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Conduction in Bi_2O_3-based oxide ion conductors under low oxygen pressure. I. Current blackening of the Bi_2O_3-Y_2O_3 electrolyte

T. TAKAHASHI, T. ESAKA, H. IWAHARA

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

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The cathodic current blackening of Bi_2O_3-based oxide ion conductors was examined for the Bi_2O_3–Y_2O_3 electrolyte at low oxygen pressure. In air, more than 500 mA cm^{-2} d.c. could be passed at 600° C without causing changes in the electrolyte itself. However, in argon gas, a limiting current of 3 mA cm^{-2} was observed and the electrolyte was blackened at the cathode side. The limiting current was ascribed to control by the diffusion of oxygen gas at the cathode. The blackened oxide was found to consist of a mixture of Bi metal and Bi_2O_3–Y_2O_3 solid solution and to exhibit the equilibrium oxygen partial pressure almost corresponding to that of the Bi, Bi_2O_3 mixture.

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1. Introduction

Takahashi and co-workers have reported the high oxide ion conduction in the sintered oxides based on Bi_2O_3 [1–4]. For example, $(Bi_2O_3)_{0\cdot75}(Y_2O_3)_{0\cdot25}$ shows an oxide ion conductivity of $6\cdot0 \times 10^{-2}\ \Omega^{-1}\,cm^{-1}$ at 600° C and its ionic transport number is close to unity in air [2]. This conductivity value is one order of magnitude higher than that of the yttria-stabilized zirconia at the corresponding temperature [5]. Therefore, many applications at lower temperatures are expected using this high conductivity conductor, e.g. in oxygen pumps and the like. However, on the basis of the thermodynamic properties of Bi_2O_3, Bi_2O_3-based conductors should be easily reduced at low oxygen pressures [6, 7]. This will lead to the cathodic decomposition of the electrolyte and subsequent colour change (current blackening) on applying high current densities at low oxygen partial pressures. In order to investigate the conduction behaviour under low P_{O_2}, we have examined this current blackening of the oxide ion conductor of the system Bi_2O_3–Y_2O_3.

2. Experimental

The preparation method for polycrystalline specimens is the same as the technique reported previously [2, 3]. The specimen containing 27 mol% Y_2O_3 was mainly used in this experiment. This was sintered at 1100° C in air; the resulting specimen had a 93% density. X-ray analysis (CuKα radiation) showed it to consist of a fcc single phase. In order to measure the current-voltage characteristics, rod (13 × 5 mm diameter) and disc samples (1 × 12 mm diameter) were used. The latter had a reference electrode of Ag, pasted on the sample laterally to measure the cathode potential (Fig. 3). The d.c. voltage was applied galvanostatically at 600° C under each equilibrium oxygen partial pressure to the sample between silver electrodes provided on the both ends, and the terminal voltage and the cathode potential against the reference electrode were measured by the high impedance recorder.

The equilibrium oxygen partial pressures (P_{O_2}, eq) of the current-blackened specimen and the other oxide systems were measured by the following cells using 10 mol% yttria-stabilized zirconia (YSZ) disks as the electrolytes.

The blackened sample | YSZ | Ag, air (I)

M, MO_x | YSZ | Ag, air. (II)

The cell assembly is shown schematically in Fig. 1.

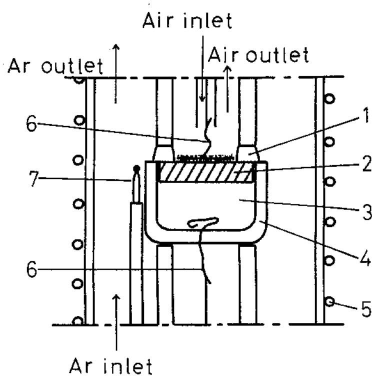

Fig. 1. Schematic cell assembly. (1) Glass packing (2) Electrolyte (3) Metal–metal oxide mixture (4) Alumina crucible (5) Heater coil (6) Ag lead (7) CA thermocouple.

Judging from the reasonable e.m.f.'s of the cells using Cu, Cu_2O and Ni, NiO as M, MO_x, the glass gasket softened at 800° C in Fig. 1 was found to be satisfactory to seal high and low P_{O_2} chambers. For the examination of the blackened sample, X-ray diffraction analysis, microscopic observation, DTA and TG were also employed.

