Electronic Conductivity Measurement of Gd– and Sm-Doped Ceria 
Ceramics by Hebb-Wagner Method

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Gadolinium- and samarium-doped ceria powders with compositions Ce$_{1-x}$Gd$_x$O$_{1.9}$ (GDC) and Ce$_{1-x}$Sm$_x$O$_{1.9}$ (SDC) were prepared by heating the oxalate solid solution $\left(Ce_{0.8}R_{0.2}O_2 \right) \left(Ce_2O_2 \right)$ ($R$: Gd, Sm) at 873 K in air. As-prepared powders with secondary particle size of 0.5–1 $\mu$m were densified to 96.6–99.4% relative density by sintering in air at 1773 K for 4 h. The electronic current of disk sample was measured in a temperature range from 773 to 1113 K by direct current polarization method using Hebb-Wagner ion blocking cell. A linear relationship, which was theoretically predicted, was measured between log I (electronic current) and E (applied voltage) for GDC and SDC in the applied voltage range of 0.2–1.4 V. The slopes of log $\sigma$ (electronic conductivity)–log Po$_2$ (oxygen partial pressure) plot for GDC agreed with the theoretically predicted value of $-1/6$. However, the slope for SDC was in the range from $-0.10$ to $-0.16$. The transport number of oxide ion for the GDC and SDC was significantly higher than the previously reported values.

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1. Introduction

The proposed solid oxide fuel cell (SOFC) consists of yttria-stabilized zirconia (YSZ) electrolyte, Ni/YSZ cermet anode, La$_{1-x}$Sr$_x$MnO$_3$ cathode, and LaCrO$_3$ interconnector.$^{1,1}$ This system is operated at about 1273 K to enhance the diffusion of oxide ions. However, the increase of oxide ion conductivity and the decrease of the thickness of solid electrolyte, lead to the decrease of operation temperature of SOFC. It is reported that rare-earth-doped ceria (RDC) has a higher oxide ion conductivity than YSZ and the transport number of oxide ion in RDC favorably approaches unit with decreasing temperature.$^{11}$ That is, RDC is a candidate of solid electrolyte for the low temperature operation of SOFC.$^{3,7}$ In the test of cell using GDC electrolyte at 873 K, the high power density of 750 and 769 mW/cm$^2$ is reported for the fuel of dry methane and wet hydrogen with 2.9 vol% H$_2$, respectively.$^8$ The problem pointed out on RDC is the increased electronic conduction at a low oxygen pressure, which is accompanied by the reduction of Ce$^{4+}$ to Ce$^{3+}$. The oxygen partial pressure at which the ionic conductivity is equal to the electronic conductivity, has been reported as follows at 1073 K: $10^{-10}$ Pa for Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$,$^9$ $10^{-8}$ Pa for Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$,$^9$ and $10^{-12}$ Pa for Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$. In our previous work,$^{10}$ the electrical conductivity of Ce$_{0.8}$Re$_{0.2}$O$_{1.8}$ ($R$ = Yb, Y, Sm, Nd) was not sensitive to the oxygen partial pressure in the range from $10^0$ to $10^{-14}$ Pa at 609–1159 K. This result suggests a relatively stable structure of RDC at a low oxygen pressure. This paper reports on the electronic conductivity of RDC measured by direct current (DC) polarization method using Hebb-Wagner ion blocking cell.

2. Experimental procedure

2.1 Sample preparation

The detailed powder preparation method of RDC with a composition Ce$_{0.8}$Gd$_{0.2}$O$_{1.8}$ (R: Gd, Sm) is reported in our previous papers.$^{11,12}$ The oxalate solid solution $\left(Ce_{0.8}R_{0.2}O_2 \right) \left(Ce_2O_2 \right)$ was produced at room temperature by adding the mixed nitrate solution (0.2 M) of Ce and R into 0.4 M oxalic acid solution. The formation of the solid solution was examined by X-ray diffraction and thermogravimetric differential thermal analysis (TG-DTA). The coprecipitated oxalate powder decomposed to polycrystalline oxide solid solution by heating upon to 873 K. Our previous observation of Y-doped ceria particles by transmission electron microscope revealed that elongated secondary particles produced at 873 K consisted of spherical primary particles of about 10 nm diameters.$^{12}$ As-prepared GDC and SDC powders consisted of platelike secondary particles of 0.5–1.0 $\mu$m and were compacted isostatically under a pressure of 294 MPa to a pellet of 10–20 mm in diameter and 2 mm in thickness. The sintering at 1773 K for 4 h in air (SPM 6512 electric furnace, Marusho Electro-Heat Co., Ltd., Japan) gave dense compacts above 97% of theoretical density. The porosity of GDC and SDC is shown in Table 1. The open pores were less than 1%. As-sintered samples were polished with diamond paste of 1 $\mu$m. Figure 1 shows the microstructures of (a) GDC and (b) SDC sintered at 1773 K for 4 h. As seen in Fig. 1, their microstructures consisted of relatively uniform grains of 0.5–4.4 $\mu$m. The median sizes of GDC and SDC were 2.0 and 2.2 $\mu$m, respectively. No sig-

