

Effects of Partial Substitution of CeO₂ with M₂O₃ (M = Yb, Gd, Sm) on Electrical Degradation of Sc₂O₃ and CeO₂ Co-doped ZrO₂

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ABSTRACT

Scandia-stabilized zirconia co-doped with CeO₂ is a promising electrolyte for intermediate temperature SOFC, but still shows rapid degradation during a long-term operation. In this study, CeO₂ (1 mol%) as a stabilizer is partially substituted with lanthanum oxides (M₂O₃, M=Yb, Gd, Sm) to stabilize a cubic phase and thus durability in reducing atmosphere. 0.5M0.5Ce10ScSZ electrolytes were prepared by solid state reaction and sintered at 1450°C for 10 h to produce dense ceramic specimens. With addition of the lanthanum oxide, 0.5M0.5Ce10ScSZ showed lower degradation rates than 1Ce10ScSZ. Since Gd₂O₃ showed the highest ionic conductivity among the co-dopants, an electrolyte-supported cell with 0.5Gd0.5Ce10ScSZ was prepared to compare its long-term performance with that of 1Ce10ScSZ-based cell. Maximum power density of 0.5Gd0.5Ce10ScSZ-based cell was degraded by about 2.3% after 250 h, which was much lower than 1Ce10ScSZ-based cell (4.2%).

Key words : SOFC, electrolyte, Sc stabilized zirconia, Co-dopant, Degradation

1. Introduction

For solid oxide fuel cells (SOFC), the problem of insufficient durability resulting from high-temperature operation remains to be a key factor impeding commercialization despite such advantages as high efficiency, possibility of internal modification, use of economic oxide electrode, etc.¹⁾ Since durability of more than about 40000 h is required for commercialization of SOFC for power generation, considerable efforts to lower operation temperatures of SOFC have been continuously made to enhance the durability of SOFC and allow the use of low-cost stack components such as stainless steels.²⁻⁴⁾

For this purpose, development of electrolyte materials showing a high ionic conductivity even at low temperatures along with ceramic manufacturing technology for preparation of thin electrolytes are required. Materials such as La_{0.8}Sr_{0.2}Ga_{0.2}Mg_{0.8}O₃ (LSGM) or Gd-doped CeO₂ (GDC) are promising as electrolytes for the low-temperature SOFC. Despite the high ionic conductivities of these materials, however, yttria-stabilized zirconia (YSZ) are still employed most universally for commercialized SOFC due to the problems with the former such as low thermo-mechanical stability and voltage loss caused by partial electronic current.⁵⁾

While YSZ shows a lower ionic conductivity compared with LSGM or GDC, studies for improving unit-cell performance have been continued through manufacturing of thick-film electrolytes having a thickness of 5 - 10 μm by thick-film processes because of their excellent thermal-mechanical stability and durability in diversified fuel conditions such as CH₄.⁶⁻⁸⁾

YSZ exhibits an ionic conductivity at high temperatures due to oxygen vacancies generated by substitution of Zr⁴⁺ sites with Y³⁺ cations through addition of metal oxides of a low valence such as Y₂O₃ in ZrO₂. Also, since Y₂O₃ increases the mobility of oxygen ions by stabilizing the cubic zirconia structure, zirconia with addition of more than 8 mol% of yttria has been generally used as an electrolyte. Meanwhile, since Sc₂O₃-stabilized zirconia (ScSZ) among cubic zirconia materials displays a higher ionic conductivity compared with YSZ, much study has been conducted for development of low-temperature SOFC using ScSZ. The high ionic conductivities of ScSZ originate from its similar ionic radius to that of Zr⁴⁺ and the resulting crystal structure stability. However, ScSZ with addition of more than 10 mol% of Sc₂O₃ has a problem of drastic reduction in electrical conductivity because of a phase transformation to a rhombohedral phase (β-phase Sc₂Zr₃O₁₇) at a temperature below 600°C.^{3,9-11)} Such martensitic phase transition (c → β) brings about 0.15% of volume change, which can cause fracture of a single cell.¹¹⁾ Arachi *et al.*¹²⁾ showed that addition of more than 0.5 mol% of CeO₂ to 10 mol% Sc₂O₃-doped zirconia could stabilize the cubic structure of ScSZ. While many studies have been conducted to stabilize the cubic ScSZ structure by co-doping of lanthanum oxides such as Gd₂O₃, Yb₂O₃, Y₂O₃ in addition to

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CeO₂. CeO₂ is known to be the most excellent co-dopant thus far.¹³ However, the rapid degradation problem in comparison with YSZ is delaying the use of 1Ce10ScSZ for low-temperature SOFC despite the high ionic conductivity of the latter.

