

# Oxygen Permeability, Electronic and Ionic Conductivities and Defect Chemistry of Ceria-Zirconia-Calcia System : $(\text{Ce}_{1-x}\text{Zr}_x\text{O}_2)_{0.9}(\text{CaO})_{0.1}$ ( $x=0, 0.1, 0.2$ )

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The total conductivity and oxygen permeation in  $(\text{Ce}_{1-x}\text{Zr}_x\text{O}_2)_{0.9}(\text{CaO})_{0.1}$  solid solutions were measured as a function of temperature and oxygen partial pressure. Empirically,  $\sigma$  at given  $x$  and  $T$  was expressed essentially by  $\sigma = \sigma_{\text{O}^{2-}} + \sigma_{\text{e}^-} P_{\text{O}_2}^{-1/4}$ , where  $\sigma_{\text{O}^{2-}}$  and  $\sigma_{\text{e}^-}$  are constant. Applying a standard defect model in which major defects are  $\text{Ca}_{\text{Ce}}''$ ,  $\text{Ce}_{\text{Ce}}'$  and  $\text{V}_{\text{O}}$  in ideal solution, we can assign  $\sigma_{\text{O}^{2-}}$  as the oxide ion conductivity and  $\sigma_{\text{e}^-}$  as the electronic conductivity at  $P_{\text{O}_2}=1$  atm. With this assignment, it was found that the oxide ion conductivity decreases while the electronic conductivity increases with the increase in Zr content. Using the oxide ion and electronic conductivities thus determined, the oxygen permeation flux was calculated for respective  $P_{\text{O}_2}$  and  $T$  conditions at which the measurements were made. The calculated values were found to agree with the observed ones.

**Key words :** Electrical conductivity,  $\text{CeO}_2$ ,  $\text{ZrO}_2$ , Fluorite structure, Chemical diffusion

## I. Introduction

Stabilized  $\text{ZrO}_2$  is well known as an oxide ion conductor. Doped  $\text{CeO}_2$  shows higher oxide ion conductivity than stabilized  $\text{ZrO}_2$ . The electronic conduction of doped  $\text{CeO}_2$ , which appears in reduced atmospheres, becomes remarkable at the oxygen partial pressure higher than that for stabilized  $\text{ZrO}_2$ . Both oxides, with  $\text{CaF}_2$ -structures, are known to be dissolved each other at high temperatures.<sup>1)</sup>

In a previous paper, the authors reported the oxygen permeation in  $(\text{Ce}_{1-x}\text{Zr}_x\text{O}_2)_{0.9}(\text{CaO})_{0.1}$  solid solutions considering applications to ceramic membrane for high temperature oxygen-separation.<sup>2)</sup> It is necessary for the membrane to have high conductivities of oxide ion and electronic defect, because permeation in oxides takes place by a simultaneous diffusion of oxide ions and electrons, so-called a "chemical diffusion".

It is considered that the oxide ion conduction is predominant in  $(\text{Ce}_{1-x}\text{Zr}_x\text{O}_2)_{0.9}(\text{CaO})_{0.1}$  solid solution. Therefore, the rate of oxygen permeation would be determined by the electronic conductivity. The electronic conductivity is expected to increase with the increase in Ce content because Ce ions easily take mixed valence state of  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  and the electronic conduction is expected to be enhanced by the electron exchange between  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ .

The observed oxygen permeation rate was rather contradictory to the prediction above. Maximum oxygen permeation rate was observed with  $(\text{Ce}_{0.9}\text{Zr}_{0.2}\text{O}_2)_{0.9}(\text{CaO})_{0.1}$ ,

and tends to decrease with the further increase in Ce content. In order to elucidate this permeation behavior and to make clear the relationship between the permeability and the conductivity, total conductivity in  $(\text{Ce}_{1-x}\text{Zr}_x\text{O}_2)_{0.9}(\text{CaO})_{0.1}$  ( $x=0, 0.1, 0.2$ ) was measured as a function of oxygen pressure.

