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Transport properties of ceria–zirconia–yttria solid solutions $\{(CeO_2)_x(ZrO_2)_{1-x}\}_{1-y}(YO_{1.5})_y$ ($x = 0$–1, $y = 0.2, 0.35$)

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Abstract

The electron and hole conductivity, oxygen transport property and thermal expansion behavior of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$ solid solution were investigated and the effect of yttrium content was examined by comparing the data with those of $\{(CeO_2)_{1-x}(ZrO_2)_x\}_{0.8}(YO_{1.5})_{0.2}$. The electron conductivity of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$ measured by ion blocking method was one order lower than that of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.8}(YO_{1.5})_{0.2}$. The increase of yttrium content suppressed the phase transition from cubic to pyrochlore structure in reducing atmosphere. The oxygen isotope diffusivity and surface exchange rate constant of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$ are considered to be comparable to those of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.8}(YO_{1.5})_{0.2}$. The chemical expansion due to the reduction of cerium ion was observed as well as for rare earth doped ceria. The compatibility of the material as an anode substrate in solid oxide fuel cells is discussed.

Keywords: SOFC; Ion-blocking; Hole conductivity; Diffusion; Thermal expansion

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1. Introduction

Ceria–zirconia solid solutions have been investigated from viewpoints of interesting catalytic activity and mixed conductivity. Ozawa et al. reported the application of CeO_2–ZrO_2 solid solutions to the three-way catalysts for automobiles [1]. Moreover, the CeO_2–ZrO_2–$YO_{1.5}$ solid solution is investigated as a promising material for oxygen permeable membranes, which can be applied to electro-catalytic reactors or oxygen gas separators. The temperature and oxygen partial pressure dependence of total and ionic conductivity of $\{(CeO_2)_{1-x}(ZrO_2)_x\}_{0.9}(Y_2O_3)_{0.1}$ have been reported by several researchers [2–4].

We have investigated the transport properties of the system $\{(CeO_2)_x(ZrO_2)_{1-x}\}_{0.8}(YO_{1.5})_{0.2}$, such as oxygen isotope diffusivity (D_O^*) and surface exchange rate (k) [5] or electron/hole conductivity (σ_e, σ_h) [6] because we think such transport properties in the oxides may affect the anode reactions of solid oxide fuel cells (SOFC) in which the fuel reacts with oxide ions come through the electrolyte. The electron conductivity (σ_e) of $\{(CeO_2)_x(ZrO_2)_{1-x}\}_{0.8}(YO_{1.5})_{0.2}$ drastically increased with cerium content (x) and had a maximum around $x = 0.5$ [6]. Concerning the oxygen transport properties, the oxygen isotope diffusivity has a minimum at $x = 0.5$ [5], however, the oxygen surface exchange rate constant (k) has a maximum around $x = 0.4$, which is similar to the compositional dependence of electron conductivity.

However, in the electron conductivity measurement of $\{(CeO_2)_x(ZrO_2)_{1-x}\}_{0.8}(YO_{1.5})_{0.2}$, it was difficult to obtain the precise data in lower oxygen partial pressures, the oxygen partial pressures lower than 10^{-8} Pa at $T = 973$–1273 K. The data exhibited some scattering and their reproducibility was poor. It indicates the phase transition from fluorite to pyrochlore structure. This phase transition has been reported for CeO_2–ZrO_2 solid solutions by several researchers including complicated metastable phases [7–11]. Ikryannikova et al., reported that 10 mole% $YO_{1.5}$ addition to CeO_2–ZrO_2

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solid solution may stabilize the cubic phase, however, it does not suppress the formation of pyrochlore phase in reducing atmosphere at high temperatures [8].

In this paper, we investigated ceria–zirconia–yttria solid solution with higher yttria content, $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$, in order to suppress the phase transition. The hole and electron conductivity, and oxygen isotope diffusivity was measured and compared with the results of samples with lower yttrium content. Since we have been interested in this material as a candidate of anode support materials in SOFC, the thermal expansion behavior was also checked in air and in reducing atmospheres.