In the present study, an attempt was made to improve the durability of ScSZ particularly under reducing atmosphere by partial substitution of CeO₂ as the stabilizer for ScSZ with different lanthanum oxides (M₂O₃, M = Yb, Gd, Sm). Ambient-temperature crystal structures were investigated as a function of the type of M₂O₃ additives, and durability was evaluated by preparing bulk ceramic specimens and measuring electrical conductivities under hydrogen atmosphere for a long time. Electrical conductivity characteristics for Gd- and Ce-doped ScSZ were considered as a function of added amounts of Gd₂O₃ showing the most excellent durability among additives. Also, electrolyte support type of single cells using electrolytes of 1Ce10ScSZ and 0.5Gd0.5Ce10ScSZ were prepared and their performance degradation characteristics at 850°C were compared.

2. Experimental Procedure

2.1. Preparation of ceramic samples

Electrolytes of 0.5M0.5Ce10ScSZ (M = Gd, Sm, Yb) where CeO₂ added to 1Ce10ScSZ (10 mol% Sc₂O₃-1 mol% CeO₂-89 mol% ZrO₂) was partially substituted with Gd₂O₃, Sm₂O₃, and Yb₂O₃ (CeO₂:MO₃ = 1 : 1 molar ratio) were synthesized by solid state reaction. Since all secondary stabilizing elements have the oxidation number of +3, and are cations having a relatively similar size (Gd⁺³: 1.053 Å, Sm⁺³: 1.079 Å, Yb⁺³: 0.985 Å) to the radius for cations of Sc⁺³ (0.87 Å) or Zr⁺⁴ (0.84 Å), a stable solid solution is formed with zirconia.¹⁴ Also, electrolytes of xGd(1-x)Ce10ScSZ (x = 0.25, 0.5, 0.75, 1.0) where the added amount of Gd₂O₃ was increased to 0.25-1.0 mol% were synthesized. Compositions of the synthesized electrolytes are summarized in Table 1.

Stoichiometry was controlled by quantitative mixing of oxide raw material powders (ZrO₂, CeO₂, Gd₂O₃, Sm₂O₃, and Yb₂O₃). The mixed raw materials were wet-milled for 24 h in ethanol, and dried at 70°C for 24 h, followed by calcination at 1100°C for 5 h. The calcined powders were ball-milled and dried for 24 h again to be prepared as electrolyte powders for ceramic manufacturing. To produce ceramic specimens to be used for evaluation of electrical conductivi-

ties, the powder was uniaxially compressed (250 kgf/cm²) to produce plates of 40 × 40 × 4 mm³ and then sintered at 1450°C for 10 h.

2.2. Characterization of ceramics

Sintered densities of ceramic electrolytes were measured by Archimedes method, and all specimens showed more than 95% of relative sintered density as shown in Table 1. Crystal structures for a sintered body of electrolyte were analyzed by X-ray diffractometry (Rigaku, Model no. D/max-2500 VL/PC, Japan). The sintered ceramics were cut into bar specimens of 3 × 3 × 20 mm, and electrical conductivities were measured by 4-probe DC method. Specimens were painted with Pt electrode (Haeraus, Model 6026) and cured at 900°C for 1 h, all of which were loaded inside a tube-type chamber by connecting Pt wire. Electrical conductivity of each specimen in the atmosphere was calculated from the slope by measuring current-voltage curves in the temperature range of 500 ~ 850°C. By using Source-Measure-Unit (Keithley, Model 2400, USA), currents in the range of 1 × 10⁻⁵ - 1 × 10⁻⁴A were applied to the electrodes at both ends of each specimen, and voltage drops between 2 middle electrodes were sequentially measured by using a multimeter (Keithley, Model 2700, US) equipped with a switching module (Keithley, Model 7700, US). To compare degradation characteristics of the electrolyte materials, H₂ gas was supplied into the chamber, and electrical conductivities were measured at 850°C for about 50 h.

