

Conduction in Bi_2O_3 -based oxide ion conductor under low oxygen pressure. II. Determination of the partial electronic conductivity

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In order to investigate the partial electronic conduction in the high oxide ion conductor of the system Bi_2O_3 - Y_2O_3 under low oxygen pressure, e.m.f. and polarization methods were employed. Although the electrolyte was decomposed when the P_{O_2} was lower than the equilibrium P_{O_2} of Bi, Bi_2O_3 mixture at each temperature, the ionic transport number was found to be close to unity above that P_{O_2} . The hole conductivity (σ_p) and the electron conductivity (σ_n) could be expressed as follows,

$$\sigma_p \Omega \text{ cm} = 5.0 \times 10^2 (P_{\text{O}_2} \text{ atm}^{-1})^{1/4} \exp [-106 \text{ kJ } (RT \text{ mol})^{-1}]$$

$$\sigma_n \Omega \text{ cm} = 3.4 \times 10^5 (P_{\text{O}_2} \text{ atm}^{-1})^{-1/4} \exp [-213 \text{ kJ } (RT \text{ mol})^{-1}]$$

These values were much lower than the oxide ion conductivity under ordinary oxygen pressure.

1. Introduction

Takahashi and co-workers have reported the high oxide ion conduction in Bi_2O_3 -based fcc solid solutions [1, 2]. As these materials are high conductivity conductors, various applications at lower temperatures are expected, e.g. in oxygen gauges, oxygen pumps and the like. For these purposes, the conduction behaviour under low oxygen pressures must be investigated, since, if an appreciable electronic conduction arises as a result of defect equilibrium at low P_{O_2} , the electrochemical measurements cannot be done correctly. In the previous paper, the current-blackening condition of the Bi_2O_3 - Y_2O_3 electrolyte was reported [3]. We have now investigated the partial electronic conduction of the above oxide by e.m.f. measurements and the polarization method.

Electromotive force of a galvanic cell using a sample as the electrolyte is a most convenient method for determining the ionic transport number of solid electrolytes. Many cells have been constructed using various metal-metal oxide mixtures as the electrode materials and the domains of oxygen partial pressure where ionic conduction pre-

dominates were determined from the e.m.f. data [4-9]. However, in the case of the Bi_2O_3 -based electrolyte, electrode materials which can be used as the P_{O_2} standard are limited to a few kinds of metal-metal oxide mixtures, since one component (Bi_2O_3) of the electrolyte is comparatively easily reduced under lower P_{O_2} , as reported in the previous paper [3] and since the mixtures having metals of low melting point are difficult to use at higher temperatures. Here, we have examined, whether the current-blackened oxide sample which exhibits an equilibrium P_{O_2} could be used as the electrode material of a galvanic cell.

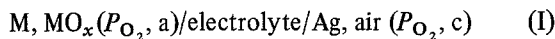
The ionic transport number (t_{ion}) can be determined generally by the above method. However, the contribution of hole and electron conduction in the solid electrolyte cannot be distinguished. Although Hebb-Wagner's polarization method can often be used for the purpose, this method requires that the ionic current is blocked [10-13]. This problem is still difficult to overcome in the case of oxide ion conductors. For this reason, Hartung employed an impervious Pt electrode covered by a high temperature glass on a hemispherical sample (yttria-stabilized zirconia) [14]. In this paper, we

describe a method using a disc specimen having Ag electrodes, one of which was covered by soda glass.

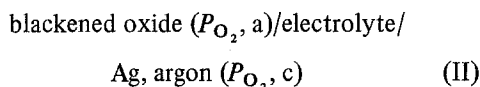
2. Experimental

2.1. Galvanic cell method

A specimen having 27 mol% Y_2O_3 was obtained by the same procedure as that reported previously [1, 3]. Two types of cells were constructed using this solid electrolyte,



and



where $P_{O_2, a}$ and $P_{O_2, c}$ are the oxygen partial pressures in the anode and the cathode, respectively. For the cell (I), $P_{O_2, c}$ was constant (0.21 atm) and $P_{O_2, a}$ was changed using various

