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Effect of aging on conductivity of yttria stabilized zirconia

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Abstract

The electrical conductivity change with annealing at 1000 °C in the Y_2O_3–ZrO_2 (YSZ) system was examined. Among the sintered samples doped with 8.0 mol% Y_2O_3 (8.0YSZ), 8.5 mol% Y_2O_3 (8.5YSZ), 9.0 mol% Y_2O_3 (9.0YSZ), 9.5 mol% Y_2O_3 (9.5YSZ) and 10.0 mol% Y_2O_3 (10.0YSZ), 9.5- and 10.0YSZ showed no conductivity decrease even for the annealing period of 1000 h, while 8.0- and 8.5YSZ showed significant decrease with time although the initial conductivities were higher than those of 9.5- and 10.0YSZ. The 9.0YSZ showed only slight conductivity decrease. The measurement of Raman spectra demonstrated that the deterioration in conductivity related to the gradual formation of fine tetragonal phase in the cubic phase. Consequently, 9.5YSZ was seemed to be optimum as the electrolyte material of solid oxide fuel cells from the point of stability in high conductivity.

Keywords: Yttria stabilized zirconia; Oxide ion conductivity; Aging; Raman spectra; Cubic phase; Tetragonal phase

1. Introduction

Solid oxide fuel cells (SOFCs) have been attracting great attention as a promising new method for electrical power generation. SOFCs can provide high total efficiency when used in a cogeneration system because their high operating temperature such as 1000 °C gives the advantage of producing high-temperature discharge gases. They also promise clean power with little NO_x emissions. The basic unit of a cell consists of a three-layer structure: anode, electrolyte, and cathode. It is necessary to achieve not only higher performance but also a more stable cell in order to apply SOFCs for practical use, because SOFCs must operate for tens of thousands of hours to be practical.

Yttria (Y_2O_3) stabilized zirconia (YSZ) is the most commonly used for an electrolyte in SOFCs because it fulfills several desired criteria [1]. In particular, 8 mol% Y_2O_3–92 mol% ZrO_2 (called 8YSZ hereinafter) has been widely used for an electrolyte in SOFCs because of its high ionic conductivity at an operating temperature about 1000 °C. However, it is also well-known that the conductivity of 8YSZ degrades after the long term operation of SOFC [2–5]. The aging process for stabilized zirconia was first investigated by Carter and Rothfor CaO–ZrO_2 system and it was concluded that defect ordering process was taking place [6]. Moghandam and Stevenson have reported the influence of annealing on the conductivity of 4.5YSZ at 1000 °C [7]. The initial decrease of conductivity was attributed to precipitation of tetragonal zirconia from cubic matrix and the further decreases to the ordering in the cubic phase. However, even after annealing for 1000 h, the slight relative X-ray diffraction (XRD) intensity changes of cubic phase are detected.

Kondoh and co-workers [8–10] have reported the detailed examination concerning the effect of aging on YSZ considering the previous many authors' works and concluded that the short range ordering of oxide ion vacancies around Zr ions as a result from relaxation of the lattice distortion is responsible for the decrease in conductivity with aging.

On the other hand, such an aging effect decreases with increase of Y_2O_3 content and looks to fade into the background in the case of 10YSZ (for example, see [9]). 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 performance of SOFCs. The optimum composition showing no change with aging,

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but relatively high oxide ion conductivity may be found between 8- and 10YSZ. However the detailed behaviors on the change of conductivity and structure for the solid solution from 8- to 10YSZ have not been clarified yet.

In this work, the conductivity change of 8.0-, 8.5-, 9.0-, 9.5- and 10.0YSZ was measured by aging at 1000 °C and the aging effect on the crystal structure was examined by Raman spectroscopy, Transmission electron microscopy (TEM) and X-ray diffraction(XRD) techniques in order to find the optimum composition.