## II. Experimental

### 1. Sample

$(\text{Ce}_{1-x}\text{Zr}_x\text{O}_2)_{0.9}(\text{CaO})_{0.1}$  ( $x=0, 0.1, 0.2$ ) was prepared by solid state reactions. Appropriate proportions of commercial  $\text{ZrO}_2$ ,  $\text{CeO}_2$  and  $\text{CaCO}_3$  powders with 99.99% purity were mixed together in an alumina mortar. The solid state reaction was carried out in an alumina crucible at 1673 K for 4 hr in air. After remixing and refiring, the powder was ground with alcohol in a ball mill with balls of  $\text{Y}_2\text{O}_3$ -partially stabilized  $\text{ZrO}_2$  for 48 hr and then dried. No diffraction peak assigned to impurities was detected in X-ray diffraction patterns. The crystal structure of the sample was confirmed to be a single phase  $\text{CaF}_2$ -structure. The powders were hydrostatically pressed at  $2 \times 10^8$  Pa into appropriate shapes. The pressed sample was sintered at 1973 K for 6 hr. The relative densities of the sintered samples turned to be 97% of the X-ray ones.

### 2. Conductivity

The samples were finished to square pillar shape (about  $4 \times 4 \times 15$  mm) by the diamond machining process. The total conductivity was measured as a function of ox-

xygen partial pressure using a standard d.c four terminal method with reversible Pt electrodes at 1173–1773 K. The oxygen partial pressure was controlled by gas-mixtures of Ar-O<sub>2</sub> or CO-CO<sub>2</sub>.

### 3. Oxygen permeation

The samples, which were hydrostatically pressed as tube shape, were finished about (13 mm (outer diameter) × 9 mm (inner diameter)) by the diamond machining process. One side of the sample was joined to Al<sub>2</sub>O<sub>3</sub> tube with Pt O-ring and another side was closed by Al<sub>2</sub>O<sub>3</sub> disk with Pt O-ring. Two samples with different length (5 and 15 mm) were simultaneously set in a furnace to eliminate influences of contact areas between sample and Al<sub>2</sub>O<sub>3</sub>. Outside of sample tube was exposed to N<sub>2</sub>-O<sub>2</sub> gas-mixtures (P<sub>O<sub>2</sub></sub>=0.2~0.5 atm) or air for oxygen source. Permeated oxygen from outside to inside of sample tube was transported by He gas flow and detected by gas chromatograph (Shimadzu GC-9A). Further details of oxygen permeation was described in ref. [2].

## III. Results and Discussion

### 1. Electrical conductivity

The total conductivity,  $\sigma$ , as a function of P<sub>O<sub>2</sub></sub> is shown in Fig. 1. At high oxygen partial pressure,  $\sigma$  is almost independent of P<sub>O<sub>2</sub></sub> and decreases with the increase in Zr content. However,  $\sigma$  increases with decreasing P<sub>O<sub>2</sub></sub> and is almost independent of Zr content at low oxygen partial pressure.

It is assumed that the increase in  $\sigma$  is caused by electronic conduction. Considering Ce<sub>Ce</sub>'<sup>+</sup>, V<sub>O</sub><sup>••</sup>, Ca<sub>Ce</sub>'<sup>+</sup> as charged defects in CaO-doped CeO<sub>2</sub>-ZrO<sub>2</sub> solid solution, the equilibrium of oxygen between the gas phase and the bulk of oxide can be expressed as

