows. Both the sintered density and the grain size increased with increasing Ga$_2$O$_3$ content up to 5 mol. %.