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Effects of lithium oxide addition on sintering behavior and electrical conductivity of yttria-doped ceria

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The densification behavior and electrical conductivity of $Ce_{0.8}Y_{0.2}O_{1.9}$ ceramics with lithium oxide concentrations ranging from 0 to 7 mol% were investigated. The sintered density was found to increase with increasing Li₂O content up to 2 mol% and then to decrease somewhat upon further Li₂O addition. It was possible to obtain dense $Ce_{0.8}Y_{0.2}O_{1.9}$ ceramics with 97% of the theoretical density using a 2 mol% Li₂O-added specimen sintered at 1300 °C for 5 hrs, whereas pure $Ce_{0.8}Y_{0.2}O_{1.9}$ ceramics needed to be sintered at 1550 °C in order to obtain an equivalent theoretical density. The electrical conductivity was measured as a function of the dopant content over the temperature range 450 °C ~ 700 °C in air. The conductivity of the 2 mol% Li₂O-added specimen showed a maximum value of $1.15 \times 10^{-2} \Omega^{-1} \cdot cm^{-1}$ at 700. The introduction of Li₂O doping had a good effect on the sintering properties and electrical conductivities of Y_2O_3 -doped CeO₂.

Key words: Yttria-doped ceria, Li₂O addition, Sintering, Electrical conductivity.

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, Y_2O_3 -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 co-fired at high temperatures.

In order to lower the sintering temperature, other methods utilizing fine starting powders and additives as sintering aids have been exploited. 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, 3, 5], combustion synthesis [6, 7] and hydrothermal synthesis [4].

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. 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.

Seo et al. [9] reported that the addition of $Sr_2Ga_2O_5$ enhanced the sinterability of yttria-doped ceria due to the presence of a liquid phase during sintering. In their study, the sintered density was found to increase rapidly at 0.5 mol% $Sr_2Ga_2O_5$ addition and then to decrease with further $Sr_2Ga_2O_5$ addition. Dense $Ce_{0.8}Y_{0.2}O_{1.9}$ ceramics with 97% of the theoretical density could be obtained by sintering the milled mixture with 0.5 mol% $Sr_2Ga_2O_5$ addition at 1250 °C for 5 hrs.

It has been reported recently that lithium oxide is effective for the densification of ceria-based ceramics [10-14]. Nicholas and De Jonghe [10] reported that a Ce_{0.9}Gd_{0.1}O_{1.95} ceramics with relative density of 99% could be sintered at 800 by adding 3 mol% LiNO₃ as a sintering aid. They used nano-sized ultra high surface area Ce_{0.9}Gd_{0.1}O_{1.95} powders and the lithium nitrate solutions as starting materials.

The effects of lithium nitrate addition on the sintering

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characteristics and electrical properties of samaria-doped ceria were investigated by Esposito et al. [11]. They reported that samaria-doped ceria could be densified at $1100 \,^{\circ}$ C with $10 \,\text{mol}\%$ LiNO₃ as an additive. Nanometric powders synthesized by a direct co-precipitation method were used.

Li et al. [13] and Le et al. [14] used Li_2CO_3 and Li_2O as sintering aids for $Ce_{0.8}Sm_{0.2}O_{2.\delta}$ electrolyte, respectively. They used fine powders prepared by combustion synthesis and co-precipitation method, respectively.

However, the reported studies were performed by the use of nano-sized fine powders prepared wet-chemical techniques such as co-precipitation method [11, 12, 14] and combustion synthesis [13], and lithium salt solutions as starting materials.

These wet-chemical methods often suffer from drawbacks, such as the need to use expensive and environmentally unfriendly organic/inorganic precursors and solvents.

In the present work, high purity commercial CeO₂, Y_2O_3 and Li₂O have been used as starting materials. It is noted that the sintering and densification behavior of ceria-based ceramics depend strongly on the characteristics of raw powders. The present work is aimed at studying the effects of Li₂O addition on the sintering behavior and electrical conductivity of Ce_{0.8}Y_{0.2}O_{1.9} ceramics prepared by the conventional mixed-oxide method.