2.3. Fabrication and characterization of single cells

Through performance evaluation of single cells using the commercial electrolyte, 1Ce10ScSZ and 0.5Gd0.5Ce10ScSZ with 0.5 mol% Gd₂O₃ addition as an electrolyte, degradation characteristics of each electrolyte were observed. Disk-shaped sintered body of electrolyte formed by uniaxial compaction was polished and electrolyte-supported cells (ESC) of 20 mm in diameter, 0.3 mm in thickness were produced. To coat Ni-ScSZ cermet anode, a slurry was prepared by mixing commercial NiO (Kceracell, 99.8%, Korea) and 1Ce10ScSZ (Daiichi Kigenso Kagaku Kogyo, 99.9%, Japan) powders with a binder in the ratio of 57 : 43 wt. The prepared anode paste was screen-printed, and then sintered at 1300°C for 3 h by 2°C/min. For the cathode functional layer, a LSM-ScSZ composite was used. The LSM-ScSZ slurry was prepared by mixing commercial LSM (Kceracell, La_{0.8}Sr_{0.2}

Table 1. Sample Notation, Composition, Crystalline Phases, and Sintered Density of M₂O₃-doped 10Sc1CeSZ Ceramics

M	Sample Notation	Composition	Crystalline Phases	Sintered Density, g/cc
Ce	1Ce10ScSZ	(CeO ₂) _{0.01} (Sc ₂ O ₃) _{0.1} (ZrO ₂) _{0.89}	cubic (+rhombohedral)	5.49 (96%)
Yb+Ce	0.5Yb0.5Ce10ScSZ	(Yb ₂ O ₃) _{0.005} (CeO ₂) _{0.005} (Sc ₂ O ₃) _{0.1} (ZrO ₂) _{0.89}	cubic, rhombohedral	5.54 (97%)
Sm+Ce	0.5Sm0.5Ce10ScSZ	(Sm ₂ O ₃) _{0.005} (CeO ₂) _{0.005} (Sc ₂ O ₃) _{0.1} (ZrO ₂) _{0.89}	cubic	5.58 (98%)
	0.25Gd0.5Ce10ScSZ	(Gd ₂ O ₃) _{0.0025} (CeO ₂) _{0.0075} (Sc ₂ O ₃) _{0.1} (ZrO ₂) _{0.89}	Cubic, rhombohedral	5.50 (96%)
Gd+Ce	0.5Gd0.5Ce10ScSZ	(Gd ₂ O ₃) _{0.005} (CeO ₂) _{0.005} (Sc ₂ O ₃) _{0.1} (ZrO ₂) _{0.89}	cubic (+rhombohedral)	5.5 (97%)
	0.75Gd0.5Ce10ScSZ	(Gd ₂ O ₃) _{0.0075} (CeO ₂) _{0.0025} (Sc ₂ O ₃) _{0.1} (ZrO ₂) _{0.87}	cubic	5.48 (96%)
Gd	1Gd10ScSZ	(Gd ₂ O ₃) _{0.01} (Sc ₂ O ₃) _{0.1} (ZrO ₂) _{0.89}	cubic (+rhombohedral)	5.25 (91%)

MnO₃, Korea) and 1Ce10ScSZ powders in the ratio of 57 : 43 wt% with plastic additives. The printed cathode layer was cured at 1200°C for 3 h. LSM paste was screen-printed as a current collector layer onto the LSM-ScSZ composite layer, and cured at 1150°C for 3 h to produce ESC. Performance of single cells was evaluated at 850°C, with the both air and fuel fed by 200 ml/min. At operating temperatures, current-voltage characteristics were continuously measured for 250 h by using a Source-Measure-Unit (Keithley, 2400, USA) for the single cell.