mixtures of metal-metal oxide. For cell (II), the equilibrium oxygen partial pressure ($P_{O_2, eq}$) in the partially blackened oxide of the Bi_2O_3 - Y_2O_3 electrolyte was used as the low P_{O_2} , a standard [3] and $P_{O_2, c}$ was variable. These cells are shown schematically in Fig. 1a and 1b. The electrolyte of the cell (I) is a disc specimen (13 mm diameter \times 2 ~ 3 mm thickness) and is 93% dense. In the case of the cell (II), one end of Pt wire (0.5 mm diameter) was buried in a rod sample (5 mm diameter \times 12 mm length) in order to obtain the blackened oxide as an electrode material directly.

The e.m.f. of the cell was measured at 500 ~ 700°C using a high impedance recorder. The P_{O_2} in argon gas used for the cell (II) was controlled by an oxygen pump employing a calcia-stabilized zirconia (CSZ) tube as an electrolyte. Argon gas introduced into the oxygen pump had been refined using spongy Ti, NaOH and P_2O_5 . The P_{O_2} was checked by a CSZ oxygen meter.

2.2. Polarization method

A specimen disc (13 mm diameter \times 1 mm thickness) containing 27 mol% Y_2O_3 was prepared by the ordinary method. The specimen was held in an electric furnace as indicated in Fig. 2. The Ag electrodes on both sample faces were 9 mm in diameter. The lower electrode was completely covered by commercial soda-glass in order to block the ionic current. The terminal voltage at a steady-state current was measured at 500 ~ 700°C under different values of P_{O_2} .

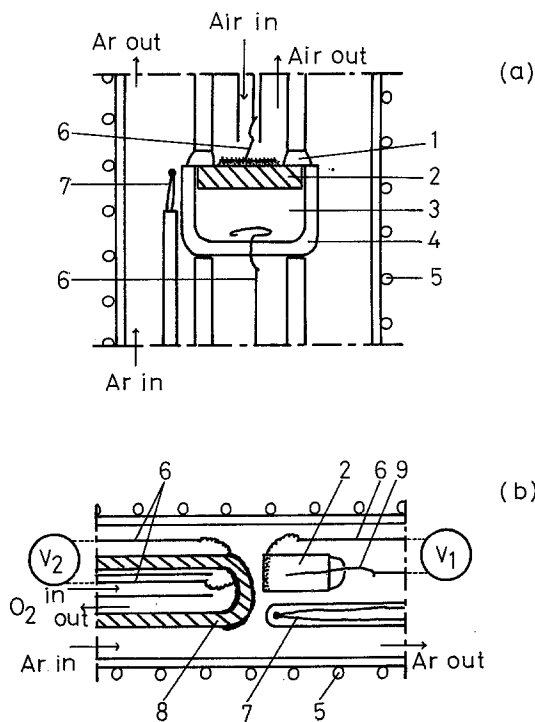


Fig. 1. Galvanic cells (schematic). (1) Glass packing; (2) sample; (3) anode material; (4) alumina crucible; (5) heater; (6) Ag lead; (7) CA thermocouple (8) CSZ tube; (9) Pt wire; (V_1) sample e.m.f.; (V_2) oxygen meter e.m.f.

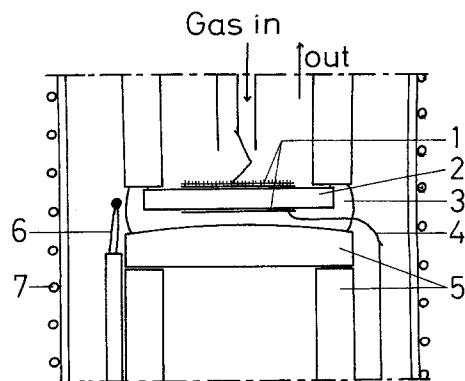


Fig. 2. Polarization cell (schematic). (1) Ag lead; (2) sample; (3) glass; (4) Pt lead; (5) alumina support (6) CA thermocouple; (7) heater.