| Table 1. Relative Density of Gd-doped Ceria (GDC) and Sm-doped Ceria (SDC), Sintered at 1500°C for 4 h in Air |
|-----------------|-------------------|-------------------|
|                | GDC               | SDC               |
| Relative density (%) | 97.75             | 97.53 – 99.41     |
| Open pore (%)    | 1.03              | 0.14 – 0.30       |
| Closed pore (%)  | 1.22              | 2.33 – 0.29       |
| Theoretical density (g/cm$^3$) | 7.246             | 7.135             |
significant pores were observed in these microstructures.

2.2 Measurement of electronic conductivity by Hebb-Wagner method

The electronic conductivity was measured by DC polarization using a Hebb-Wagner ion blocking cell in the temperature range from 773 to 1113 K under the oxygen partial pressure range of PO2 = 10^{-2} \text{--} 10^{-32} \text{Pa}. The ion blocking cell is schematically shown in Fig. 2. Au paste (TR-1301, Tanaka Kikinzoku Kogyo Co., Japan) was painted on both surfaces of a disk sample with 8 mm diameter and 1.5 mm thickness and fired at 1223 K in air. The Au electrode surface area was about 0.2 cm². The sample with Au electrodes was attached to a high purity alumina holder (Al₂O₃ > 99.99 mass%) using glass O-ring (HV10R, Iwaki Glass Co., Japan). The sample on the O-ring was heated to 1223 K under the application of the stress through SiO₂–Al₂O₃ tube and cooled to 773–1113 K to measure the electronic conductivity. The DC polarization measurement was performed with potentiometer (HA–501G, Hokuto Denko Co., Japan). The applied voltage (E) varied from 0.2 to 1.4 V. When the voltage was applied to the sample, the oxygen gas inside of the sealed holder is exhausted through RDC sample toward the outer side. In the equilibrium state, the oxygen chemical potential at the inner Au electrode/sample interface is reduced against the outer Au electrode (reversible electrode). However, the oxide ion flow is blocked at the inner electrode because of the applied potential difference (See Section 3.1). The measured current should be electronic current, governed by electrons or holes in the sample.

3. Theoretical approach to electronic conduction

3.1 Electronic conductivity and applied voltage

The electronic conductivity (σₑ) at a low oxygen partial pressure is expressed by Eq. (1) as a function of oxygen partial pressure (PO₂),

\[ \sigmaₑ = C₁PO₂^{-n} \]  

(1)

where C₁ and n are the constants. The oxygen partial pressure at the inner and outer electrodes of sample in Fig. 2 is related to the applied voltage (E), Faraday constant (F), gas constant (R) and temperature (T) by Eq. (2) (Nernst equation),

\[ E = \frac{RT}{4F} \ln \left( \frac{PO₂(\text{outer})}{PO₂(\text{inner})} \right) \]  

(2)

Combination of Eqs. (1) and (2) gives Eq. (3),

\[ \sigmaₑ = C₁PO₂(\text{outer})^{-1/n} \exp \left( \frac{4FE}{nRT} \right) \]  

(3)

Since PO₂ (outer) is equal to 0.21 × 10⁵ Pa in air, Eq. (3) indicates a linear relationship between ln σₑ and E. On the other hand, σₑ is defined by Eq. (4),

\[ \sigmaₑ = \frac{L}{A} \frac{dl}{dE} \]  

(4)

where A is the surface area of electrode, L the thickness of sample and I the electronic current. Substitution of Eq. (3) into Eq. (4) provides Eq. (5),

\[ dl = \frac{A}{L} C₁PO₂(\text{outer})^{-1/n} \exp \left( \frac{4FE}{nRT} \right) dE \]  