3. Results and Discussion

3.1. Phase and electrical properties of 0.5M0.5Ce10 ScSZ (M= Yb, Sm, Gd)

While 1Ce10ScSZ electrolyte is known to have a stable cubic phase crystal structure which shows a high ionic conductivity, the cubic phase (c) and the rhombohedral phase (β) are known to be intermingled as a function of temperature for its crystal structures.¹³⁾ In the present study, the characteristics of 0.5M0.5Ce10ScSZ electrolyte were evaluated where CeO₂ was partially substituted with M₂O₃ (M = Yb, Sm, Gd) to improve the mixed phase crystal structures (c+β) in the 1Ce10ScSZ electrolyte and the resultant degradation problem in electrical conductivities.

Ambient-temperature XRD analysis result for the sintered specimen of 0.5M0.5Ce10ScSZ electrolyte with substitutional solid-solution of 0.5 mol% of secondary stabilizer (Gd, Sm, Yb) is shown in Fig. 1. As reported in the literature, 1Ce10ScSZ specimen was shown to have a mixture of cubic phase and some β phase. No β phase was detected in the electrolyte where 0.5 mol% Sm₂O₃ was substitutionally solid-solutioned among the sintered specimens of electrolyte with some CeO₂ substituted by secondary stabilizer. However, β phase was detected in the specimens with addition of Gd₂O₃ or Yb₂O₃.

Figure 2 shows the electrical conductivities in air for 0.5M0.5Ce10ScSZ ceramics with addition of 0.5 mol% of M₂O₃. In a high-temperature section above 700°C, 0.5Gd0.5Ce10ScSZ with addition of Gd₂O₃ and 0.5Yb0.5Ce10ScSZ with addition of Yb₂O₃ showed slightly higher electrical conductivities compared with 1Ce10ScSZ. Electrical conductivities for the electrolytes with addition of 0.5 mol% of M₂O₃ were highest in the order of M = Gd > Yb > Sm. As shown in Table 1, such differences in electrical conductivities would not have been caused by the fraction of pores present inside the specimens, since all specimens fired at 1450°C for 10 h showed high sintered densities of more than 95%. In that case, the differences in electrical conductivities should be considered by division into grain conductivity and grain boundary conductivity. Grain boundary conductivity is determined by size of the grain, impurities in the grain boundary, space charge layer, etc. However, since the grain boundary resistance for zirconia is not large at a high temperature above 700°C,^{9,15,16)} its effect may be excluded.

First, grain conductivity is affected by the symmetry

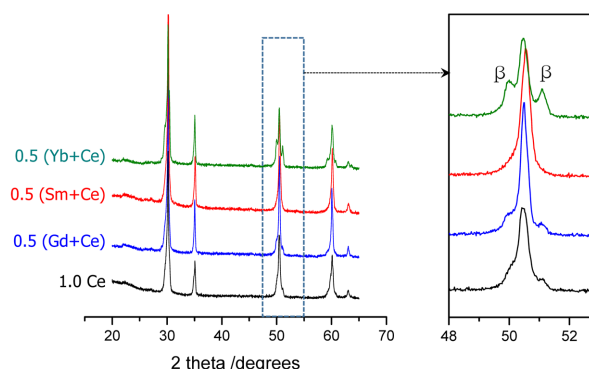


Fig. 1. X-ray diffraction patterns of 0.5M0.5Ce10Sc SZ (M= Yb, Sm, Gd) and 1Ce10ScSZ.