2. Experimental

The sample was prepared by solid-state reaction of CeO_2 (Wako), Y_2O_3 (Wako) and ZrO_2 (TOSOH TZ-0). The powders in appropriate amounts were mixed in TZP ball mill with ethanol as solvent. The dense polycrystalline body of the solid solution was prepared by pressing the powder mixture into pellets by one-axial press under 150 MPa and cold iso-static press (CIP) at 300 MPa, and then sintered in air at $T = 1873$ K for 10 h. Over 99% of theoretical density was obtained. The phase purity of sintered sample was checked by X-ray diffraction analysis (XRD), which exhibited a single phase of fluorite structure without any secondary peaks.

The surface of the pellet was polished by diamond pastes. For comparison of the thermal expansion behavior, the dense polycrystalline bodies of yttria stabilized zirconia (YSZ, $Zr_{0.8}Y_{0.2}O_{1.9}$), and yttria doped ceria (CYO, $Ce_{0.8}Y_{0.2}O_{1.9}$) were prepared by the same method.

The electric and hole conductivities as minor carrier were determined by a dc-polarization method using a Hebb–Wagner ion blocking cell at 1173 and 1273 K. The detail of the ion blocking cell is described in our previous paper [6]. Platinum paste was painted on both surfaces of a sample pellet and fired at 1273 K in air. The oxygen partial pressure at the outer electrode ($p_{out}(O_2)$) was fixed around $p_{out}(O_2) = 1$ kPa by flowing 1% O_2–Ar. The dc-polarization measurements were performed with a potentiostat (Toho Technical Research, potentiostat/galvanostat 2020). When the electric voltage was applied to the samples, the current changed until the steady state was established. In the equilibrium state, the oxygen chemical potential at the inner platinum electrode/sample interface was reduced against the outer electrode. The oxide ion flow was blocked at the inner electrode, because no electrochemical potential gradient of oxide ion exists inside the samples. The measured current should be electronic current governed by electrons or holes in the sample. The electronic or hole conductivity ($\sigma_e + \sigma_h$) was determined by the following equation:

$$\sigma_e + \sigma_h = \frac{L}{A}\left(\frac{\partial I_e}{\partial E_{app}}\right) \tag{1}$$

where A and L are the electrode area and the thickness of the sample, E_{app} the applied voltage and I_e is the steady current. The oxygen partial pressure at the inner electrode $p(O_2)$ was calculated by using the following equation:

$$E_{app} = \frac{RT}{4F}\ln\left(\frac{p_{out}(O_2)}{p(O_2)}\right) \tag{2}$$

where R is the gas constant, T the absolute temperature, F the Faraday's constant and $p_{out}(O_2)$ is the oxygen partial pressure in outer atmosphere, which was fixed to 1 kPa.

The oxygen isotope diffusivity and oxygen surface exchange coefficient were determined by using $^{18}O_2$ exchange. The sample was cut into small pieces (3 mm × 3 mm × 1 mm), and placed in a small cell attached in a closed system. The 21 kPa of oxygen gas (O_2) was introduced in the system and the cell was kept at $T = 973$ K for 1 h. Then the atmosphere is changed to 21 kPa of $^{18}O_2$ (ISOTEC Ltd., 99.7% enriched $^{18}O_2$) at the same temperature and kept for 300 s and quenched. The depth profiles of the secondary ion intensities ($I(^{16}O^-)$, $I(^{18}O^-)$) were collected by secondary ion mass spectrometry (SIMS, CAMECA ims5f, Cameca Instruments Co., France, primary ion Cs^+: 10 kV, secondary ion accelerating voltage −4.5 kV). The oxygen isotope diffusivity (D_O^*) and oxygen surface exchange rate constant (k) were determined by fitting the obtained profile to the diffusion equation suggested by Crank [12]:

$$\frac{X - X_{bg}}{X_g - X_{bg}} = \operatorname{erfc}\frac{z}{2\sqrt{(D_O^* t)}} - \exp(bz + b^2 D_O^* t)\operatorname{erfc} \times \left\{\frac{z}{2\sqrt{(D_O^* t)}} + b\sqrt{(D_O^* t)}\right\} \tag{3}$$

$$b = \frac{k}{D_O^*} \tag{4}$$

where X corresponds to the normalized ^{18}O concentration derived from the intensity ratio of SIMS secondary ion $I(^{18}O)/\{I(^{16}O) + I(^{18}O)\}$, X_{bg} the natural abundance of ^{18}O (=0.002), X_g the ^{18}O concentration in gaseous phase which was fixed at $X_g = 0.97$ in all experiments, t the annealing time and z is the depth from the surface.