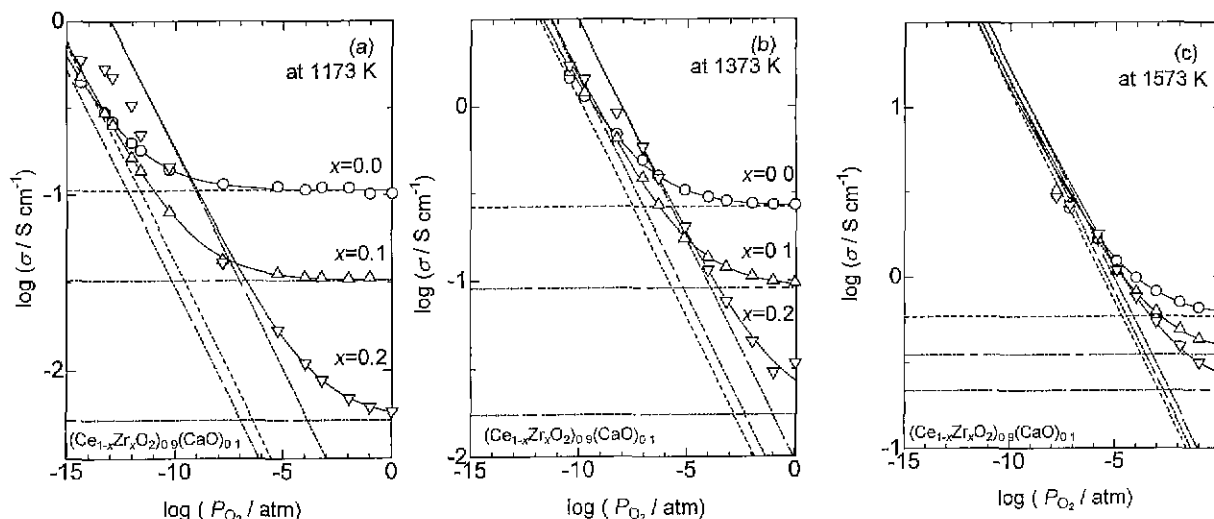
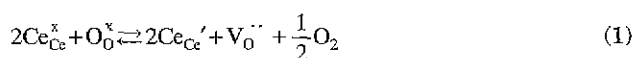


Fig. 1. Total conductivity of (Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub>)<sub>0.9</sub>(CaO)<sub>0.1</sub> (x=0, 0.1, 0.2) as a function of partial oxygen pressure.

where Kröger-Vink<sup>81</sup> notation is adopted. Using activities of each defects, a, the equilibrium constant, K, is written as follows.

$$K_{(1)} = \frac{a_{\text{Ce}_{\text{Ce}}^{\times}}^2 a_{\text{V}_0^{\bullet\bullet}} P_{\text{O}_2}^{1/2}}{a_{\text{Ce}_{\text{Ce}}^{\prime}}^2 a_{\text{O}_0^{\times}}} \quad (2)$$

Assuming that Henry's law is valid, Raoult's law also expected to hold. Then, using the concentration, the equilibrium constant, K<sub>(1)</sub>, is rewritten as follows.

$$K_{(1)}' = \frac{[\text{Ce}_{\text{Ce}}^{\times}]^2 [\text{V}_0^{\bullet\bullet}] P_{\text{O}_2}^{1/2}}{[\text{Ce}_{\text{Ce}}^{\prime}]^2 [\text{O}_0^{\times}]} \quad (3)$$

where "[ ]" designates a mole quantity in one mole of (Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub>)<sub>0.9</sub>(CaO)<sub>0.1</sub>.

The defect equilibrium of doped CaO is given as



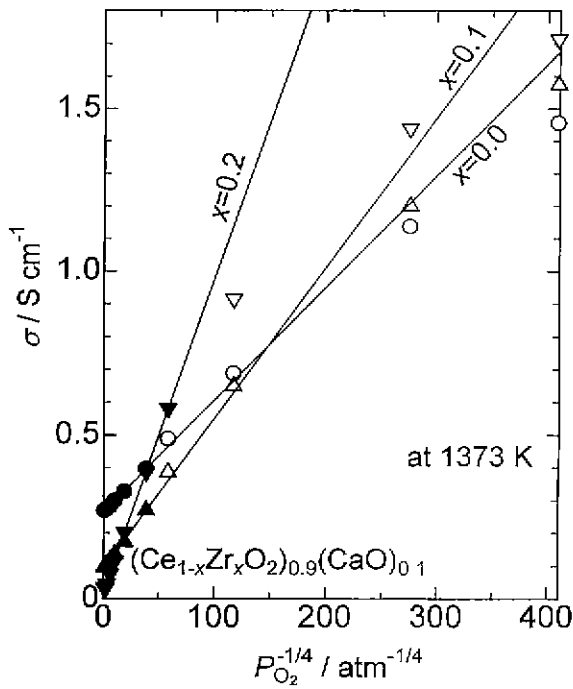
The electroneutrality can be expressed as

$$2[\text{V}_0^{\bullet\bullet}] = [\text{Ce}_{\text{Ce}}^{\prime}] + 2[\text{Ca}_{\text{Ce}}^{\prime}] \quad (5)$$