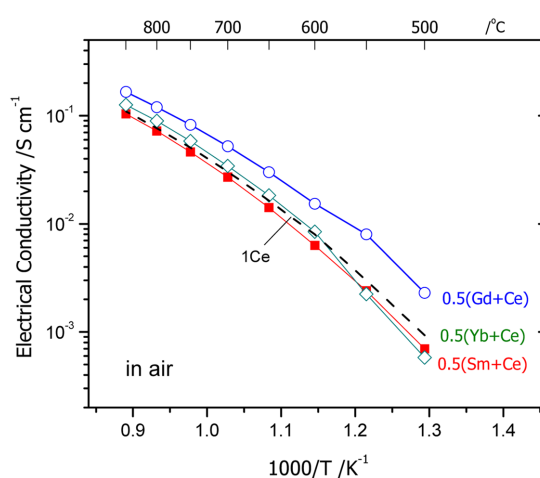


Fig. 2. Temperature dependence of electrical conductivity of 0.5M0.5Ce10ScSZ (M = Yb, Sm, Gd) and 1Ce10ScSZ in ambient air.

caused by phase transition from the cubic fluorite structure to the tetragonal or rhombohedral phase. This is because the mobility of ions shows a higher value in a symmetrical structure. In Fig. 2, electrical conductivities of other specimens showed a gradual change as a function of temperature unlike 0.5Yb0.5Ce10ScSZ which showed a marked change in the slopes below 600°C. Also, activation energy values at high temperatures did not show a large difference, suggesting that there was no large difference in the crystal phases at a high temperature being attributable to additives. In Fig. 1, a rhombohedral phase (β phase) was observed when CeO₂ was partially substituted with Yb₂O₃, Sm₂O₃, or Gd₂O₃. However, since the specimen with addition of Yb₂O₃ where a relatively large amount of rhombohedral phase was observed showed a higher conductivity than the specimen with addition of Sm₂O₃, the effects of existence of β phase present at ambient temperature on electrical conductivity are presumably not large. However, in view that the specimen with addition of Yb₂O₃ exhibited a drastic reduction in conductivities below 600°C, the content of β phase with a relatively large resistance appears to have been increased. Based on the high-temperature XRD results, Yarmolenko *et*

*al.*¹³⁾ reported that the commercial 1Ce10ScSZ ceramic electrolyte showing a metastable cubic phase at ambient temperature was transitioned back to a cubic phase at a higher temperature after transition to a rhombohedral phase around 300 - 500°C. These authors demonstrated it by obtaining 95% of rhombohedral phase after annealing the 1Ce10ScSZ electrolyte at 400°C for 12 h. Therefore, the ambient-temperature crystal phases of 0.5M0.5Ce10ScSZ shown in Fig. 1 appear to be metastable phases, most of which were transitioned to a cubic phase at temperatures above 500°C where electrical conductivities were measured. However, even if a small change in the amount of additives may not greatly affect the crystal structures at a high temperature in the present study, the fine difference in symmetry of a cubic structure can bring about a change in the electrical conductivities. Since lanthanide ions substituted for Zr sites have respectively different ionic radii, the effects of the added stabilizers on lattice distortion and the corresponding reduction in oxygen ion mobility should be considered. However, additional studies such as high-temperature XRD analysis and impedance analysis are required for the clearer analysis.

To consider the degradation characteristics of 0.5M0.5Ce10ScSZ where a part of Ce was substituted from 1Ce10ScSZ electrolyte, changes in electrical conductivity at 850°C under hydrogen atmosphere were observed. Fig. 3 represents normalized (σ/σ_0) electrical conductivities for electrolyte specimens of each formulation under H₂ atmosphere. (σ_0 being the initial conductivity value.) Whereas 1Ce10ScSZ electrolyte exposed to H₂ atmosphere at 850°C for about 50 h showed the highest degradation rate (~28%), 0.5Gd0.5Ce10ScSZ with substitution of Gd showed the lowest degradation rate.

A study on the degradation phenomenon of 1Ce10ScSZ has been conducted by Omar *et al.*¹⁷⁾ These authors reported that continued reduction in conductivities was observed in air and the degradation progressed faster particularly under the reducing atmosphere although addition of 1mol% CeO₂ improved the phase stability of scandia stabilized zirconia. The cause for such degradation in a long term test at 600°C for 3,000 h was considered to be caused by an increase in grain boundary resistance, which was attributed to formation of blocking layers impeding diffusion of oxygen vacancies as Ce⁺³ was gradually diffused to the grain boundary from inside the grain. Also, Ni solid solution from an anode material such as Ni-based cermet was reported to affect the phase transition of ScSZ and the corresponding degradation characteristics.^{15,18)} Therefore, since the concentration of Ce⁺³ was reduced when a part of CeO₂ was substituted with lanthanum oxide (M₂O₃, M = Yb, Gd, Sm), more excellent durability is expected to be observed in comparison with 1Ce10ScSZ. However, additional studies are required to find the causes for delaying of the degradation rates by addition of Gd₂O₃ in comparison with that of Yb₂O₃ or Sm₂O₃.