2. Experimental

2.1. Samples preparation

The samples used in this study are 8.0-, 8.5-, 9.0-, 9.5- and 10.0YSZ. All starting powders of sub-micron order, which were prepared by the solid state reaction of Y_2O_3 and ZrO_2, were supplied by Kyoritsu Ceramic Material Co. Ltd. Each starting powder was uni-axially pressed at 25 MPa, and then isostatically pressed by cold isostatic press (CIP) method at 300 MPa followed by sintering at 1500 °C for 10 h in air. In order to obtain the high density sintered body, the temperature was increased with the rate of 200 °C/h between room temperature and 1000 °C, and 50 °C/h between 1000 and 1500 °C. The cooling rate was settled at 200 °C/h.

2.2. Conductivity measurements

The stability of conductivity was continuously measured by the direct current (dc) four-probe technique at 1000 °C for 1000 h in air for the samples cut to rectangular form of 4 mm × 3.5 mm × 20 mm. Platinum was used as electrodes and the length between voltage terminals was fixed about 10 mm. Current density was settled at 200 mA/cm^2. The conductivity was measured automatically every 10 min using two digital multimeters (ADVANTEST TR6851). The electrical conductivity was also measured by the complex impedance method in order to estimate the activation energy. The size of the samples was the same as that for dc four-probe technique. The frequency response analyzer (Soratlon 1260) was used and impedance spectroscopy was collected from 350 to 1000 °C in air atmosphere using platinum electrodes.

2.3. Characterization of microstructures

XRD, TEM and Raman spectroscopy were measured for YSZ samples before and after aging of 1000 h. XRD patterns were measured using Rigaku X-ray diffractometer with Cu Kα radiation from 20 to 80 degrees in 2θ. TEM (JEOL; JEM-4000FX) was used for an observation of the microstructure and a measurement of the electron diffraction patterns. The samples for TEM observation were prepared by an argon ion thinning method. The Raman spectroscopy was measured to identify the existing phase, because the vibrational modes are strongly dependent on the crystal structure. Raman spectra in the wavenumber 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 exited by an argon-ion laser source (wavelength of 488.0 nm) at 500 mW.

3. Results and discussion

All sintered samples showed a density of more than 99 % by the Archimedes' method. Fig. 1 shows the conductivity change of YSZ with time at 1000 °C. The initial values of conductivity for 8.0- and 10.0YSZ were almost the same as those of the previous reports [1,8]. The conductivity of 0.155 S/cm of as sintered 8.0YSZ decreases with time to 0.100 S/cm after 1000 h and shows the decreasing behavior on further annealing. The conductivity of 8.5YSZ also decreases significant with time, but keeps the higher value of 0.115 S/cm than that of 8.0YSZ after 1000 h. The samples with higher Y_2O_3 content show no significant conductivity decrease with annealing time. Although 9.0YSZ shows only slight conductivity decrease, 9.5YSZ keeps the initial conductivity (0.135 S/cm) even after the annealing period of 1000 h. In the view point of the stability in conductivity, 9.5YSZ seems to be optimum as the electrolyte material of SOFCs.

Fig. 2 shows the Arrhenius plots of the electrical conductivity for 8.0- and 9.5YSZ before and after aging. The plots show a slight curvature at around 700 °C. The activation energy of higher temperature region reflects the migration of oxide ions (E_m), while the association at lower temperature region ($E_a + E_m$). In higher temperature region, the value (83 kJ/mol) of E_m for 8.0YSZ after annealing was higher than that (75 kJ/mol) before annealing. By the way, E_m for 9.5 YSZ had the same value before and after annealing (76 kJ/mol). This behavior seems to be good agreement with

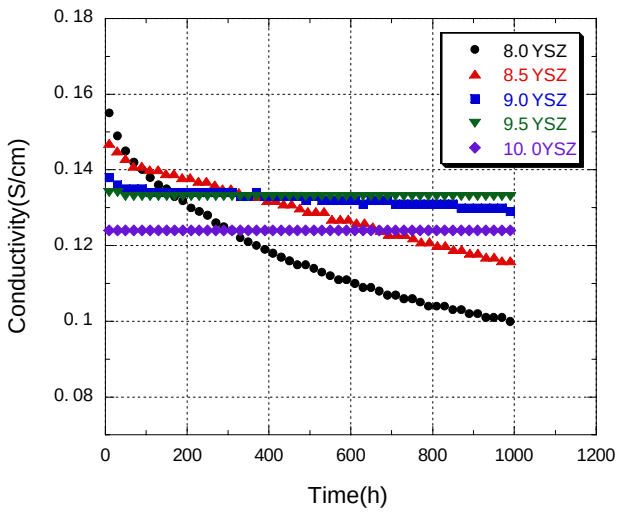

Fig. 1. Time dependence of conductivity of YSZ annealed at 1000 °C.