When  $[\text{Ca}_{\text{Ce}}^{\prime}] \gg [\text{Ce}_{\text{Ce}}^{\prime}]$ ,  $[\text{V}_0^{\bullet\bullet}]$  is essentially constant and  $[\text{O}_0^{\times}]$  is also constant. At the region where  $[\text{Ce}_{\text{Ce}}^{\times}]$  is higher enough than  $[\text{Ce}_{\text{Ce}}^{\prime}]$ ,  $[\text{Ce}_{\text{Ce}}^{\times}]$  can be considered as constant. Transforming eq. (3), a left side in the following equation is regarded as constant.

$$\frac{K_{(1)}' [\text{Ce}_{\text{Ce}}^{\times}]^2 [\text{O}_0^{\times}]}{[\text{V}_0^{\bullet\bullet}]} = [\text{Ce}_{\text{Ce}}^{\prime}]^2 P_{\text{O}_2}^{1/2} \quad (6)$$

On ZrO<sub>2</sub>-CeO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> system, Calès and Baumard<sup>82</sup> explained that the electronic conductivity is caused by a hopping mechanism between Ce<sub>Zr</sub><sup>•</sup> and Ce<sub>Zr</sub>' and proportional to the product of  $[\text{Ce}_{\text{Zr}}^{\bullet}] \cdot [\text{Ce}_{\text{Zr}}']$ . At the region of  $[\text{Ce}_{\text{Ce}}^{\times}] \gg [\text{Ce}_{\text{Ce}}^{\prime}]$ , the conductivity of electron is proportional to  $[\text{Ce}_{\text{Ce}}^{\times}]$ . Therefore, the electronic conductivity is proportional to P<sub>O<sub>2</sub></sub><sup>-1/4</sup>.



**Fig. 2.**  $P_{O_2}^{-1/4}$  dependence of total conductivity. The solid marks were used for the least squares fits.

The total conductivity is represented by

$$\sigma = \sigma_{ion} + \sigma_e^0 P_{O_2}^{-1/4} \quad (7)$$

where  $\sigma_{ion}$  is the ionic conductivity and  $\sigma_e^0$  is the electronic conductivity at  $P_{O_2}=1$  atm. Fig. 2 shows  $P_{O_2}^{-1/4}$  dependence of  $\sigma$ . There are linear relations at the high  $P_{O_2}$  region. It is considered that the decrease in  $\sigma$  at low  $P_{O_2}$  region is caused by the influence of the decrease in  $[Ce_{Ce}^{\cdot}]$ , that is, it is difficult for  $[Ce_{Ce}^{\cdot}]$  to be regarded as constant in this region.

