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Effect of annealing on the electrical conductivity of the Y_2O_3–ZrO_2 system

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Abstract

The effect of annealing on the electrical conductivity of the Y_2O_3–ZrO_2 system (8.0–10.0 mol% Y_2O_3) was investigated by the direct current four-probe technique at several temperatures for 1000 h. The difference of the crystal structure before and after annealing was investigated by X-ray diffraction (XRD), Raman spectroscopy, and transmission electron microscopy (TEM). The decrease of the conductivity for the specimens with composition of 8.0–9.0 mol% Y_2O_3 was caused by the formation of a fine tetragonal phase. On the other hand, the sample of 9.5 mol% Y_2O_3 after annealing for 1000 h supported a single phase with cubic structure. Therefore, the optimum composition as electrolyte for solid oxide fuel cell in the Y_2O_3–ZrO_2 system was considered to be 9.5 mol% Y_2O_3 from the viewpoint of long-term stability with the relatively high conductivity.
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1. Introduction

The solid oxide fuel cells (SOFCs) have received the interest for electric power generation systems with the advantages of high energy conversion and low emissions. The unit cell consists of three-layer structures: anode, electrolyte, and cathode. An electrolyte with a high conductivity and long-term stability should be provided for developing a high performance SOFC, because the electrolyte resistance is predominant in the total cell resistance of SOFCs.

Yttria stabilized zirconia (YSZ) is the most commonly used for an electrolyte in SOFCs, because it satisfies several desired criteria [1]. In the Y_2O_3–ZrO_2 system, the composition of 8.0 mol% Y_2O_3 (8.0YSZ: hereafter, x mol% Y_2O_3 was denoted as xYSZ) is widely used for an electrolyte material in SOFCs, because of the highest conductivity at an operating temperature (1000 °C). However, it is well known that the conductivity of 8.0YSZ and other ZrO_2 based materials degrades after the long-term operation of SOFC [2–5]. In general, the annealing effect (isothermal decrease of conductivity with annealing time) can be attributed to following two possible effects: (1) the formation and growth of microdomains and (2) the formation and growth of ordered phase (phase decomposition).

As the practical use of YSZ for the electrolyte, the stability in conductivity as well as the value itself is an important factor satisfied in order to maintain the long-term performance of SOFCs. The optimum composition in the Y_2O_3–ZrO_2 system showing no change with aging but relatively high oxide ion conductivity may be found between 8.0 and 10.0YSZ. Recently, we reported that the optimum composition was found at 9.5YSZ sample with relatively high conductivity and long-term stability at 1000 °C [6,7].

In this work, the conductivity change in 8.0–10.0YSZ was reported in detail about annealing effect at several temperatures for 1000 h. The annealing effect before and after the samples was synthesized by X-ray powder diffraction (XRD), Raman spectroscopy, and transmission electron microscopy (TEM).

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2. Experimental

All starting powders with sub-micron order were prepared by the solid state reaction of Y_2O_3 and ZrO_2 (Kyoritsu Ceramic Material Co.). The compositions used in this study were 8.0, 8.5, 9.0, 9.5, and 10.0YSZ. Each starting powder was uni-axialy pressed at 25 MPa, and then isostatically pressed by cold isostatic press (CIP) method at 300 MPa followed by sintering at 1500 or 1400 °C for 10 h in air.

The conductivity was continuously measured by the direct current (dc) four-probe technique at several temperatures for 1000 h in air. The specimens were fabricated to rectangular from of 4 mm × 3.5 mm × 20 mm. The length between voltage terminals with platinum electrodes was fixed about 10 mm. Current density was settled at 200 mA/cm^2. The conductivity was recorded automatically by home-made program at every 10 min using two digital multimeters (Advantest TR6851).

The samples that were obtained by this procedure were analyzed at room temperature via XRD technique, using Cu Kα radiation and graphite curved monochromator (Rigaku). The Raman spectroscopy was also measured to identify the existing phase. Raman spectra in the wave number range of 140–860 cm^{-1} were obtained using a Raman system (JASCO; NR-1800) with a double spectrometer and a charge-coupled device (CCD) detector. The Raman scattering was excited by an Ar^+ laser source (wavelength of 488.0 nm) at 500 mW. TEM (JEOL; JEM-4000FX) was used for an observation of the microstructure and a measurement of the electron diffraction patterns.