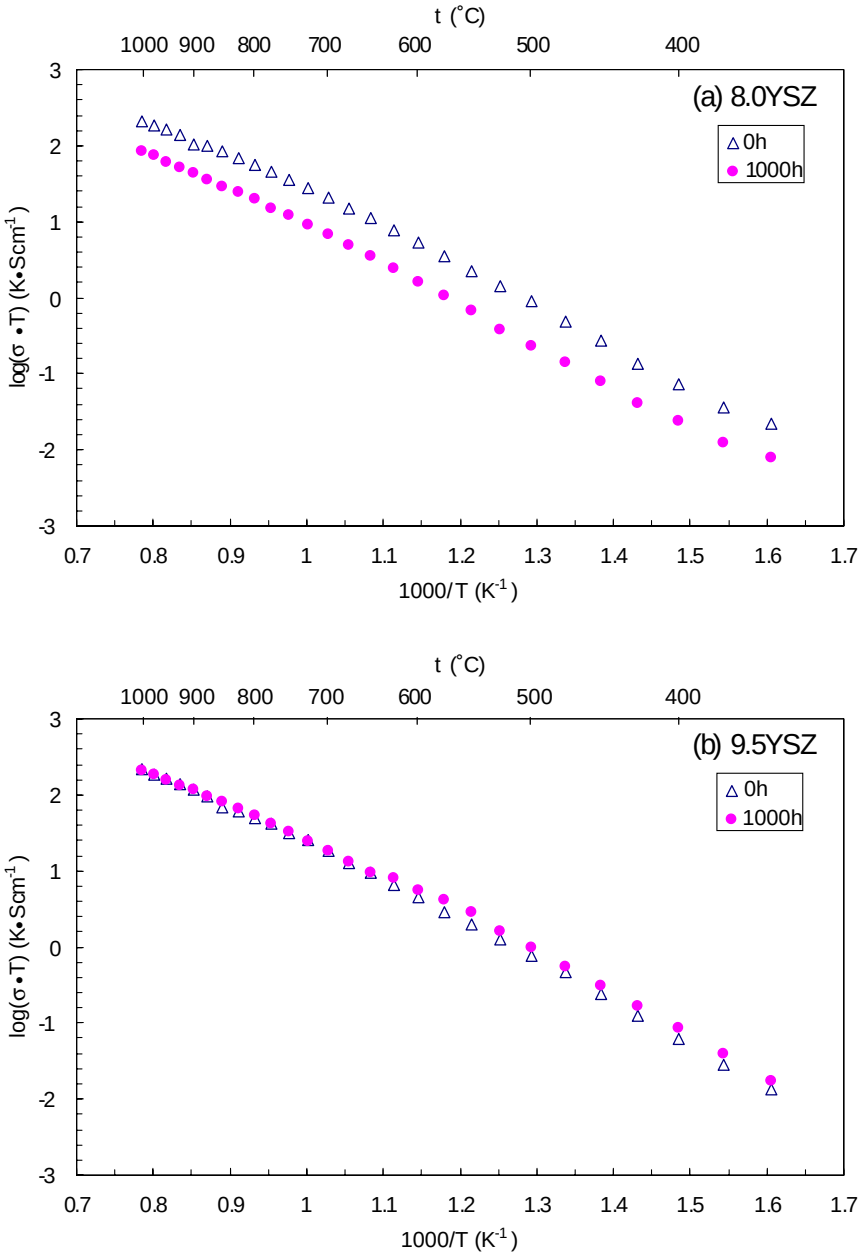

Fig. 2. Arrhenius plots of the conductivity in 8.0- and 9.5YSZ.

the results of stability of conductivity for 8.0- and 9.5YSZ, as seen in Fig. 1. On the other hand, in lower temperature region, no remarkable difference in the samples between before and after aging is observed for $E_a + E_m$ (104 kJ/mol) in both 8.0- and 9.5YSZ, which indicate that the deterioration in conductivity of 8.0- and 9.5YSZ by aging is so small that the mechanism of oxide ion conduction does not change.