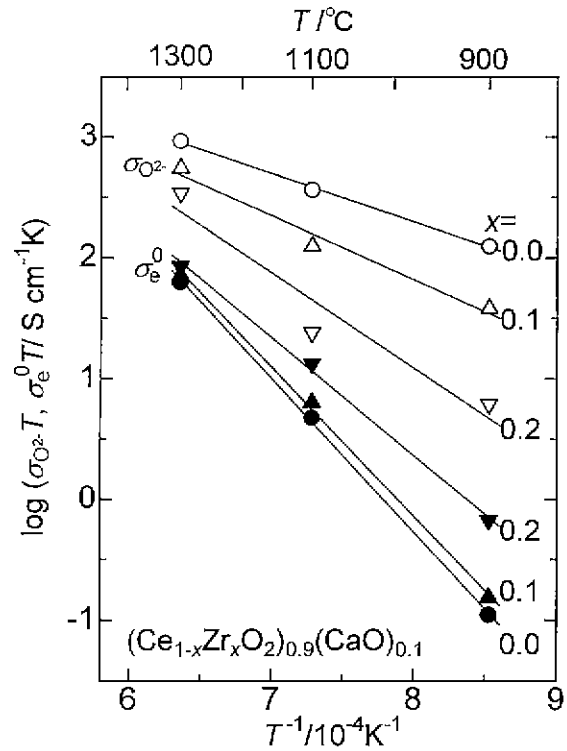
The least squares fits give  $\sigma_{ion}$  and  $\sigma_e^0$ . Horizontal and straight lines in Fig. 1 are drawn by using obtained  $\sigma_{ion}$  and  $\sigma_e^0$ , respectively. Curves are calculated from eq. (7).

The ionic and electronic conductivities at  $P_{O_2}=1$  atm as a function of temperature are shown in Fig. 3. The parameters are shown in Table 1. With this assignment, it is found that the oxide ion conductivity decreases while the electronic conductivity increases with the increase in Zr content.

**2. Oxygen permeability**

When two gas-phases different in oxygen pressures are separated by  $(Ce_{1-x}Zr_xO_2)_{0.9}(CaO)_{0.1}$ , the chemical potential gradient of oxygen is formed in it, which causes flux of oxygen. At the region of the oxygen partial pressure in which the oxide ion conduction is predominant, the oxide ions flow from high to low oxygen partial pressure accompanied by the electron flow of counter direction to compensate the balance of the charge in the oxide.

Using  $\sigma_{O^{2-}}$  and  $\sigma_e$ , the flux,  $j$ , of oxide ion and electron



**Fig. 3.** Temperature dependence of ionic and electronic conductivity

**Table. 1.** The Oxide Ion and Electronic Conductivity in  $(Ce_{1-x}Zr_xO_2)_{0.9}(CaO)_{0.1}$

x	$\sigma_{O^{2-}}/S cm^{-1} = \frac{A}{T} \exp(-\frac{Q}{RT})$		$\sigma_e^0/S cm^{-1} = \frac{A}{T} \exp(-\frac{Q}{RT})$	
	A S cm <sup>-1</sup> K	Q J mol <sup>-1</sup> K	A S cm <sup>-1</sup> K	Q J mol <sup>-1</sup> K
0	$3.12 \times 10^5$	$7.65 \times 10^4$	$8.03 \times 10^9$	$2.44 \times 10^5$
0.1	$1.11 \times 10^6$	$1.01 \times 10^5$	$5.36 \times 10^9$	$2.36 \times 10^5$
0.2	$2.44 \times 10^7$	$1.51 \times 10^5$	$1.47 \times 10^9$	$1.87 \times 10^5$

are represented by

$$j_{O^{2-}} = - \frac{\sigma_{O^{2-}}}{(z_{O^{2-}}F)^2} \frac{d\eta_{O^{2-}}}{dx} \quad (8)$$

$$j_e = - \frac{\sigma_e}{(z_e F)^2} \frac{d\eta_e}{dx} \quad (9)$$

where  $F$  is Faraday constant and  $z$  and  $\eta$  are electrical charge and electrochemical potential of species shown as the subscript.

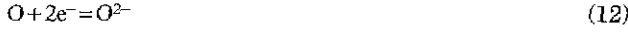
To maintain the electroneutrality,  $j_{O^{2-}}$  and  $j_e$  are related by the following equation.

$$z_{O^{2-}} j_{O^{2-}} = -z_e j_e \quad (10)$$

Substituting eq. (10) into eq. (9),  $\eta_e$  can be related to the  $j_{O^{2-}}$ :

$$j_{O^{2-}} = \frac{z_e}{z_{O^{2-}}} \frac{\sigma_e}{(z_e F)^2} \frac{d\eta_e}{dx} \quad (11)$$

Generally, we assume the local equilibrium in the material. An equilibrium reaction is represented by



The relation between respective potentials is expressed as follows.