3. Results and discussion

The samples of 8.0–9.0YSZ showed significant decrease with annealing time, however, in the case of 9.5 and 10.0YSZ samples, the initial conductivity was maintained constant value even after the annealing period of 1000 h [6,7]. The conductivity change of each composition before and after annealing was shown in Fig. 1. The meaning of before and after annealing in Fig. 1 indicates that holding time at 1000 °C is 0 and 1000 h, respectively.

The conductivity was dependent on the concentration of Y_2O_3. The conductivity change at low concentration of Y_2O_3 (8.0–9.0YSZ) was higher than that at high concentration (9.5 and 10.0YSZ). In the case of 9.5 and 10.0YSZ, the initial conductivity keeps even after the annealing period of 1000 h. The rate of conductivity change between before and after annealing had the maximum value at 8.0YSZ and the rate decreased with increasing Y_2O_3 content.

In 8.0 and 9.5YSZ, the annealing time dependence of conductivity at each operating temperatures was also carried out in this work. Fig. 2 shows the conductivity change at each temperature for 1000 h. At temperatures above 900 °C,

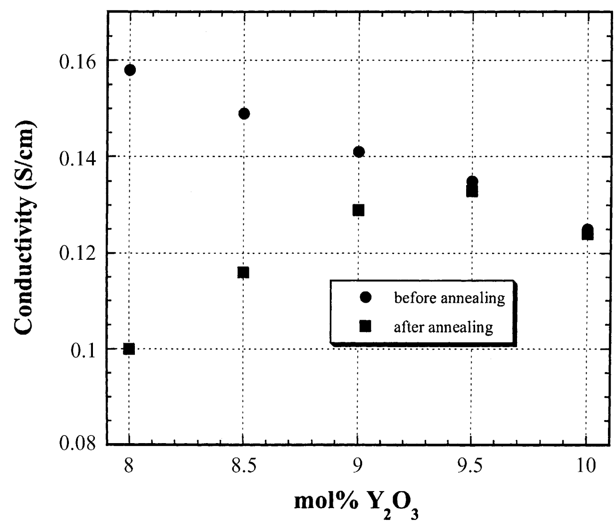

Fig. 1. The conductivity change of each composition (8–10 mol% Y_2O_3) before and after annealing at 1000 °C for 1000 h.

8.0YSZ observed significant conductivity decrease after annealing, however, the change at low temperatures (below 800 °C) appeared a slight decrease according to annealing time. On the other hand, no significant conductivity decrease after annealing at each temperature was shown in the case of 9.5YSZ. Therefore, in the view point of the long-term stability in conductivity, 9.5YSZ in the Y_2O_3–ZrO_2 system seems to be an optimum composition as the electrolyte material of SOFCs.

The phase identification of 8.0 and 9.5YSZ was estimated by the XRD and TEM, and some results were reported in our previous work [6,7]. In both samples, the XRD peaks corresponding to the monoclinic or tetragonal phase did not appear and only the cubic phase was observed even after annealing for 1000 h. At the case of TEM photograph, the

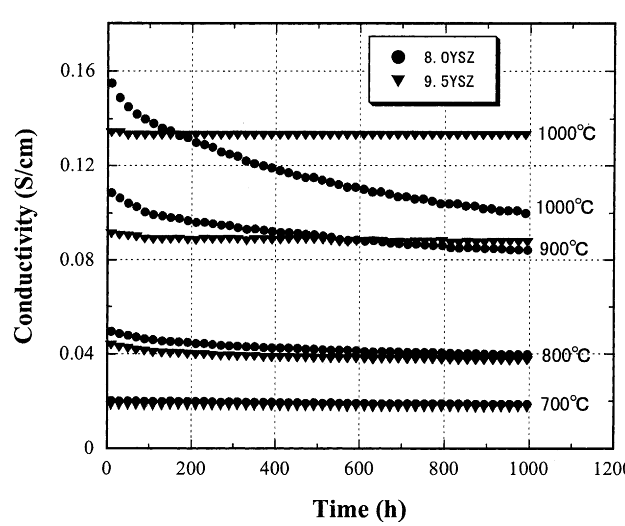

Fig. 2. Time and temperature dependence of the conductivity of 8.0 and 9.5YSZ annealed at 1000 °C.

electron diffraction pattern of the initial 8.0YSZ suggests the existence of only cubic phase, however, the tetragonal phase is considered in the 8.0YSZ after annealing because the striped patterns are observed.