Meanwhile, concerning the degradation phenomenon under an oxidizing atmosphere, Du *et al.* reported that

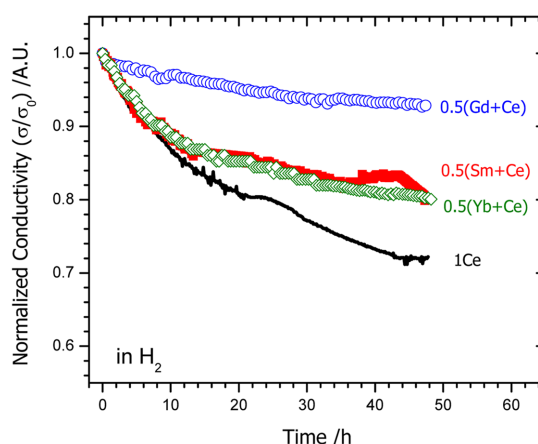


Fig. 3. Degradation of electrical conductivity of 0.5M0.5Ce10ScSZ (M = Yb, Sm, Gd) and 1Ce10ScSZ at 850°C in H₂ atmosphere.

almost no effects of aging were observed in 1Ce10ScSZ while tetragonal → monoclinic phase transition and serious degradation phenomenon occurred only in ScSZ with additions of 4 mol% and 6 mol% Sc₂O₃.³⁾ Such results are in agreement with the results of Haering and Yamamoto on the effects of aging at 1000°C in air.^{11,19)} Haering *et al.* attributed such degradation in the electrical conductivities to the lowered mobility of oxygen vacancies as dipoles [Sc'_{Zr} - V_O'] formed a strong defect association with tripoles [Sc'_{Zr} - V_O' - Sc'_{Zr}]^X. According to their analysis, no severe degradation occurred due to the already high ratio of tripole/dipole when Sc₂O₃ dopant of a high concentration of more than 10 mol% was added. In the present study, the degradation progressed more slowly, although the electrolytes doped with Sm₂O₃ and Yb₂O₃ showed a lower ionic conductivity compared with 1Ce10ScSZ. In terms of the cause, there is a possibility that acceptor concentrations, [Sm'_{Zr}] and [Sb'_{Zr}] were increased as Ce⁺⁴ was substituted with Yb⁺³ or Sm⁺³, resulting in a slight increase in oxygen vacancy concentrations, [V_O']. Since, however, the effect of co-doping with 0.5 mol% on the oxygen vacancy concentration of zirconia stabilized with 10 mol% Sc₂O₃ will be around 5%, the effect is considered to be not large. Meanwhile, the degradation occurring in YSZ or ScSZ may be attributed to formation of the tetragonal or the ordered rhombohedral phase.¹⁹⁾ As with Ce, Yb or Gd apparently suppresses transition from a cubic phase to a rhombohedral phase, and maintenance of a cubic structure is known to occur at higher concentrations compared with Sc.⁹⁾ For a clear explanation, however, studies of high-temperature structure analysis need to be implemented in the future.

3.2. Effects of Gd₂O₃ co-dopant substituted into 1Ce10ScSZ

In the 3.1 above, 0.5Gd0.5Ce10ScSZ with addition of Gd₂O₃ showed the lowest degradation rate. To investigate the effects of Gd content on electrical conductivity, xGd(1-x)Ce10ScSZ specimens were prepared with the added

amounts of Gd_2O_3 being varied within 0.25 - 1 mol%. In Fig. 4, XRD analysis results for the ceramic specimens are shown as a function of the amounts of Gd-substituted solid-solution. In the specimens with formulations of 0.25 - 0.5 mol% for the substituted solid-solution amount of Gd_2O_3 , the metastable β phase was observed, while a single cubic phase was confirmed with a formulation of more than 0.75 mol% for the substituted solid-solution amount. Namely, the amounts of metastable phase (rhombohedral, β) at ambient temperature were reduced, as the more Gd_2O_3 was substituted in lieu of CeO_2 as a structure stabilizer.