(5)

Integration of Eq. (5) between I = 0 at E = 0 and I = I at E = E results in Eq. (6)

\[ I = \frac{nAC₁RTPO₂(\text{outer})^{-1/n}}{4FL} \left[ \exp \left( \frac{4FE}{nRT} \right) - 1 \right] \]  

(6)

Equation (6) represents the I-E relation for electronic conduction and is transformed into Eq. (7),

\[ \ln I = \ln C₂ + \ln \left[ \exp \left( \frac{4FE}{nRT} \right) - 1 \right] \]  

(7)

where C₂ is equal to nAC₁RTPO₂(outer)^{-1/n}/4FL in Eq. (6). For the condition of exp (4FE/nRT) > 1, Eq. (7) is approximated to Eq. (8),
\[ \ln I = \ln C_2 + \frac{4FE}{nRT} \]  

(8)

Equation (8) is useful to determine both the values of \( C_2 \) and \( n \) from the linear relationship between \( \ln I \) and \( E \). The condition of \( \exp \left( \frac{4FE}{nRT} \right) \geq 100 \) in Eq. (7) can reduce the analysis error below 0.2% for the approximation of \( \ln \left( \exp \left( \frac{4FE}{nRT} \right) - 1 \right) = \left( \frac{4FE}{nRT} \right) \). The allowed applied voltage \( E \) is given by Eq. (9) for the approximation error below 0.2% and plotted in Fig. 3 as a function of measurement temperature:

\[ E \geq 9.921 \times 10^{-7} \text{ nT} \]  

(9)

The measurement temperature of electronic conduction was changed in the range from 773 to 1113 K. As \( n \) value, which was discussed in Section 3.2, 4 and 6 were substituted in Eq. (9) to clarify the allowed applied voltage range. The allowed applied voltage for the precise analysis of electronic conductivity by Eq. (8), which depends on the \( n \) value, should be increased at a higher measurement temperature. In the present experimental condition, the electronic conductivity measured at the applied voltage higher than 0.5 V has a high reliability. In this applied voltage range (\( >0.5 \text{ V} \)), the oxygen partial pressure becomes lower than \( 10^{-7} \text{ Pa} \) at 873 K and \( 10^{-3} \text{ Pa} \) at 1073 K (Eq. (2)).

3.2 Possible interactions between RDC and electron

The possible interaction between electron and Ce site or O site in RDC is expressed by Eqs. (10) and (11).

\[ \text{Ce}_{\text{Ce}^+} + e^- \rightleftharpoons \text{Ce}_{\text{Ce}^+} \]  

(10)

\[ \text{O}_2^- + 2e^- + \frac{1}{2} \text{O}_2 \]  

(11)

Equation (12) provides the total reaction of Eqs. (10) and (11).

\[ \text{Ce}_{\text{Ce}^+} + 2\text{O}_2^- \rightleftharpoons \text{Ce}_{\text{Ce}^+} + 2\text{V}_{\text{O}^2-} + 3e^- + \text{O}_2 \]  

(12)

The equilibrium constant \( K \) for Eq. (12) is expressed by Eq. (13).

\[ K = \frac{(\text{Ce}_{\text{Ce}^+})(\text{V}_{\text{O}^2-})^2(\text{e}^-)^3}{\text{Ce}_{\text{Ce}^+}} \]  

(13)

The substitution of \( R \) for Ce in CeO\(_2\) fluorite structure produces oxygen vacancy by Eq. (14),

\[ \text{CeO}_2 \rightleftharpoons 2\text{Ce}_{\text{Ce}^+} + 3\text{O}_2^- + \text{V}_{\text{O}^2-} \]  

(14)

That is, the concentration of oxygen vacancy is a total by Eqs. (12) and (14).

\[ [\text{V}_{\text{O}^2-}] = \frac{1}{2} [\text{Ce}_{\text{Ce}^+}] + \frac{3}{2} \left[ \text{e}^- \right] \]  

(15)

When the concentration of oxygen vacancy is dominated by Eq. (14), the following relation is derived from Eqs. (13) and (14).

\[ [\text{e}^-] = \left( \frac{4K}{[\text{Ce}_{\text{Ce}^+}]^2} \right)^{1/3} \left( \frac{([\text{Ce}_{\text{Ce}^+}][\text{O}_2^-]^2)^{1/3}}{[\text{Ce}_{\text{Ce}^+}]} \right) \]  