The XRD patterns and electron diffraction is not very sensitive to difference of the tetragonal and cubic phases. On the other hand, the Raman spectroscopy has been utilized as a powerful tool to observe the phase transformation and boundary of tetragonal and cubic of zirconia [8,9]. The reason is that the Raman spectroscopy is related to the atomic vibration of the cations and oxygen. The relationship between symmetries and Raman active modes of the polymorphs of zirconia was summarized by the previous work [8]. The Raman active mode of well ordered monoclinic phase has $9A_g + 9B_g$ symmetry with 18 sharp and intense. Tetragonal phase shows six broad bands, which is consistent with the number of its Raman active frequencies ($A_{1g} + 2B_{1g} + 3E_g$). The Raman spectra of cubic phase show broad bands with background profile, although the ideal cubic phase gives only one Raman band with T_{2g} symmetry.

Based on the Raman study in the ZrO_2 system, all the samples sintered at 1500 °C in this work was indicated the Raman band of cubic structure with a broad band near 640 cm^{-1} together with a background profile as reported in the previous works [8–11]. However, after ageing at 1000 °C for 1000 h, the spectra of 8.0, 8.5, 9.0YSZ samples except 9.5, 10.0YSZ changed and the Raman bands of about 260 and 460 cm^{-1} appeared [7]. Two Raman bands of 260 and 460 cm^{-1} were included in six broad bands predicted by group theory for the tetragonal structure. It is considered that fine cubic phase of 8.0YSZ after annealing is decomposed to tetragonal phase in cubic matrix. Based the result of conductivity and Raman spectra, the conductivity decrease during annealing is related to phase decomposition of fine tetragonal structure in cubic matrix because the tetragonal phase is lower conductivity than cubic one.

The annealing effect of 8.0 and 9.5YSZ specimens sintered at 1300, 1400, 1500 °C was also investigated. As shown in Fig. 3, the initial conductivity of all the samples was dependant on the sintering temperature ($\sigma_{1300\,^\circ C} < \sigma_{1400\,^\circ C} < \sigma_{1500\,^\circ C}$). The conductivity of all as-sintered 8.0YSZ decreases with annealing time during 1000 h and shows the decreasing behavior on further annealing. However, no significant decrease in the conductivity during annealing was observed in all as-sintered 9.5YSZ.

The Raman spectra before and after annealing of all as-sintered 8.0YSZ were shown in Fig. 4a and b, respectively. The Raman modes of as-sintered samples (initial

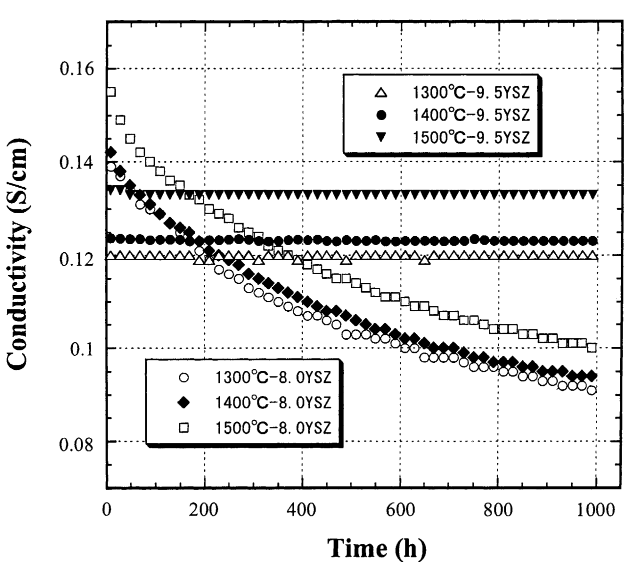

Fig. 3. Conductivity changes of 8.0 and 9.5YSZ during annealing at 1000 °C for 1000 h, which were sintered at 1300, 1400, and 1500 °C.