Figure 5 shows changes in the electrical conductivity and the activation energy at 600, 700, and 800°C as a function of an increase in added amounts of Gd_2O_3 . When the Gd_2O_3 addition were 0.25 - 0.5 mol%, the highest electrical conductivity occurred, and a tendency for reduction was observed with an increase in the concentrations. Such feature is a typical phenomenon occurring when the acceptor concentra-

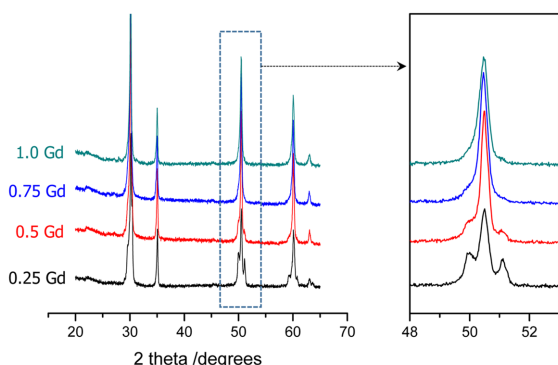


Fig. 4. X-ray diffraction patterns of $(Gd_2O_3)_x(CeO_2)_{0.01-x}(Sc_2O_3)_{0.1}(ZrO_2)_{0.89}$ ($x = 0.0025 \sim 0.01$) sintered pellet at room temperature.

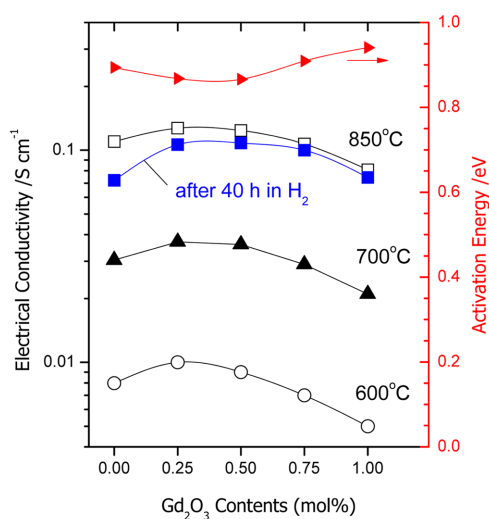


Fig. 5. Electrical conductivity and activation energy as a function of Gd_2O_3 addition in $(Gd_2O_3)_x(CeO_2)_{0.01-x}(Sc_2O_3)_{0.1}(ZrO_2)_{0.89}$ ($x = 0 \sim 0.01$) in air at 600, 700, and 850°C. The blue line presents the electrical conductivity values after measurement for 40 h in hydrogen.

tions are increased in YSZ or ScSZ, and caused by reduction in the concentration of mobile oxygen vacancies due to association of oxygen vacancies $[M'_{Zr} - V_O^{\bullet}]$ or short-range-ordering at high defect concentrations.^{11,16,20} When the added amounts of Gd_2O_3 were increased to more than 0.5 mol%, the gradually increased activation energies showed an evidence for supporting such explanation.

Meanwhile, addition of 0.25 - 0.5 mol% Gd_2O_3 not only enhanced the conductivity of 1Ce10ScSZ, but also improved the durability under hydrogen atmosphere. Also, the durability was increased under hydrogen atmosphere, the more increased the added amount of Gd_2O_3 . This is probably associated with stabilization of the cubic structure resulting from an increase in Gd_2O_3 contents as shown in Fig. 4.