3. Results and discussion

3.1. *Current blackening*

Fig. 2 shows the measured current density versus terminal voltage relations for a rod sample at 600° C. An ohmic relation is observed in air up to 500 mA cm^{-2} at least. In argon gas, however, a limiting current and the subsequent decomposition voltage are observed at about 3 mA cm^{-2} and 600 mV, respectively. Using a disc specimen with the reference electrode mentioned above, the limiting current was shown to be associated with the cathode. The cathode potential versus current density relation, measured at 600° C under various

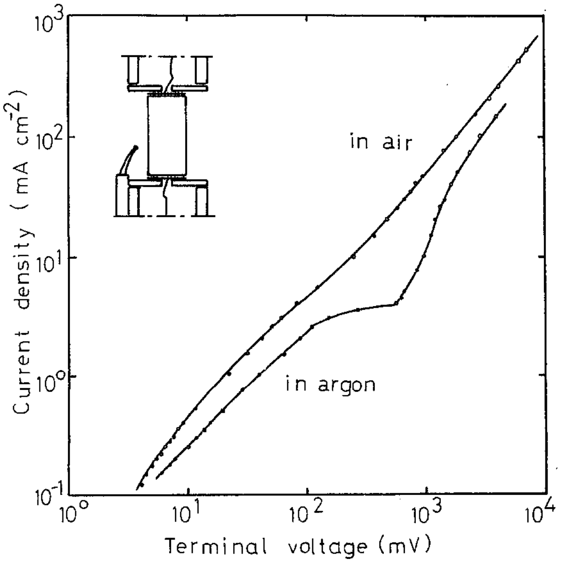

Fig. 2. Current density versus terminal voltage relations at 600° C.

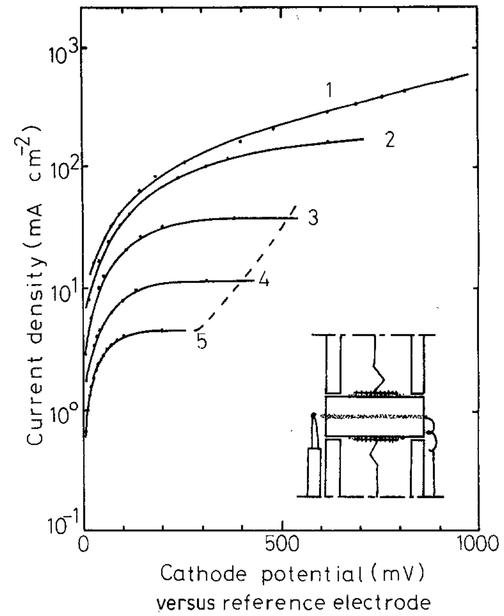

Fig. 3. Current density versus cathode potential relations at 600° C. (1) $P_{O_2} = 2{\cdot}1 \times 10^{-1}$ atm (2) $5{\cdot}1 \times 10^{-2}$ atm (3) $1{\cdot}1 \times 10^{-2}$ atm (4) $3{\cdot}7 \times 10^{-3}$ atm (5) $1{\cdot}3 \times 10^{-3}$ atm

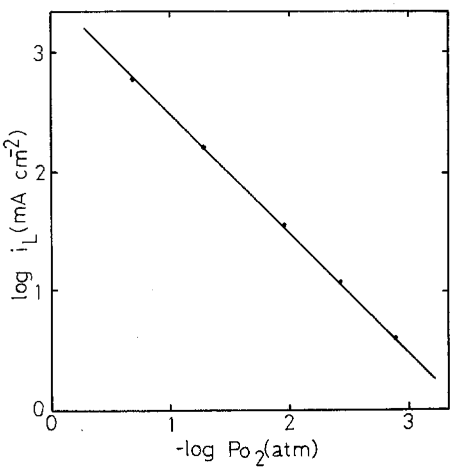

Fig. 4. P_{O_2} dependence of limiting current density (i_L) at 600° C.