(16)

For the condition of [\text{e}^-] \( \geq 3([\text{Ce}_{\text{Ce}^+}] \) in Eq. (12), Eq. (16) is converted to Eq. (17), giving a linear relation with \(-1/4\) of slope in the log [\text{e}^-] \(-\log \text{P}_{\text{O}_2}\) plot.

\[ [\text{e}^-] = \left( \frac{12K([\text{Ce}_{\text{Ce}^+}][\text{O}_2^-]^2)^{1/4}}{[\text{Ce}_{\text{Ce}^+}]^2} \right) \]  

(17)

On the other hand, when Eq. (12) dominates the concentration of oxygen vacancy, the following relation is derived from Eq. (13).

\[ [\text{e}^-] = \left( \frac{9K}{4} \right)^{1/5} \left( \frac{([\text{Ce}_{\text{Ce}^+}][\text{O}_2^-]^2)^{1/5}}{[\text{Ce}_{\text{Ce}^+}]} \right) \]  

(18)

For the condition of [\text{e}^-] \( \geq 3([\text{Ce}_{\text{Ce}^+}] \) in Eq. (12), Eq. (18) is written as Eq. (19), giving a linear relation with \(-1/6\) of slope in the log [\text{e}^-] \(-\log \text{P}_{\text{O}_2}\) plot.

\[ [\text{e}^-] = \left( \frac{27K([\text{Ce}_{\text{Ce}^+}][\text{O}_2^-]^2)^{1/6}}{4} \right) \]  

(19)

Therefore, the above possible interactions between RDC and electron predicts the electronic conduction in proportion to \text{P}_{\text{O}_2}^{-1/4} or \text{P}_{\text{O}_2}^{-1/6} of oxygen partial pressure.

4. Results and discussion

4.1 Electronic conductivity

Figure 4 shows the current decay of SDC at 0.6 V in the temperature range from 773 to 1073 K, measured with the Hebb-Wagner ion blocking cell as a function of measuring time. When an electric potential was applied, the current decreased within 10 min of measuring time and approached a constant value after 30 min. The early stage current includes both the motion of oxide ion and electron. The latter constant current corresponds to the electronic current because of the blocking of oxide ion. The electronic conductivity increased at a higher heating temperature and also at a large applied voltage (See Figs. 5 and 6). A similar result was also measured in GDC sample. This result is explained by the influence of T (1st term) and E (2nd term) in the right side of Eq. (6). The increase of these factors enhances the electronic conductivity.
linearity with 0.993–0.999 of the correlation coefficient in a wide applied voltage range of 0.2–1.4 V. This result supports the good approximation by Eq. (8) for the measured electronic conductivity. From the intercept at \( E = 0 \) in Figs. 5 and 6, the \( n \) value in Eq. (8) was determined and shown in Fig. 7 as a function of measuring temperature. The \( n \) value measured in GDC was close to 6 in the temperature range from 873 to 1113 K, except for the measurement at 773 K. This result strongly supports the interaction between \( \text{Ce}^{4+} \) and electron as expressed by Eq. (19). That is, oxygen vacancy, electron, and \( \text{Ce}^{4+} \) were formed according to Eq. (12) at a low oxygen partial pressure. On the other hand, the \( n \) value in SDC was higher than 6 and approached 6 as the heating temperature was increased to 1073 K. The reason for this tendency of \( n \) value is not explained by the interaction between SDC and electron discussed in Section 3.2.

Xiong et al.\(^{14} \) reported that the electronic conduction of Y-doped ceria (\( \text{Ce}_{0.85}\text{Y}_{0.15}\text{O}_{2} \), YDC) was in proportion to \( \text{Po}_{2}^{-1/4} \) in the \( \text{Po}_{2} \) range from 10 to \( 10^{-2} \) Pa at 973–1273 K. This result agreed with the theoretical prediction by Eq. (17) where the concentration of oxygen vacancy is dominated by the amount of the doped rare-earth element (Eq. (14)). As discussed in Section 4.2, the present experiment covers the electronic conduction in the \( \text{Po}_{2} \) range from 10 to \( 10^{-2} \) Pa at 773–1113 K for GDC (Fig. 8) and from \( 10^{2} \) to \( 10^{-2} \) Pa at 773–1073 K for SDC (Fig. 9). The kinds of rare earth elements were different between the samples by Xiong et al. and present experiment. However, both the data on \( n \) values in Eq. (1) lead to the conclusion that \( n \) value changes from 4 to 6 or more large value with decreasing \( \text{Po}_{2} \).