The thermal expansion measurements of dense polycrystalline bodies of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$, $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.8}(YO_{1.5})_{0.2}$ and $(CeO_2)_{0.8}(YO_{1.5})_{0.2}$ was carried out by thermal mechanical analysis (TMA 320, Seiko Instruments, Ltd., Japan) in the temperature range from 300 to 1273 K under the load of 1 g. Since the samples are prepared by sintering in air, the sample heating in TMA measurement in air results in the thermal expansion coefficients (TECs) of normal composition with a good reproducibility. However, when the sample is heated in a reducing atmosphere, a rare earth doped ceria exhibits a very large expansion in the first heating, which includes thermal expansion and chemical expansion with the formation of additional oxygen vacancy. Hence, the apparent thermal expansion coefficient in a reducing atmosphere in the first heating is extraordinary

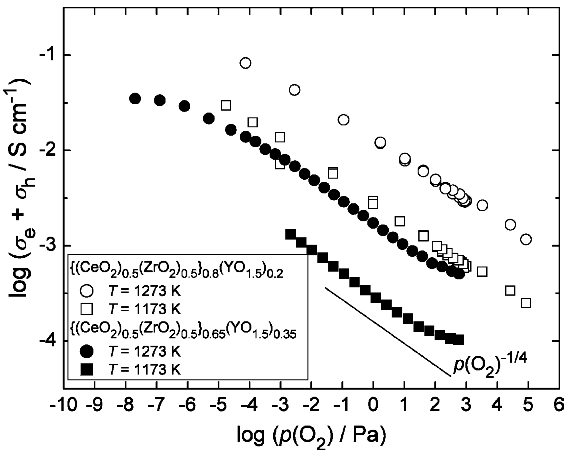

Fig. 1. Hole and electron conductivity of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$ (closed symbols) as a function of oxygen partial pressure ($p(O_2)$). The literature data of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.8}(YO_{1.5})_{0.2}$ are shown as open symbols [6].

higher than the thermal expansion coefficient in air. The chemical expansion in a reducing atmosphere causes the dimensional instability of the materials in anode atmospheres of SOFC, in which the oxygen potential may drastically change with operation modes. Our interest is if such a chemical expansion of rare earth doped ceria can be suppressed by increasing yttrium content. Hence, we carried out the TMA measurements for the samples first in air, and then in a reducing atmosphere ($1\%H_2 + 2\%H_2O + 97\%Ar$) to check the difference of expansion behavior among different atmospheres.

3. Results and discussion

The electronic and hole conductivities of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$ measured by Hebb–Wagner method were shown in Fig. 1, and they are compared with the data of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.8}(YO_{1.5})_{0.2}$ reported in our previous paper [6]. The electronic conductivity data of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$ are ca. one-tenth of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.8}(YO_{1.5})_{0.2}$. The hole conductivity was detected for $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$ at $p(O_2) > 10^2$ Pa, whereas no hole conductivity was detected for $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.8}(YO_{1.5})_{0.2}$ even at $p(O_2) = 10^5$ Pa.

Moreover, it should be noted that the increasing yttrium content resulted in the stabilization on fluorite cubic phase of ceria–zirconia–yttria solid solution. The electronic conductivity measurement for $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$ was possible until the oxygen partial pressure lower than 10^{-8} Pa at $T = 1273$ K as shown in Fig. 1. For $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.8}(YO_{1.5})_{0.2}$ the reproducible data could not be obtained at $p(O_2) < 10^{-5}$ Pa because the data exhibited irreversible scattering. We think that this scattering is due to the phase formation from cubic to pyrochlore phase transition. According to the literatures, this phase transition mechanism is governed by small change of oxide ion coordination, therefore it is sometimes hard to observe by conventional XRD. However, the data scattering of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.8}(YO_{1.5})_{0.2}$ in reducing atmosphere indicates that such a small structure change is enough to affect the transport properties. The present data of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$ indicates that the increase of yttrium content in ceria–zirconia–yttria solid solution may suppress the pyrochlore phase formation.