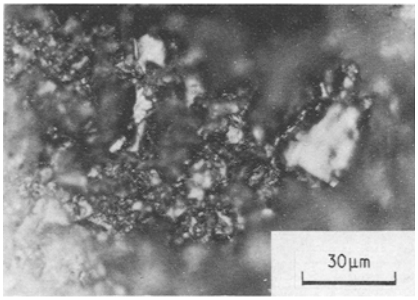

Fig. 5. Microstructure of blackened sample.

P_{O_2}, is given in Fig. 3. The potential values were corrected for the *IR* drops. The lower the P_{O_2}, the smaller and the more obvious, is the limiting current density (i_L). Fig. 4 indicates the P_{O_2} dependence of the i_L shown in Fig. 3. Apparently, the cathodic limiting current density is proportional to the P_{O_2}. This indicates that the limiting current is due to control by the rate of diffusion of oxygen gas at the cathode, since the i_L is related to P_{O_2} by Fick's law in the case of diffusion control i.e.

$$i_L = 4FD\frac{P_{O_2}}{\delta} \tag{1}$$

where F is the Faraday constant, D the diffusion coefficient and δ the thickness of the diffusion layer.

Further application of d.c. voltage beyond the limiting current in each case made the slope of the i–V curve steep as shown by a broken line in Fig. 3, and the resultant specimen was blackened from the catholyte surface towards the bulk, except for the sides. The blackened part was electrically conductive even at room temperature. Microscopic analysis showed that every part of the sample was not completely blackened even at the catholyte surface (Fig. 5). Fig. 6 represents the X-ray diffraction patterns of an unblackened and a blackened oxide, and of Bi metal (from the ASTM card). The blackened part was found to consist of two phases, a fcc solid solution of the Bi_2O_3–Y_2O_3 system and Bi metal. The diffraction pattern, corresponding to a lower valence oxide such as Bi_2O or BiO, was not observed in any case. The results of DTA or TG for the blackened oxide examined in air are indicated in Fig. 7. The mass of the sample increases as an exothermic reaction proceeds. As an endothermic peak at 271° C corresponds to the melting point of Bi metal, the exothermic reaction is due to the oxidation of Bi metal.

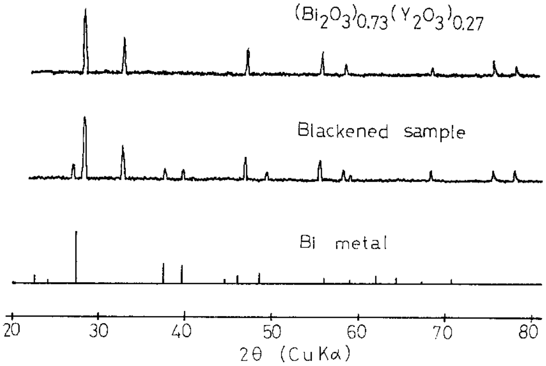

Fig. 6. X-ray diffraction patterns of an unblackened and a blackened sample and Bi metal.

As a result, it is concluded that the oxide is partially reduced to Bi metal by applying a high d.c. voltage under low P_{O_2}. From TG data, in particular, only about 30% of the Bi_2O_3 of the Bi_2O_3–Y_2O_3 solid solution was found to be decomposed into Bi metal even in the catholyte. The reason why Bi metal (271° C m.p.) is retained in the blackened oxide at high temperature is explained as follows: (1) the side of the sample is not electrolysed in argon gas; (2) the matrix of the fcc phase remains in the blackened region as mentioned above.

The current blackening condition of the oxide ion conductor has been examined for stabilized zirconia by several investigators [8, 9]. According to these authors, the current blackening was not accompanied by significant variations in the fcc

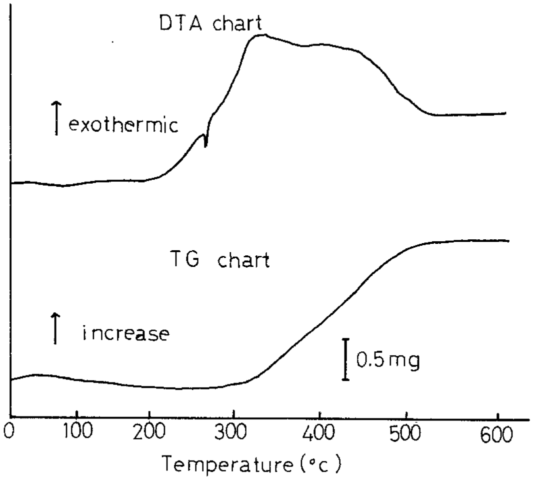

Fig. 7. DTA and TG charts of blackened sample.

lattice and, moreover, no evidence of reduction to free Zr metal was obtained, although the zirconia electrolyte exhibited a considerable colour change. The reduction to metal is considered to be a characteristic property of the oxide electrolyte based on Bi_2O_3 which has a small free enthalpy of formation $|\Delta G_f^0|$.