3.3. Electrolyte-supported cell with 0.5Gd0.5Ce10ScSZ

In Fig. 6, a change in output performance as a function of time for ESC where 1Ce10ScSZ electrolyte and 0.5Gd0.5Ce10ScSZ electrolyte were used is shown along with a current-voltage curve. Considering the thickness of electrolyte (300 μm), a relatively high output density of more than 0.8W/cm² was observed at 850°C. Open-circuit voltages (OCV) of two cells were different, being 1.08 Vand about 1.31 V, respectively. The low OCV observed with 1Ce10ScSZ was caused by an increase in the electronic concentrations due to a reduction of Ce^{+4} ($Ce_{Zr}^x \rightarrow Ce_{Zr}^{\bullet} + e^-$) under the reducing atmosphere and the resulting decrease in Nernst potential. Despite the difference in OCV, however, the two cells showed almost similar maximum outputs. Actually, the difference in conductivities between the two electrolytes was not large, and the out performance may be considered almost the same when other variables in the single cell preparation processes are considered. However, it is noteworthy that the single cell of 0.5Gd0.5Ce10ScSZ with substitution by Gd_2O_3 showed a lower degradation rate compared with the single cell of 1Ce10ScSZ. After measurement for about 250 h, the single cell with application of

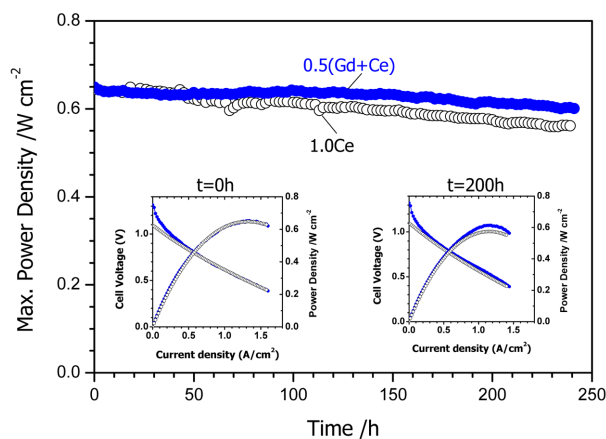


Fig. 6. Long term stability of cell performance of ESCs with 0.5Gd0.5Ce10ScSZ and 1Ce10ScSZ electrolytes (thickness $\sim 300 \mu m$) at 850°C. Initial and final current-voltage curves are inserted.

10Sc0.5Gd0.5CeSZ electrolyte showed a performance reduction by 2.3%, while the single cell with application of 1Ce10ScSZ electrolyte showed a degradation rate (4.2%) which was about twice as fast. Such result is in agreement with the earlier result where addition of Gd₂O₃ suppressed the degradation in electrical conductivities for 1Ce10ScSZ. Degradation of a single cell is caused primarily by an increase in ohmic resistance due to electrolyte and by an increase in polarization resistance resulting from degradation in catalyst characteristics of the electrode. Generally, the increase in polarization resistance arises from coarsening of electrode particles due to high-temperature operation or reduction in active areas due to deposition of impurities from outside and reaction, etc. Since the same electrodes were used on both faces of each electrolyte support in the present study, the difference observed between the two types or cells was presumably caused by an increase in ohmic resistance of the electrolyte.

4. Conclusions

1Ce10ScSZ stabilized to a cubic structure by CeO₂ co-dopant showed a rapid degradation in the electrical conductivities particularly under the reducing atmosphere. In the present study, all of Gd₂O₃, Sm₂O₃, and Yb₂O₃ added to partially substitute for CeO₂ showed stable electrical conductivities compared with 1Ce10ScSZ, and 0.5Gd0.5Ce10ScSZ showed the highest ionic conductivity together with the lowest degradation rate. In the investigation of electrical conduction characteristics as a function of added amounts of Gd₂O₃, addition of 0.25 - 0.5 mol% Gd₂O₃ was observed to exhibit the highest electrical conductivity, and degradation rates under the hydrogen atmosphere was affirmed to be lowered as a result of addition of Gd₂O₃. In agreement with an increase in durability under the hydrogen atmosphere, the single cell using 0.5Gd0.5Ce10ScSZ electrolyte showed an improved durability as compared with 1Ce10ScSZ.

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