Destabilization and ion conductivity of yttria-stabilized zirconia for solid oxide electrolyte under thermal stress

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Research Article

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Abstract

The degradation behavior of yttria-stabilized zirconia under thermal stress was investigated in terms of phase transformation, local atomic structure, and electrical conductivity. The average grain size of 8YSZ were increased from 20.83 μm to 25.81 μm with increasing aging temperature. All 8YSZ samples degraded at different temperatures had a predominantly cubic structure. The (400) peak of 8YSZ deteriorated at 1300 and 1400°C shifted to high angle, and the peak of tetragonal was not indexed. For 8YSZ degraded at 1500°C, the (400) peak shifted to a lower angle, and the peak of tetragonal was identified. In the local atomic structure of the aged 8YSZ with extended X-ray absorption fine structure, the intensity of the Zr-O peak gradually increased, and the intensity of the Zr-Cation peak decreased as the aging temperature increased. The changes in the peaks indicate that the oxygen vacancies were reduced and Y^{3+} ions escaped from the lattice, leading to destabilization of 8YSZ. The activation energies of 8YSZ at 1300°C and 1400°C were derived to be 0.86 and 0.87 eV, respectively, and the activation energy of 8YSZ at 1500°C increased significantly to 0.92 eV. With the thermal deterioration of 8YSZ, the cation (Y^{3+}) escaped from the lattice and the number of oxygen vacancies decrease, resulting in the formation of a tetragonal structure and high activation energy at 1500°C.

1. Introduction

Oxygen sensors operating in harsh conditions have been extensively developed in recent years, and zirconia electrolytes are in the spotlight because of their high ionic conductivity and excellent reliability [1, 2]. Zirconia electrolytes are exposed to hazardous chemicals and extreme temperatures depending on the operating environment and operate in such environments for several years [3]. Long-term exposure to high temperatures causes degradation of the solid electrolyte, and the degradation changes the conductivity, affecting the accuracy and stability of the sensor [4]. In addition, the solid oxide membrane (SOM) process, which is an environmentally friendly metal electrolysis process using yttria-stabilized zirconia as an oxygen-conducting membrane, has been studied recently [5, 6]. Thus, ensuring the stability of YSZ at high temperatures is becoming more important.

The electrical properties and stability of zirconia-based electrolytes depend on the dopant type and concentration [7]. Zirconia-based electrolytes are stabilized by doping zirconia with binary oxides such as CaO , MgO , Sc_2O_3 , and Y_2O_3 . Among them, yttria-stabilized zirconia has high ionic conductivity at high temperatures and is the most widely studied as a zirconia solid electrolyte [8, 9].

It is well known that the conductivity of 8YSZ decreases during aging at high temperatures (approximately 1000°C). Moghdam et al. [10] reported that the precipitation of the tetragonal phase in a cubic matrix decreased the conductivity of 8YSZ. Kondoh et al. [11] suggested the oxygen ion vacancies ($V_{\text{O}}^{\bullet\bullet}$) around dopant cations (Y^{3+}) are trapped in the dopant cations owing to columbic forces, that is, short-range ordering. In addition, it has been reported that the grain boundary resistance increases by glassy phase segregation and $\text{Y}_2\text{Zr}_2\text{O}_7$ or $\text{Y}_4\text{Zr}_3\text{O}_{12}$ phase precipitation by the formation of oxygen

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 s factors, as described above, resulting in a

decrease in the conductivity. Many studies on the degradation mechanism have been conducted at temperatures below 1000°C, whereas studies of the aging behavior at high temperatures above 1200°C are required.

We studied thermal stress-induced degradation behavior of 8YSZ at 1300, 1400, and 1500°C in terms of phase transformation, local atomic structure, and conductivity. XRD analysis is performed to confirm the phase transformation induced by thermal stress, and the change in the local atomic structure is analyzed by the extended X-ray absorption fine structure (EXAFS). The changes in the electrical conductivity and activation energy with aging were investigated using impedance spectroscopy.

2. Experimental

YSZ powder (TZ-8Y, Tosoh Corporation) was uniaxially pressed at 3 ton/m² to produce a 20 mm disk specimen. The green body was sintered at 1600°C for 6 h and polished to a thickness of 1 mm. The polished specimens were heated in a tube furnace at 1300, 1400, and 1500°C for 100 h. The X-ray diffraction (XRD) patterns of the degraded specimens were collected at room temperature using a step scan procedure ($2\theta = 10\text{--}90^\circ$, step interval: 0.02° , Cu-K α radiation, Rigaku Ultima-IV, Rigaku), and extended x-ray absorption spectroscopy (EXAFS) experiments were performed at the Zr K-edge using the EXAFS facility of the 10C wide-XAFS beamline in the Pohang Accelerator Laboratory (PLS-II, Pohang, Korea). The storage ring was operated at 3.0 GeV with an injection current of 350 mA. The sample surfaces were observed using field-emission scanning electron microscopy (FESEM, MIRA3, TESCAN). The grain size was determined from the SEM images based on ISO 13383–1 [14]. AC impedance measurements were performed with an Ivium-Stat (Ivium, Netherlands) instrument in the frequency range of 10^6 Hz to 10^{-2} Hz using an excitation voltage of 10 mV, at an operating temperature of 1,000°C, in air.

3. Results And Discussion

SEM images of 8YSZ aged at 1300, 1400, and 1500°C for 100 h (hereinafter termed 1300°C 8YSZ, 1400°C 8YSZ, and 1500°C 8YSZ) are shown in Fig. 1. The grain size increased from 10.53 μm to 25.81 μm by thermal stress and the average grain sizes for 10 grains of the 8YSZ specimen at 1300, 1400, and 1500°C were 20.83, 22.17, and 25.81 μm , respectively. This shows that the grain size gradually increased according to the thermal stress.