3. Results and discussion

3.1. E.M.F. studies

According to Wagner's expression for oxide mixed-conductors, the steady-state open circuit e.m.f. (E) may be written as

$$E = \frac{1}{4F} \int_{\mu_{\text{O}_2, a}}^{\mu_{\text{O}_2, c}} t_{\text{ion}} d\mu_{\text{O}_2} \\ = \frac{RT}{4F} \int_{\ln P_{\text{O}_2, a}}^{\ln P_{\text{O}_2, c}} t_{\text{ion}} d \ln P_{\text{O}_2} \quad (1)$$

where F is Faraday's constant, R the gas constant, T the absolute temperature, t_{ion} the ionic transport number within the mixed conductor, and μ_{O_2} and P_{O_2} the oxygen chemical potential and oxygen partial pressure, respectively. If the average ionic transport number is used, Equation 1 is rewritten as Equation 2.

$$E = t_{\text{ion}} \frac{RT}{4F} \ln \frac{P_{\text{O}_2, c}}{P_{\text{O}_2, a}} \quad (2)$$

For a predominantly ionic conductor ($t_{\text{ion}} \approx 1$), the e.m.f. is given as follows,

$$E_o = \frac{RT}{4F} \ln \frac{P_{\text{O}_2, c}}{P_{\text{O}_2, a}} \quad (3)$$

Therefore, the ionic transport number for various electrolytes can be calculated from the ratio of E to E_o .

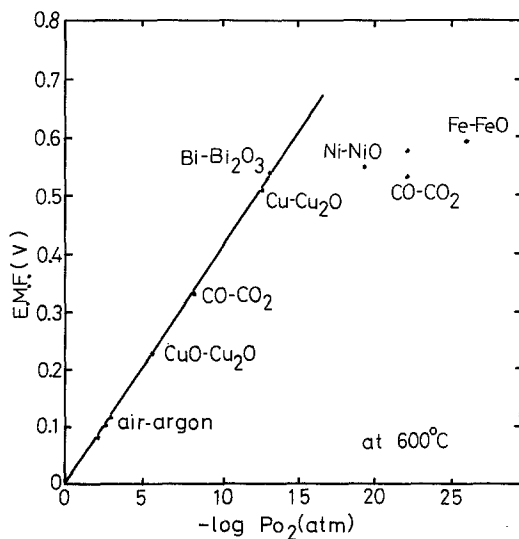


Fig. 3. Open circuit e.m.f. versus $P_{\text{O}_2, a}$ relation for the cell (I) at 600°C .

Figure 3 indicates the e.m.f.'s of cell (I) at 600°C under various values of $P_{\text{O}_2, a}$. The $P_{\text{O}_2, a}$ was changed from 10^{-2} atm (air-argon mixture) to 10^{-20} atm (Fe, FeO mixture). The measured values were almost equal to that calculated from Equation 3 (solid line) and were stable with time above $10^{-13.1}$ atm, indicating that t_{ion} is nearly unity. But below $10^{-13.1}$ atm, the e.m.f. values deviated from the calculated ones and were almost independent of $P_{\text{O}_2, a}$. The critical $P_{\text{O}_2, a}$ of $10^{-13.1}$ atm is the $P_{\text{O}_2, \text{eq}}$ in the Bi, Bi_2O_3 mixture. The electrolyte samples of such cells had been blackened on the anode sides and X-ray diffraction analysis showed partial decomposition into Bi metal. According to our previous paper [3], the blackened oxide containing Bi metal and Bi_2O_3 - Y_2O_3 solid solution had a $P_{\text{O}_2, \text{eq}}$ almost equal to that of a Bi, Bi_2O_3 mixture. Therefore, it is apparent that the blackening was caused by the contact of the electrolyte with the metal-metal oxide mixtures having lower $P_{\text{O}_2, \text{eq}}$ than $10^{-13.1}$ atm at 600°C . This can be also supported by the fact that the e.m.f. values of such cells correspond almost to the value at $P_{\text{O}_2, a} = 10^{-13.1}$ atm at 600°C .