Fig. 3 shows the XRD patterns (a raw datum) of 8.0- and 9.5YSZ as sintered and after annealing for 1000 h in the range of 2θ angles of 72°–76°. In both samples, the peaks corresponding to the monoclinic or tetragonal phase do not appear and only the cubic phase is observed even after annealing for 1000 °C. Fig. 4 shows the TEM images and electron diffraction patterns from an 8.0YSZ grain as sintered and after annealing. The electron diffraction pattern of the initial 8.0YSZ suggests the existence of only cubic phase. However, the spot correspond to 102 plane was revealed in the 8.0YSZ after annealing for about 1000 h. The change of electron diffraction pattern seems to be coursed by the formation of tetragonal phase and/or the ordering of oxide ion vacancies.

Raman spectroscopy is useful technique to observe the local structural change because it is directly related to the atomic vibration of the cations and oxygen in the crystal structure. The information of XRD patterns is related to the total structural change of the sample. It is enable to detect the severe local structural change. Fig. 5 shows the Raman spectra of YSZ samples of as sintered and after annealing

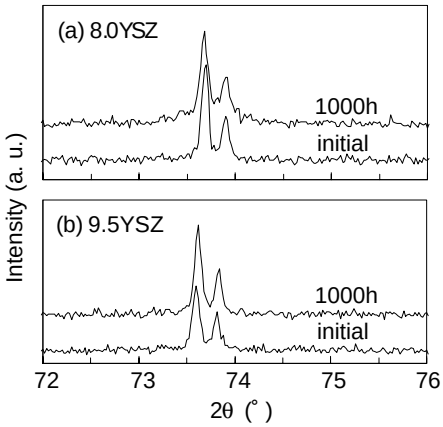

Fig. 3. XRD patterns of 8.0- and 9.5YSZ of as sintered and after annealing for 1000 h.

for 1000 h and that of tetragonal 3.0YSZ as the reference. Although all the as-sintered samples seem to indicate the typical cubic structure, after aging for 1000 h, the patterns of 8.0-, 8.5- and 9.0YSZ change and the bands of about 260 and 460 cm^{-1} appear. The similar peaks are observed in the pattern of 3.0YSZ having tetragonal symmetry and these peaks correspond to tetragonal phase [11,12]. Yashima et al. reported that the determination of cubic-tetragonal phase boundary in ZrO_2 based materials by Raman spectroscopy [11,13]. According to them tetragonal phase is classified as two type, t′ and t″, and t″ metastable phase can not distinguish by XRD because the axial ration c/a for t″ phase which

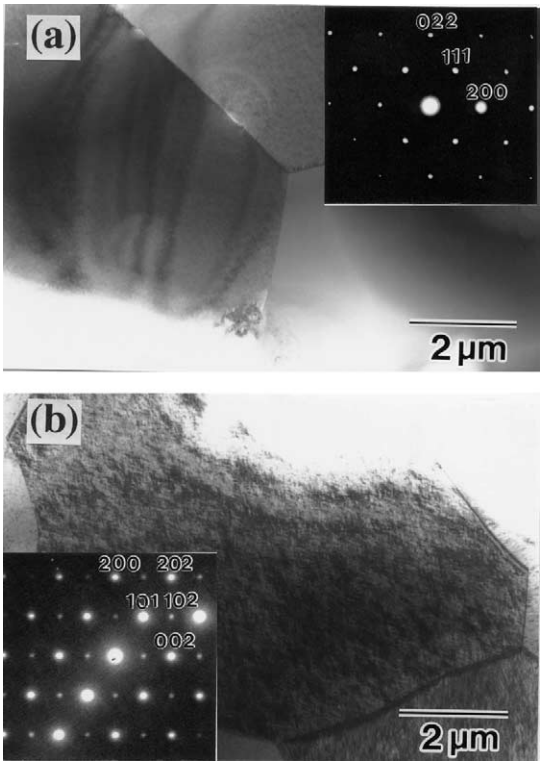

Fig. 4. TEM pictures and electron diffraction patterns of 8.0YSZ before (a) and after (b) annealing for 1000 h.