$$\frac{d\mu_{\text{O}}}{dx} + 2 \frac{d\eta_{e^-}}{dx} = \frac{d\eta_{\text{O}^{2-}}}{dx} \quad (13)$$

Substituting  $z_{e^-} = -1$ ,  $z_{\text{O}^{2-}} = -2$ , eq. (8) and (11) into eq. (13), we can obtain the relation between  $j_{\text{O}^{2-}}$  and  $\mu_{\text{O}}$ :

$$j_{\text{O}^{2-}} = -\frac{1}{4F^2} \left( \frac{\sigma_{\text{O}^{2-}} \sigma_e}{\sigma_{\text{O}^{2-}} + \sigma_e} \right) \frac{d\mu_{\text{O}}}{dx} \quad (14)$$

Integrating from end to end in the material and using a definition of  $\mu_{\text{O}} = \mu_{\text{O}}^{\circ} + \frac{1}{2} RT \ln P_{\text{O}_2}$ , we can calculate as

$$J_{\text{O}^{2-}} = -\frac{RT}{8F^2 L} \int_{\ln P_{\text{O}_2}^{\text{H}}}^{\ln P_{\text{O}_2}^{\text{L}}} \frac{\sigma_{\text{O}^{2-}} \sigma_e}{\sigma_{\text{O}^{2-}} + \sigma_e} d \ln P_{\text{O}_2} \quad (15)$$

where  $L$  is thickness of the material. Here  $P_{\text{O}_2}^{\text{H}}$  and  $P_{\text{O}_2}^{\text{L}}$  indicate the  $P_{\text{O}_2}$  in the gas phase of higher and lower  $P_{\text{O}_2}$ , respectively. The oxygen permeation,  $j_{\text{O}_2}$ , is related to  $j_{\text{O}^{2-}}$  as  $2j_{\text{O}_2} = j_{\text{O}^{2-}}$ . The oxygen permeation normalized by thickness,  $J_{\text{O}_2}$ , is represented by

$$J_{\text{O}_2} = j_{\text{O}_2} L = -\frac{RT}{16F^2} \int_{\ln P_{\text{O}_2}^{\text{H}}}^{\ln P_{\text{O}_2}^{\text{L}}} \frac{\sigma_{\text{O}^{2-}} \sigma_e}{\sigma_{\text{O}^{2-}} + \sigma_e} d \ln P_{\text{O}_2} \quad (16)$$

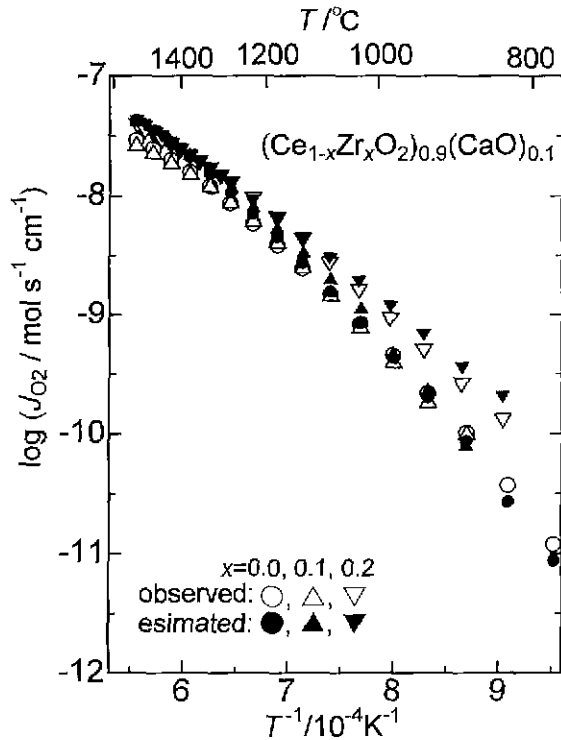


Fig. 4. Oxygen permeation as a function of temperature.