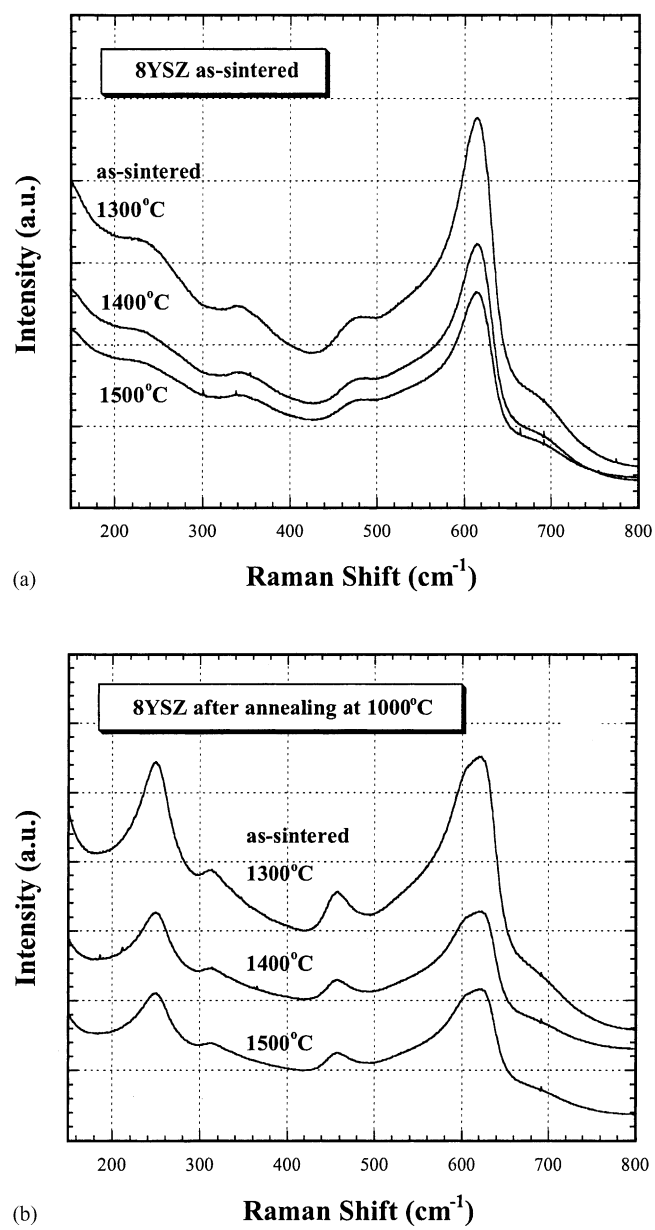

Fig. 4. Raman spectra of 8.0YSZ sintered at 1300, 1400, and 1500 °C: (a) before annealing (initial) and (b) after annealing at 1000 °C for 1000 h.

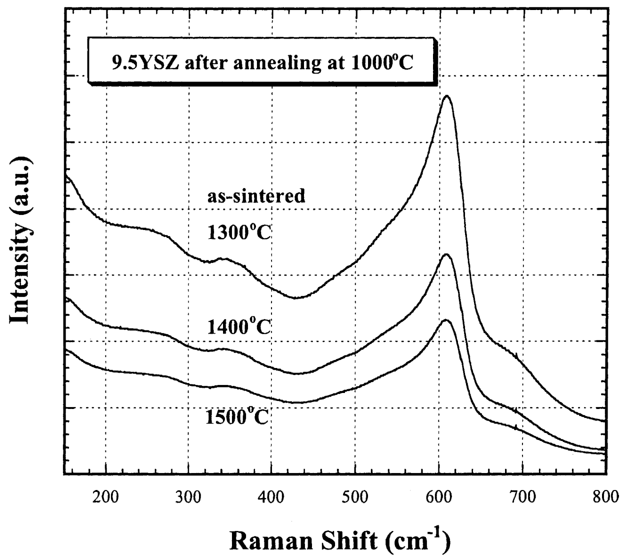

Fig. 5. Raman spectra of 9.5YSZ after annealing at 1000 °C for 1000 h. The 9.5YSZ samples were sintered at 1300, 1400, and 1500 °C.

samples before annealing) were similar results (Fig. 4a). In the case after annealing (Fig. 4b), the 260 cm^{-1} band indexed to tetragonal phase was appeared and increased as decrease of sintering temperature. On the other hand, no change of Raman spectra before and after annealing was observed in 9.5YSZ (Fig. 5).

Therefore, the optimum composition as electrolyte materials for SOFC in the Y_2O_3–ZrO_2 system was considered to be 9.5 mol% Y_2O_3 (9.5YSZ), because of long-term stability with the relatively high conductivity.

4. Conclusions

The conductivity change in the Y_2O_3–ZrO_2 system was measured during continuous current loading at several temperatures for 1000 h. The conductivity change at low concentration of Y_2O_3 (8.0–9.0YSZ) was higher than that at high concentration (9.5 and 10.0YSZ). From the results of the Raman spectra and XRD patterns, the conductivity decrease for the specimens with composition of 8.0–9.0 mol% Y_2O_3 was caused by the formation of fine tetragonal phase. The composition with 9.5 mol% Y_2O_3 was suggested to the electrolyte for SOFC operated at high temperature (above 900 °C).

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