In order to obtain the low P_{O_2} standard directly in the blackened oxide, the oxide sample around the Pt wire in the case of the cell (II) was electrolysed partially into Bi metal under unpurified argon gas ($P_{\text{O}_2} \approx 10^{-4}$ atm). Fig. 4 represents the temperature dependence of the e.m.f. of cell (II) at $P_{\text{O}_2, c} = 10^{-4}$ atm. The e.m.f. at each temperature coincides with the value calculated from Equation 3 using the P_{O_2} in the blackened oxide (solid line)

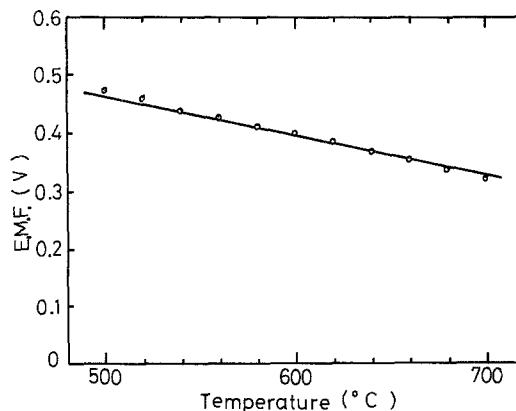


Fig. 4. Open circuit e.m.f. versus temperature relation for the cell (II) at $P_{\text{O}_2, c} = 10^{-4}$ atm.

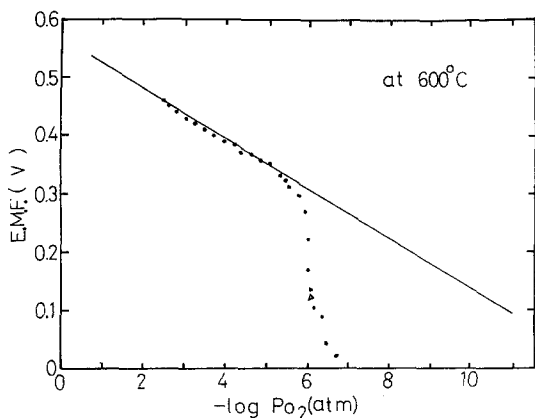


Fig. 5. Open circuit e.m.f. versus P_{O_2} , c relation for the cell (II) at 600°C (Δ) the e.m.f. of the cell (IV).

[3]. Therefore, these results show that: (i) this type of sample can retain the low P_{O_2} in the blackened oxide, which can be used as the P_{O_2} standard of a galvanic cell; (ii) t_{ion} of this sample is close to unity at P_{O_2} , c $\geq 10^{-4}$ atm between 500 and 700°C even when P_{O_2} , a is very low ($\approx 10^{-13}$ atm).

When the P_{O_2} , c of cell (II) was lowered, the e.m.f. variation in Fig. 5 was observed at 600°C . If the t_{ion} of the electrolyte is unity and the electrode reaction of oxygen is reversible over a wide range of P_{O_2} , c, the e.m.f. relation shown by the solid line should be observed. The measured e.m.f. is obviously much lower than this below a certain P_{O_2} . This denotes the presence of mixed ionic and electronic conduction in the sample. However, if the partial electronic conduction causes electrode polarization, the ratio of ionic and electronic conduction cannot be determined in this case. The following cells were constructed to measure the ionic transport number at lower oxygen pressure,

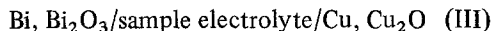
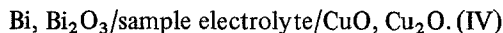


Table 1. Electronic conductivity (σ_e) and ionic transport number (t_{ion}) calculated using the cells [III] and [IV].

| $^\circ\text{C}$ | Cell III | | Cell IV | |
|------------------|---------------------------------------|-----------|---------------------------------------|-----------|
| | $\sigma_e(\Omega^{-1}\text{cm}^{-1})$ | t_{ion} | $\sigma_e(\Omega^{-1}\text{cm}^{-1})$ | t_{ion} |
| 500 | 4.16×10^{-5} | 0.995 | — | 0.999 |
| 600 | 1.64×10^{-4} | 0.997 | 3.57×10^{-6} | 0.999 |
| 700 | 9.20×10^{-4} | 0.995 | 1.90×10^{-5} | 0.999 |