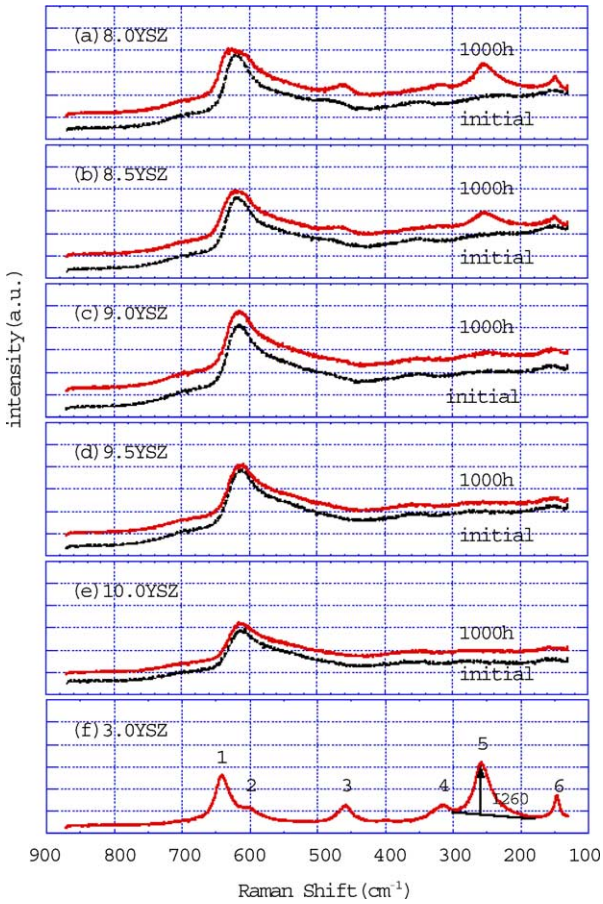

Fig. 5. Raman spectra of YSZ of as sintered and after annealing for 1000 h.

induced by the oxygen displacement along *c*-axis from the ideal fluorite site equals 1. The degree of conductivity decrease with time correspond the intensity of the peaks at about 260 and 460 cm^{-1} in Raman spectra, and similar behavior for 8YSZ and scandia (Sc_2O_3) stabilized zirconia (ScSZ) was reported by Yamada et al. [2] and Mizutani [14], respectively. Based on the results of conductivity and Raman spectroscopy of YSZ of as sintered and after annealing for 1000 h, Fig. 6 shows the relationship between deterioration in conductivity and formation of tetragonal phase. In this figure, the peak intensity ratio of I_{260}(1000 h)/I_{260}(initial) is plotted as vertical axis and deterioration ratio of conductivity (σ(1000 h)/σ(initial)) is plotted as horizontal axis. It was clearly observed that the peak ratio of I_{260}(1000 h)/I_{260}(initial) is increased with increasing the deterioration ratio of conductivity. Therefore, it was suggested in this study that the degradation of the conductivity for YSZ materials was caused by the formation of fine tetragonal phase. Many different phase diagrams for the ZrO_2–Y_2O_3 system were reported on the basis of experimental results and they were summarized by Yoshimura [15]. However, it is not clear the phase boundary between cubic and tetragonal at 1000 °C in the phase diagrams, because the diagrams contain some frozen and/or metastable phase boundaries at temperatures of below 1200 °C. In order to be clear the