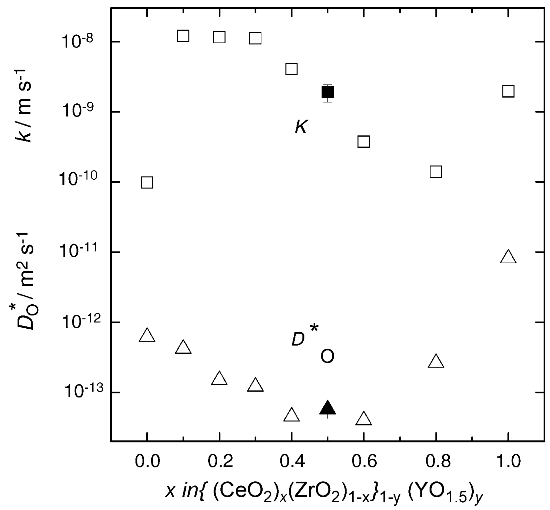

Fig. 2. Oxygen diffusivity (D^*_O, triangles) and oxygen surface exchange rate constant (k, squares) of $\{(CeO_2)_x(ZrO_2)_{1-x}\}_{1-y}(YO_{1.5})_y$ at $T = 973$ K as a function of cerium content (x). Open symbols: $y = 0.2$ [5] and closed symbols: $y = 0.35$ (present data).

The oxygen isotope diffusivity (D^*_O) and oxygen surface exchange rate constant (k) of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$ in air were plotted in Fig. 2 and compared with those of $\{(CeO_2)_x(ZrO_2)_{1-x}\}_{0.8}(YO_{1.5})_{0.2}$ as a function of cerium content (x). The oxygen isotope diffusivity and surface of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$ are just between those of $\{(CeO_2)_{0.4}(ZrO_2)_{0.6}\}_{0.8}(YO_{1.5})_{0.2}$ and $\{(CeO_2)_{0.6}(ZrO_2)_{0.4}\}_{0.8}(YO_{1.5})_{0.2}$. It indicates that the increase of yttrium content does not significantly affect the oxygen transport properties. Since the oxygen isotope diffusivity can be correlated with the oxide ion conductivity by Nernst–Einstein theory, it can be suggested that $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$ has a comparable conductivity to $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.8}(YO_{1.5})_{0.2}$.

The apparent thermal expansion coefficients of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$ in air and reducing atmosphere (first time only) are shown in Table 1. It should be noted that the TEC in reducing atmosphere is apparently larger than in air. This is because the tetravalent cerium ion (Ce^{4+}) is reduced to trivalent ion (Ce^{3+}), which is accompanied with the oxygen vacancy formation. The data of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.8}(YO_{1.5})_{0.2}$ and YDC ($(CeO_2)_{0.8}(YO_{1.5})_{0.2}$) are also shown in Table 1, and they exhibited larger TECs in reducing atmosphere than $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$, which is probably due to the larger amount of cerium content.

Table 1
Thermal expansion coefficients (TECs) of CeO_2–ZrO_2–Y_2O_3 solid solutions

Composition	Atmosphere	Temperature range (K)	TEC (MK^{-1})
$\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$	Air	333–1283	11.47
	Ar–1%H_2–1%H_2O	338–1234	14.22
$\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.8}(YO_{1.5})_{0.2}$	Air	351–1108	12.37
	Ar–1%H_2–1%H_2O	336–1278	14.34
$(CeO_2)_{0.8}(YO_{1.5})_{0.2}$	Air	346–1243	12.16
	Ar–1%H_2–1%H_2O	342–1260	15.18

4. Summary

The present investigation clarified some physico-chemical properties of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$. Considering these materials as a SOFC component, the following facts should be emphasized.

The electron conductivity of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$ was one-tenth of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.8}(YO_{1.5})_{0.2}$, which indicates that the increase of yttrium content may stabilize the tetravalent cerium ion (Ce^{4+}) in the fluorite structure. Furthermore, the fluorite structure of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$ has better stability than $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.8}(YO_{1.5})_{0.2}$ in reducing atmosphere. As the result, it is supposed that the conductivity of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.65}(YO_{1.5})_{0.35}$ in strongly reducing atmosphere will be better than that of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.8}(YO_{1.5})_{0.2}$.

However, the increase of yttrium content does not perfectly suppress the Ce^{3+} formation, hence the isothermal expansion is observed for the present composition as well as the cases of $\{(CeO_2)_{0.5}(ZrO_2)_{0.5}\}_{0.8}(YO_{1.5})_{0.2}$ or yttrium doped ceria. The compositions with higher yttrium content should be examined to clarify the possibility to overcome this problem.

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