These galvanic cells showed much lower e.m.f.'s than the E_0 values calculated from the ΔG_f values of the anode and cathode materials (Fig. 5). However, if each E_0 is applied to the cell from an outer source in changing the polarity, no ionic current passes through the sample and the observed current is electronic. In this condition, the electronic conductivity (σ_e) of the sample is obtained from the electronic current and the terminal voltage [15]. In Table 1, this result and t_{ion} calculated using the above parameters are presented. As a result, the sample electrolyte used here was found to be a predominantly ionic conductor over a wide range of P_{O_2} (e.g. $\geq 10^{-13.1}$ atm at 600°C). At lower values of P_{O_2} than that, the oxide sample was reduced and decomposed partially into Bi metal. Thus, the small e.m.f. in the low P_{O_2} , c range in Fig. 5 can be explained by the polarization of the electrode reaction caused by partial electronic conduction.

3.2. Hole and electron conduction

The steady-state polarization current density in an anionic conductor has been shown by Patterson *et al.* [13] to obey the following relation:

$$J_{ss} = K\sigma_n(\exp U - 1) + K\sigma_p(1 - \exp - U) \quad (4)$$

in which $K = RT/LF$ and $U = EF/RT$, and E is the e.m.f. applied to the cell, L the thickness of electrolyte, and σ_n and σ_p the electron and hole conductivities for the electrolyte, equilibrated with oxygen at the appropriate pressure. Equation 4 can be changed into Equation 5:

$$J_{ss}/K(1 - \exp - U) = \sigma_n \exp U + \sigma_p \quad (5)$$

Therefore, σ_n and σ_p can be obtained from the slope and intercept of the $J_{ss}/K(1 - \exp - U)$ versus $\exp U$ relation.

In order to perform polarization measurements, a blocking electrode must be established. Here, the ionic current was blocked by covering the Ag electrode on a disc specimen with a commercial soda-glass softened at 800°C . No chemical reaction between the electrolyte and the glass was observed below 700°C . Fig. 6 represents the data at $500 \sim 700^\circ\text{C}$ in air. The same measurements were done in oxygen and argon gas and in the P_{O_2} , eq of the CuO, Cu₂O mixture. However, as the CuO, Cu₂O

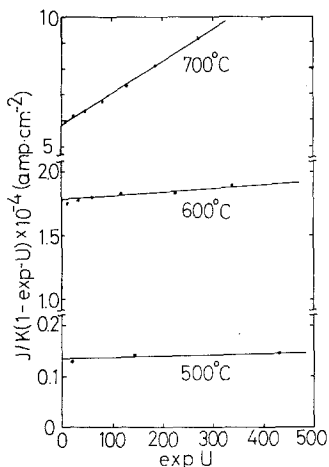


Fig. 6. Data for the polarization studies in air.

did not behave as a reversible electrode as mentioned above, no satisfactory measurements could be made in this case. Values of σ_n and σ_p calculated from the slopes and the intercepts are presented in Fig. 7, with the oxide ion conductivity of this material, as a function of the reciprocal of the absolute temperature [1]. The activation energies under different P_{O_2} values for hole or electron conduction are almost comparable and they are calculated to be 106 kJ mol⁻¹ and 213 kJ mol⁻¹, respectively. The σ_p and σ_n versus P_{O_2} data are indicated in Fig. 8. The slopes show the relations of $\sigma_p \propto P_{O_2}^{1/4}$ and $\sigma_n \propto P_{O_2}^{-1/4}$, indicating that the following defect equilibria are established in the presence of a large number of oxide ion vacancies due to the fluorite-type structure of the sesquioxide.

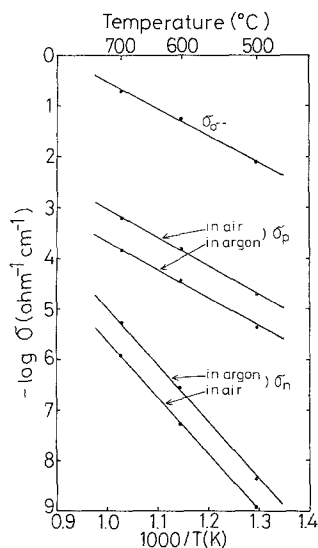


Fig. 7. Hole and electron conductivity of the Bi₂O₃-Y₂O₃ electrolyte in air and argon.