Experimental Procedure

Fig. 1 shows a schematic flow diagram of the experimental procedures used in this study. Mixtures having a composition corresponding to $(Ce_{0.8}Y_{0.2}O_{1.9})_{1-x}(Li_2O)_x$ (x = 0 ~ 0.07) were prepared using the conventional mixed-oxide method. High purity commercial CeO₂ (Aldrich Chemical Co., 99.9%), Y₂O₃ (Aldrich Chemical Co., 99.99%), and Li₂O (Alfa Aesar, 99.5%) powders were

Y203 CeO₂ Li₂0 milling in ethanol, for 24h drying 120°C, for 10h screening 325 mesh pressing 196 MPa sintering 1300°C, for 5h density, SEM, XRD characterization onductivity

Fig. 1. Flow chart of experimental procedures.

used as the starting materials.

These mixtures were then ball-milled in ethanol using a plastic jar and zirconia balls for 24 hrs. 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 1300 °C for 5 hrs 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 the five specimens was used.

The fracture surface of the sintered specimens was observed using a scanning electron microscope (SEM, S-2400, Hitachi). The X-ray diffraction (XRD) technique was employed to identify the phases. XRD was performed on the milled powders of specimens using a Rigaku D/MAX IIIA diffractometer with Ni-filtered Cu K_{α} radiation.

The electrical conductivities were measured using the conventional dc four-probe method. The measurement was performed in air over the temperature range of $450 \text{ }^{\circ}\text{C}$ to $700 \text{ }^{\circ}\text{C}$ at $50 \text{ }^{\circ}\text{C}$ intervals.

Results and Discussion

Fig. 2 shows the relative density as a function of Li_2O content. It can be seen that the sintered density increases with increasing Li_2O content up to 2 mol% and then decreases somewhat upon further addition of Li_2O . However, the sintered density of the Li_2O -added specimens was higher than that of the pure specimen.

By applying the measured lattice parameter into the oxygen vacancy model, the theoretical densities of $Ce_{0.8}Y_{0.2}O_{1.9}$ ceramics were calculated. From the theoretical



Fig. 2. Relative density as a function of Li₂O content.



(a)



(b)

Fig. 3. SEM micrographs of the fracture surface of the sintered specimens; (a) $0 \mod \% (\times 3,000)$ and (b) $2 \mod \% (\times 1,500)$.

density, the relative density of the pure $Ce_{0.8}Y_{0.2}O_{1.9}$ specimens was calculated and found to be 81%, while the specimen containing 2 mol% Li₂O had a higher density of 97%. Furthermore, high densities of over 90% were obtained with the addition of up to 7 mol% Li₂O.

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 [2], whereas for the 2 mol% Li₂O-added specimen 97% of the theoretical density was achieved at just 1300 °C. This result suggests that the addition of Li₂O can reduce the sintering temperature by about 250 °C.

The relative densities of the specimen containing $2 \text{ mol}\% \text{ Li}_2\text{O}$ were 89% at 1100 and 92.9% at 1200 °C. The enhanced sinterability of the Li₂O-added specimens was also verified by microstructural observations of the sintered specimens. The SEM micrographs of the fracture surface of pure and 2 mol% Li₂O-added specimens are shown in Fig. 3. There is an obvious difference



Fig. 4. X-ray diffraction patterns of the sintered specimens with different $\rm Li_2O$ contents.



Fig. 5. Temperature dependence of electrical conductivity.

in the microstructures of the specimens. Higher densification is observed in the Li_2O -added specimens. The specimen containing 2 mol% Li_2O exhibits a morphology corresponding to a high value of 97% in relative density.

It is well known that the melting point of lithium oxide is 1427 °C. In this work, the enhanced densification temperature occurred at <<1100 °C. It is difficult for the formation of a liquid phase at this temperature. No evidence from phase diagram or experimental analysis reveals the existence of liquid phases in the $Li_2O-Y_2O_3$ -CeO₂ system below 1300 °C.

In this work, it is believed that the reduction of sintering temperature is due to viscous flow sintering predominantly taking place in the early stage sintering, as it was reported elsewhere for other sintering aids [15, 16]. Lithium oxide will easily diffuse on the surface of matrix particles during subsequent sintering to form a very thin amorphous film between matrix particles. This very thin amorphous layer reduces the friction between matrix particles, causing the rearrangement of particles

into a more compact structure and promotes mass diffusivity of the matrix. Thus, the densification is further enhanced.