Figure 2 shows the XRD patterns of the aged 8YSZ. Higher angle shift of (400) peak occurred in 1300, 1400 °C 8YSZ, and the second phase was not identified. It was reported that lattice distortion by formation of a solid solution by the yttrium ions, which are larger than the zirconium ions, was subsequent relaxed by aging [15]. However, the peak shifted to lower angle for the 1500°C 8YSZ. It is related to the tetragonal peak observed at 1500°C 8YSZ, the lower angle shift occurred by the formation of the tetragonal phase, which has a larger lattice [16].

The Zr K-edge Fourier transform analysis using EXAFS was performed to confirm the degradation behavior according to thermal stress (Fig. 3); EXAFS signals were obtained in the range of $3 < k < 11.5 \text{ \AA}^{-1}$ using a Hanning window. The 1st peak at $1.7 \text{ \AA}$ is attributed to Zr-O bonding, and the 2nd peak at $3.31 \text{ \AA}$ was appeared by the Zr-Cation (Zr, Y) [17, 18]. The interatomic distance from the Zr ion to the first nearest neighbor were decreased in 1300, 1400°C 8YSZ by degradation. It was analyzed that the lattice distortion caused by the substitution of Y^{3+} ions larger than that of Zr^{4+} ions is relaxed by aging, resulting in short-range ordering of the oxygen vacancies [19]. But for 1500°C 8YSZ, the interatomic distance to the first nearest neighbor of Zr increased by the formation of the tetragonal phase. As the thermal stress increased, the distance to the second nearest neighbor was shortened, the intensity of Zr-Cation peak decreased, and the intensity of the Zr-O peak increased. These results mean the number of oxygen vacancies decreased due to the formation of a disordered phase by extraction of the cation dopant (Y^{3+}). The increase in the intensity of the Zr-O peak for 1500°C 8YSZ compared to that of 8YSZ treated at 1300°C and 1400°C corresponds to the previous XRD results [20].

Figure 4(a) shows the Nyquist plot from the impedance data for aged 8YSZ. The ohmic resistance (Rohm) appeared in the intercept on the real axis in the high frequency-region, and electrode polarization resistance (R_{pol}) was measured as the difference between the intercepts with the real axis at low and high frequencies [21]. R_{ohm} and R_{pol} increased as the thermal stress increased, and the values of R_{pol} were 6.82, 8.81, and $18.25 \text{ } \Omega \text{ cm}^2$ for 8YSZ and the samples treated at 1300, 1400 and 1500°C, respectively. The grain sizes increased with aging, but the area-specific resistance increased without decreasing. The increase in area-specific resistance by thermal degradation has a greater effect than the decrease in area-specific resistance due to the increase in grain size. Figure 4(b) shows the total ASR Arrhenius plots of 8YSZ before and after degradation. The activation energy of 1300 and 1400°C 8YSZ was 0.86 and 0.87 eV respectively, and the activation energy of 8YSZ at 1500°C was significantly increased to 0.92 eV. These results indicate that the short-range ordering hindered the diffusion of oxygen vacancies and increased the activation energy for 1300, 1400°C 8YSZ, but for 1500°C 8YSZ, the activation energy was significantly increased according to the formation of the tetragonal phase by Y^{3+} destabilization [22].

4. Conclusions

We investigated degradation behavior of yttria stabilized zirconia by thermal stress in terms of phase transformation, local atomic structure, and electrical conductivity. The average grain size of 8YSZ aged for 100h at 1300–1500°C increased from $20.83 \text{ } \mu\text{m}$ (1300°C) to $25.81 \text{ } \mu\text{m}$ (1500°C). The cubic phase was predominant in all aged 8YSZ, and a higher angle shift of the (400) peak occurred with thermal stress at 1300°C and 1400°C 8YSZ, where peak of the tetragonal phase was not identified. For 1500°C 8YSZ, the peak shifted to lower angle by the formation of a tetragonal phase with a large lattice. Zr K-edge EXAFS analysis of the Zr-O local atomic structure showed that the intensity of the Zr-O peak increased and the intensity of the Zr-Cation peak decreased as the aging temperature increased. The changes in the peaks indicate the Y^{3+} ions escaped from the lattice and the oxygen vacancies were reduced, resulting in 8YSZ

thermal stress increased. The activation energy of 1300 and 1400°C 8YSZ was 0.86 and 0.87 eV respectively, and the activation energy of 8YSZ at 1500°C was significantly increased to 0.92 eV. The difference in the activation energy of the specimens depending on the deterioration conditions is attributed to the decrease in oxygen vacancies and the increase in lattice distortion by formation of the tetragonal phase.

Declarations

Acknowledgements

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Figures

Figure 1

SEM images of specimens: (a) 8YSZ, (b) 1300 °C 8YSZ, (c) 1400 °C 8YSZ, (d) 1500 °C 8YSZ.

Figure 2

(a) XRD diffraction patterns and (b) (400) peaks of 8YSZ specimens after thermal stress for 100 h.

Figure 3

Zr K-edge Fourier-transform data for 8YSZ before and after thermal stress for 100 h.

Figure 4

(a) Nyquist plot of 8YSZ before and after thermal stress; obtained in air at 1000 $^{\circ}\text{C}$, (b) Arrhenius plots of the total ASR for 8YSZ before and after thermal stress.