Fig. 4 shows the normalized oxygen permeation as a function of temperature (open marks). The sides of high and low oxygen partial pressure are  $P_{\text{O}_2}^{\text{H}} = 0.2 \sim 0.5$  and  $P_{\text{O}_2}^{\text{L}} = 4 \times 10^{-2} \sim 3 \times 10^{-4}$  atm. It is necessary for taking into account  $\sigma_{\text{O}^{2-}}$  and  $\sigma_e$  to compare between conductivity and oxygen permeability, because the difference between  $\sigma_{\text{O}^{2-}}$  and  $\sigma_e$  is about one order.

### 3. Comparison between conductivity and oxygen permeation

When the conductivities of conduction species except oxide ion and electron, the oxide ion and electron transference number is represented as follows.

$$t_{\text{O}^{2-}} = \frac{\sigma_{\text{O}^{2-}}}{\sigma_{\text{O}^{2-}} + \sigma_e} \quad (17)$$

$$t_e = \frac{\sigma_e}{\sigma_{\text{O}^{2-}} + \sigma_e} \quad (18)$$

where the sum of  $t_{\text{O}^{2-}}$  and  $t_e$  is equal to unity. Using  $t_{\text{O}^{2-}}$ , eq. (16) can be arranged as follows.

$$J_{\text{O}_2} = -\frac{RT \sigma_{\text{O}^{2-}}}{16F^2} \int_{\ln P_{\text{O}_2}^{\text{H}}}^{\ln P_{\text{O}_2}^{\text{L}}} (1 - t_{\text{O}^{2-}}) d \ln P_{\text{O}_2} \quad (19)$$

In stabilized  $\text{ZrO}_2$ , the partial electronic conduction parameter is introduced to represent the influence of electronic conduction.<sup>5,6)</sup> The partial electronic conduction parameter,  $P_e$ , is defined as the oxygen pressure at which the ionic and the electronic transference numbers are equal.

$$0.5 = \frac{\sigma_{\text{O}^{2-}}}{\sigma_{\text{O}^{2-}} + \sigma_e^2 P_e^{-1/4}} \quad (20)$$

Using the value in Table 1,  $P_e$  is expressed as shown in Fig. 5.

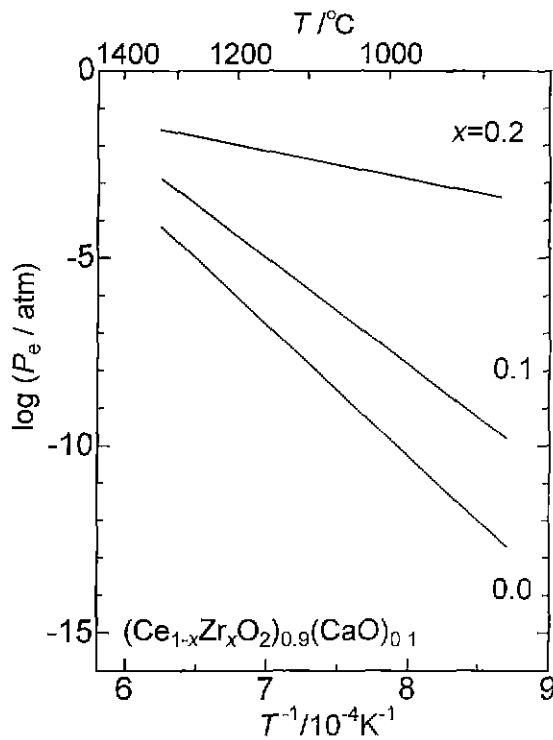
We can apply  $P_e$  to eq. (19) and calculate as

$$J_{\text{O}_2} = -\frac{RT \sigma_{\text{O}^{2-}}}{16F^2} \left( \ln \frac{P_{\text{O}_2}^{\text{H}}}{P_{\text{O}_2}^{\text{L}}} - 4 \ln \frac{P_e^{1/4} + P_{\text{O}_2}^{\text{H}1/4}}{P_e^{1/4} + P_{\text{O}_2}^{\text{L}1/4}} \right) \quad (21)$$

Fig. 4 includes the estimated values (solid marks) at each experimental condition by using obtained conductivities and eq. (21). The estimated  $J_{\text{O}_2}$  shows good agreement with observed  $J_{\text{O}_2}$ .