3.2. P_{O_2}, *eq in the blackened oxide*

One of the possible reactions during the above electrolysis is

$$(Bi_2O_3)_{1-x}(Y_2O_3)_x \rightarrow 2(1-x)Bi + [3(1-x)]/2\ O_2 + xY_2O_3. \tag{2}$$

However, as free Y_2O_3 is not shown to be present by X-ray diffraction, the overall decomposition reaction may be

$$(Bi_2O_3)_{1-x}(Y_2O_3)_x \rightarrow (Bi_2O_3)_{1-x-\alpha}(Y_2O_3)_x + 2\alpha Bi + 3\alpha/2\ O_2. \tag{3}$$

The P_{O_2}, eq of a mixture of Bi metal and oxide in the blackened specimen was examined using the cell [I]. Fig. 8 shows that the measured e.m.f. coincides with the value calculated from the free enthalpy of formation (ΔG_f^0) of Bi_2O_3 between 580 and 700° C within an accuracy of ± 5 mV. In order to evaluate the ΔG_f^0 value of Bi_2O_3, we used the data given by Chatterji and Smith [7], which was obtained using the following cell,

Bi, Bi_2O_3 | CaO-stabilized ZrO_2 tube | Pt, air. [III]

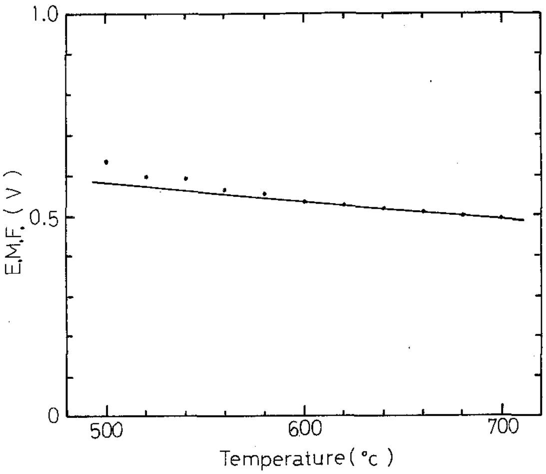

Fig. 8. Electromotive force versus temperature relation of the cell (I); a solid line shows the value calculated from the ΔG_f^0 of Bi_2O_3.

The P_{O_2}, eq of Bi, Bi_2O_3 is, for example, $10^{-13 \cdot 1}$ atm at 600° C. Therefore, the blackened sample has the same P_{O_2} value at the corresponding temperature. A deviation from the calculated value was observed at lower temperatures. Such behaviour has been observed sometimes for solid state galvanic cells of high impedance at lower temperatures.

The partially blackened specimen may be used as the low P_{O_2} standard for galvanic cells, since Bi metal does not escape from the blackened body at high temperature and the blackened oxide has the P_{O_2}, eq at each temperature. We will discuss this property in detail in the subsequent paper.

4. Conclusion

More than 500 mA cm^{-2} d.c. could be passed through the Bi_2O_3–Y_2O_3 electrolyte at 600° C in air without current blackening. However, a limiting current (≈ 3 mA cm^{-2}) was observed at $P_{O_2} \approx 10^{-4}$ atm and the electrolyte decomposed and blackened. The limiting current was found to be caused by a cathodic reaction controlled by the diffusion of oxygen gas, and the blackening was due to the partial reduction of the electrolyte into Bi metal. The blackened specimen exhibited the equilibrium P_{O_2} ($10^{-13 \cdot 1}$ atm at 600° C) which almost corresponded to that of the Bi, Bi_2O_3 mixture. This may be used as a low P_{O_2} standard for galvanic cells.

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