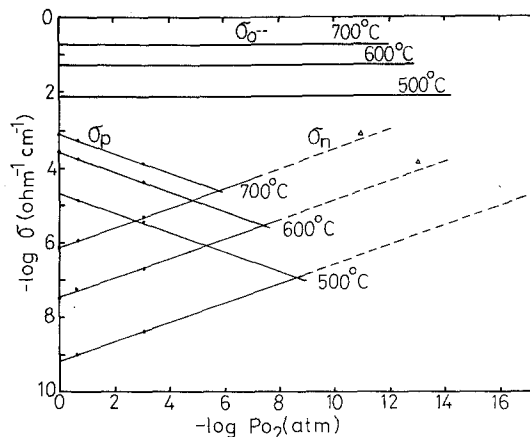
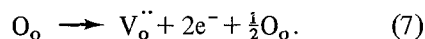
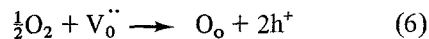


Fig. 8. P_{O_2} dependence of the hole and electron conductivities of the Bi₂O₃-Y₂O₃ electrolyte; (Δ) the electronic conductivity obtained using the cell (III).



The electronic conductivity (σ_e), calculated from the e.m.f. (E_o) for the cell [III], (see Equation 3), is considered to correspond to the electron conductivity (σ_n), since the $P_{O_2, a}$ and $P_{O_2, c}$ values of the cell [III] are low and close to one another. The σ_e values are also plotted against the $P_{O_2, eq}$ values of the Cu, Cu₂O mixtures at each temperature in Fig. 8, and lie almost on the extrapolated lines. These results also indicate partial non-stoichiometry as expressed in Equations 6 and 7. However, the contribution of electronic conduction to the total conductivity was found to be rather lower in the higher P_{O_2} range than in the $P_{O_2, eq}$ of the Bi, Bi₂O₃ mixture. The hole and electron conductivity of the Bi₂O₃-Y₂O₃ electrolyte can be expressed using the results of the temperature and P_{O_2} dependence of both conductivities as follows;

$$\sigma_p \Omega \text{ cm} =$$

$$5.0 \times 10^2 (P_{O_2} \text{ atm}^{-1})^{1/4} \exp [-106 \text{ kJ} (RT \text{ mol}^{-1})^{-1}] \quad (8)$$

$$\sigma_n \Omega \text{ cm} =$$

$$3.4 \times 10^5 (P_{O_2} \text{ atm}^{-1})^{-1/4} \exp [-213 \text{ kJ} (RT \text{ mol}^{-1})^{-1}] \quad (9)$$

4. Conclusion

As a result of this investigation, it can be stated that the electrolyte domain (where $t_{ion} \geq 0.99$)

for the $\text{Bi}_2\text{O}_3\text{-Y}_2\text{O}_3$ oxygen ion conductor extends down to the P_{O_2} given by the decomposition of the oxide electrolyte ($10^{-13.1}$ atm at 600°C). That is, the oxide ion conductivity of the electrolyte is, at least, two orders of magnitude higher than the partial electronic conductivity between 500 and 700°C under a non-reducible P_{O_2} atmosphere. The hole and electron conductivity can be expressed by the following equations:

$$\sigma_p \Omega \text{ cm} = 5.0 \times 10^2 (P_{\text{O}_2} \text{ atm}^{-1})^{1/4}$$

$$\times \exp [-106 \text{ kJ } (RT \text{ mol})^{-1}]$$

$$\sigma_n \Omega \text{ cm} = 3.4 \times 10^5 (P_{\text{O}_2} \text{ atm}^{-1})^{-1/4}$$

$$\times \exp [-213 \text{ kJ } (RT \text{ mol})^{-1}].$$

This oxide ion conductor can be used as the electrolyte of an oxygen gauge to measure comparatively high P_{O_2} at lower temperatures using a high P_{O_2} , c standard e.g. oxygen or air.

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