4.2 Transport number of oxide ion

Figures 8 and 9 show the comparison of oxide ion conductivity and electronic conductivity for GDC and SDC, respectively, as a function of oxygen partial pressure. The open circles for electronic conduction represents the \( \text{Po}_{2} \) (inner) range in this experiment at a given applied voltage range (Eq. (2)). The electronic conductivity was calculated by substituting the experimentally measured \( n \) and \( C_1 \) (derived from \( C_2 \) in Eq. (8)) into Eq. (1). On the other hand, we reported the electrical conductivity of GDC and SDC in air in a previous paper.\(^{15} \) This value represents the oxide ion conductivity. The compari-
Fig. 10. Transport number \( t_1 \) of oxide ion for GDC as a function of oxygen partial pressure at 773–1113 K. The solid lines correspond to the \( P_{O_2} \) range measured for the electronic conduction. The dashed lines were extrapolated by Eq. (1) from the measured electronic conductivity.

Fig. 11. Transport number \( t_1 \) of oxide ion for SDC as a function of oxygen partial pressure at 773–1073 K. The solid lines correspond to the \( P_{O_2} \) range measured for the electronic conduction. The dashed lines were extrapolated by Eq. (1) from the measured electronic conductivity.

The obtained conductivities of oxide ion and electron were coupled to clarify the transport number of oxide ion.

**Figures 10 and 11** show the transport number \( t_1 \) of oxide ion for GDC and SDC, respectively, as a function of oxygen partial pressure. The solid lines in Figs. 10 and 11 correspond to the \( P_{O_2} \) range measured for the electronic conduction in the present experiment. The dashed lines were extrapolated from the measured oxide ion conductivity and electronic conductivity (Eq. (1)). Both the results for GDC and SDC indicate that the \( t_1 \) value decreases with increasing temperature and decreasing oxygen partial pressure. The previously reported oxygen partial pressure for \( t_1 = 0.5 \) at 1073 K is \( 10^{-10} \) Pa for SDC,\(^3\) \( 10^{-8} \) Pa for GDC,\(^5\) and \( 10^{-12} \) Pa for GDC.\(^6\) Compared with these oxygen partial pressures, a significantly low oxygen partial pressure of \( \sim 10^{-13} \) Pa was calculated for \( t_1 = 0.5 \) of both the samples of GDC and SDC. That is, the transport number of the oxide ion was significantly enhanced in the present samples. This result is favorable to apply RDC for the solid electrolyte of SOFC. In Fig. 11, the \( t_1 \) value previously measured by electromotive force (EMF) method\(^{20}\) was also plotted to compare with that by Hebb-Wagner method. Although the \( t_1 \) values by EMF method showed a scattering at near the corresponding line by Hebb-Wagner method at 973 and 1073 K, both the data were close each other. That is, it was shown from the two measurement methods that present SDC had a high transport number of oxide ion reaching 0.83 at 973 K under an oxygen partial pressure of \( \sim 10^{-15} \) Pa. In the significantly low oxygen pressure range below \( 10^{-20} \) Pa at 773 and 873 K, the \( t_1 \) values between the two methods showed a relatively large difference. Currently, the reason for this discrepancy between the two methods is not understood and under investigation.

5. Conclusions

The electronic conductivity of GDC and SDC was measured in a temperature range from 773 to 1113 K by direct current polarization method using the Hebb-Wagner ion blocking cell.

(1) A high linearity between \( \ln I \) (electronic current)–\( E \) (applied voltage), which was theoretically predicted, was measured for GDC and SDC in the applied voltage of 0.2–1.4 V.

(2) The slope of log electronic conductivity-log \( P_{O_2} \) plot for GDC agreed well with the theoretically predicted value of \(-1/6\) in the temperature range from 873 to 1113 K. However, the slope for SDC was in the range from \(-0.10\) to \(-0.16\) and increased with increasing temperature.

(3) The transport number \( t_1 \) of oxide ion for the present GDC and SDC was significantly higher than the previously reported values. The \( t_1 \) value calculated for present GDC and SDC at 973 K was 0.83–0.85 under a oxygen partial pressure of \( 10^{-15} \) Pa.

References