Furthermore, the addition of Li_2O may induce the distortion of the surrounding lattice because Li^+ (0.092 nm) ion has smaller size compared to that of Ce^{4+} (0.097 nm) ion and Y^{3+} (0.102 nm) ion [17]. It is expected that the lattice distortion promotes the grain boundary mobility and the grain growth, which is caused by the effect of severely undersized dopants [18].

Nicholas and De Jonghe [10] reported that lithium oxide is a good sintering aid which possess both a high vapor pressure and a low Vegard's Slope. Due to the high volatility of lithium oxide at low temperatures, the mobility of lithium becomes quite high and the high diffusivity rates of lithium on matrix particles promote viscous flow sintering at the early and intermediate sintering stage.

Fig. 4 shows the XRD patterns of the specimens with different Li₂O contents. All the patterns show peaks of cubic fluorite type. No peaks corresponding to a new phase appeared.

The temperature dependence of the electrical conductivity is shown in Fig. 5. The conductivities all increase with increasing temperature. No deviations from linearity are observed in the Arrhenius plots between 450 °C and 700 °C. The conductivities of the specimen containing 2 mol% Li₂O are higher than the conductivities of the pure Ce_{0.8}Y_{0.2}O_{1.9} specimens. This is consistent with the results for the variation of the sintered density. From the Arrhenius plot in Fig. 5, the activation energies for 0 mol% and 2 mol% Li₂O-added specimens were around 0.96 eV and 0.97 eV, respectively.

Eguchi et al. [19] reported that the conductivity of yttria-doped ceria sintered at 1650 °C for 15 hrs was $\sim 1.02 \times 10^{-2} \ \Omega^{-1} \cdot \text{cm}^{-1}$ at 700 °C. Gao et al. [8] also reported a conductivity of $\sim 2.8 \times 10^{-2} \ \Omega^{-1} \cdot \text{cm}^{-1}$ at 700 °C. They used specimens sintered at 1600 °C for 20 hrs.

In this work, a conductivity of $1.15 \times 10^{-2} \ \Omega^{-1} \cdot \text{cm}^{-1}$ was observed at 700 °C for the 2 mol% Li₂O-added specimens sintered at 1300 °C. This value obtained for the specimen sintered at 1300 °C is close to the value obtained for the pure Ce_{0.8}Y_{0.2}O_{1.9} specimen sintered at 1600 °C (~ $2.8 \times 10^{-2} \ \Omega^{-1} \cdot \text{cm}^{-1}$ [8]). Seo et al. [9] reported a conductivity of ~ $4.43 \times 10^{-3} \ \Omega^{-1} \cdot \text{cm}^{-1}$ at 700 °C for the 0.5 mol% Sr₂Ga₂O₅-added specimens sintered at 1250 °C. A conductivity of $1.15 \times 10^{-2} \ \Omega^{-1} \cdot \text{cm}^{-1}$ obtained in this work is higher than a value obtained in the Sr₂Ga₂O₅-added specimens (~ $4.43 \times 10^{-3} \ \Omega^{-1} \cdot \text{cm}^{-1}$ [9]).

The addition of Li_2O significantly promoted the densification and conductivity of Y_2O_3 -doped CeO_2 . It is suggested that the addition of Li_2O has an affirmative effect on the sintering behavior and electrical conductivity of Y_2O_3 -doped CeO_2 .

Conclusions

We investigated the effects of lithium oxide addition on sintering behavior and electrical conductivity of yttria-doped ceria. The sintered density increased with increasing Li₂O content up to 2 mol%. Li₂O was found to be an effective sintering promoter for the densification of Y₂O₃-doped CeO₂ ceramics. It was confirmed that a small amount of Li₂O reduces the sintering temperature by about 250 °C. The conductivity of the 2 mol% Li₂Oadded specimen showed a maximum value of 1.15×10^{-2} $\Omega^{-1} \cdot cm^{-1}$ at 700 °C. The addition of Li₂O was found to promote the sintering properties and electrical conductivities of Y₂O₃-doped CeO₂.

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