Fig. 6 shows normalized oxygen permeation of  $(\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2)_{0.9}(\text{CaO})_{0.1}$  with various  $P_{\text{O}_2}^{\text{H}}$  and  $P_{\text{O}_2}^{\text{L}}$ . The estimated  $J_{\text{O}_2}$  at 1400 K also indicates good agreement with observed  $J_{\text{O}_2}$ . At 1726 K, the deviation of the estimated  $J_{\text{O}_2}$  from the observed  $J_{\text{O}_2}$  is larger than at 1400 K. It is considered two reasons for the deviation in high temperature.

One is considered that  $\sigma_e$  was estimated higher than the true value. Since  $\sigma_e$  would be proportional to  $[\text{Ce}_2^{\cdot}] \cdot [\text{Ce}_2^{\cdot}]$ , the electronic conductivity should be decrease



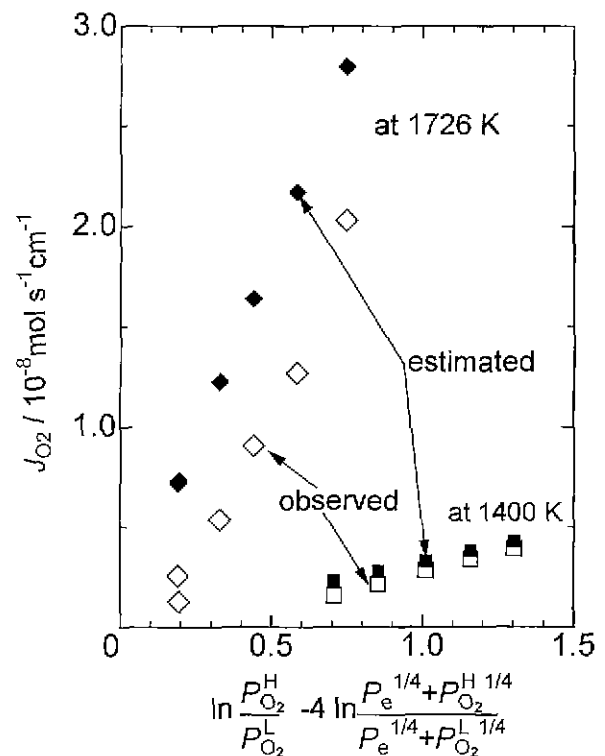
**Fig. 5.** The partial electronic conduction parameter as a function of temperature.

with decrease in  $P_{O_2}$  at low  $P_{O_2}$  region. Another reason is considered as an influence of surface reaction of oxygen: Both the surface reaction rate and the diffusion flux increase with temperature in Arrhenius-type relationships. When the activation energy for the surface reaction is smaller than that for the chemical diffusion, the effect of surface reaction would be remarkable at the higher temperatures.

To make clear this point, it is necessary to clarify the electric properties in the sample at high temperatures. Despite the deviation between estimated  $J_{O_2}$  and observed  $J_{O_2}$  at high temperatures, the estimated  $J_{O_2}$  interprets the magnitude and the  $P_{O_2}$  and temperature dependence of the observed  $J_{O_2}$ .

#### IV. Conclusion

The total conductivity and oxygen permeation in  $(Ce_{1-x}Zr_xO_2)_{0.9}(CaO)_{0.1}$  ( $x=0, 0.1, 0.2$ ) solid solutions were measured as a function of temperature and oxygen partial pressure. With the increase in Zr content, the assigned electronic conductivity from total one increased and the oxygen permeation also increased. The estimated oxygen permeability, which was calculated with assigned oxide ion and electronic conductivity by using the standard theory of charged particles, agreed with the



**Fig. 6.** Oxygen permeation in  $(Ce_{0.9}Zr_{0.2}O_2)_{0.9}(CaO)_{0.1}$  as a function of oxygen partial pressure.

observed oxygen permeability.

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