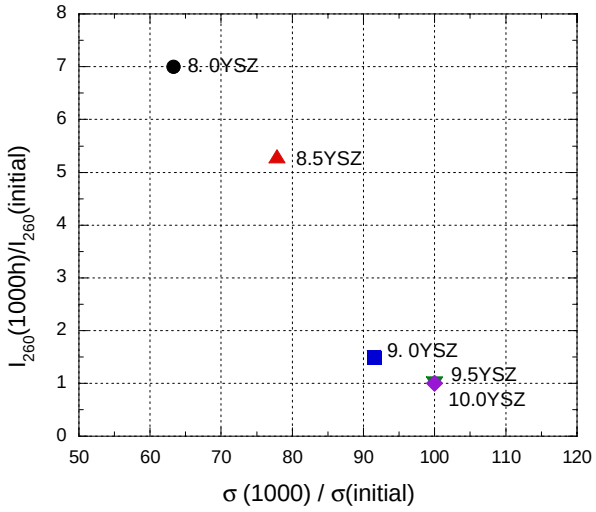

Fig. 6. The relationship between the peak intensity ratio of I_{260} and deterioration of conductivity for YSZ of as sintered and after annealing for 1000 h.

phase boundary in ZrO_2 based materials, Yashima et al. have proposed the new phase diagram considering the metastable phase such as t″ and supposed that the cubic-tetragonal phase boundary at 1000 °C is around the 9 mol% Y_2O_3 in ZrO_2 [16]. Therefore, our results that 9.5- and 10.0YSZ showed no conductivity decrease at 1000 °C seem to be correspondence with their phase diagram. In addition, based on their phase diagram, it is expected that the conductivity with low value of 8.0YSZ after annealing is recovered by heat treatment for above 1200 °C, because the cubic phase for 8.0YSZ is stable at temperatures of above 1200 °C. After annealing at 1000 °C for 1000 h, the conductivity of the annealed sample 8.0YSZ was measured in the temperature range of 700–1400 °C during heating and cooling. The heating and cooling rate is 2 °C/min. The temperature dependence of the conductivity for the annealed sample 8.0YSZ was shown in Fig. 7. As evident from Fig. 7, it is confirmed that the conductivity of the annealed sample 8.0YSZ has recovered during heating above 1200 °C and the conductivity at 1000 °C after heat treatment at 1400 °C is same as initial value as shown in Fig. 1. This result is also supported that the degradation of the conductivity for YSZ materials as shown in Fig. 1 is caused by the formation of tetragonal phase in cubic matrix. Now, we are examining the annealing effect of conductivity at temperatures of below 1000 °C in the YSZ system. This will be reported in the near future.

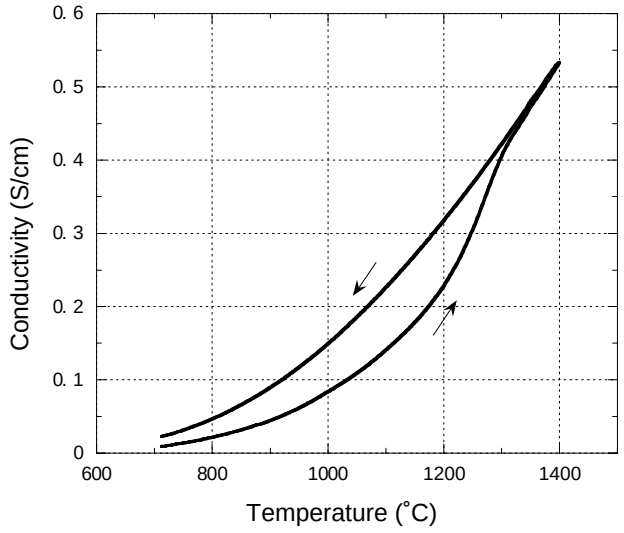

Fig. 7. Temperature dependence of the conductivity for 8.0YSZ after annealing for 1000 h.

4. Conclusion

The electrical conductivity change with annealing at 1000 °C in the YSZ system as electrolyte material for SOFCs was examined. The 9.5- and 10.0YSZ showed no conductivity decrease even for the annealing period of 1000 h, while 8.0- and 8.5YSZ showed significant decrease with time although the initial conductivities were higher than those of 9.5- and 10.0YSZ. The 9.0YSZ showed only slight conductivity decrease. Consequently, it was concluded that 9.5YSZ was optimum as the electrolyte material of SOFCs from the point of stability in high conductivity. In addition, it was demonstrated that the deterioration in conductivity related to the gradual formation of fine tetragonal phase in the cubic phase by Raman spectroscopy.

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