OXYGEN DIFFUSION THROUGH THE ELECTROLYTE BULK IN NOBLE METAL/(Bi₂O₃)₀.₈(Er₂O₃)₀.₂ AIR ELECTRODES

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ABSTRACT

The current decay curves of Au/(Bi₂O₃)₀.₈(Er₂O₃)₀.₂ and Pt/(Bi₂O₃)₀.₈(Er₂O₃)₀.₂ electrodes measured by potential-step chronoamperometry were analyzed by assuming a reaction model of oxygen diffusion through the electrolyte bulk. The theoretical decay curves calculated from this model give a better fit to experimental ones than those derived from the widely used adsorption model. Rate parameters involved in the decay equation were determined by curve-fitting. The time constant of diffusion obtained is independent of the electrode materials used, as predicted from the model. Permeability of oxygen in (Bi₂O₃)₀.₈(Er₂O₃)₀.₂ estimated from the rate parameter essentially agreed with known experimental values. These facts strongly suggest that the electrode performance is determined by the oxygen diffusivity of the electrolyte bulk.

INTRODUCTION

The performance of high temperature air electrodes is highly dependent on the solid electrolyte used. Not only the ohmic drop, but also the polarization loss is influenced by the electrolyte. For instance, a platinum electrode sintered on a Sc₂O₃-doped Ta₂O₅ electrolyte gives an order of magnitude greater polarization resistance than that on a Y₂O₃-stabilized ZrO₂(YSZ), while the same electrode on an Er₂O₃-doped Bi₂O₅ (EDB) shows an order of magnitude smaller polarization resistance than the Pt/YSZ electrode (1,2). Microscopic observation from the top of these electrodes indicates that these electrodes are in contact with the electrolyte surface in a comparable area, and therefore the performance difference is unascribable to a geometrical effect. Recently, it has been found that YSZ and EDB are oxygen-permeable (3,4). One can expect that the oxygen permeation also occurs in the SOFC electrodes incorporating these electrolytes. This study aims to understand the high performance of electrodes using EDB as the electrolyte in terms of its high oxygen diffusivity in the electrolyte bulk.
EXPERIMENTAL

Measurement of oxygen permeability in $\text{Bi}_2\text{O}_3$

A gold paste (Tokuriki Chemical Co., No.8570) was sintered at 850°C over a 2 cm$^2$ area of YSZ single crystal plate. A counter electrode was sintered on the other side of the crystal and a reference electrode on the peripheral area, using the same gold paste. A bismuth oxide slurry was painted over the gold electrode in full coverage. After dried, it was heated at 830°C to melt $\text{Bi}_2\text{O}_3$, and thereby the gold electrode was covered by a dense $\text{Bi}_2\text{O}_3$ layer. The layer thickness was estimated from the weight. This electrode was used to measure the oxygen permeability in $\text{Bi}_2\text{O}_3$ by potential-step chronoamperometry.

Preparation of the Electrodes

$\text{Er}_2\text{O}_3$-doped $\text{Bi}_2\text{O}_3$ electrolytes (80mol% $\text{Bi}_2\text{O}_3$ + 20mol% $\text{Er}_2\text{O}_3$) were prepared from reagent grade oxide powders, which were well mixed in a mortar and pressed into green pellets. They were then sintered at 1000°C for 24h. The faces of the sintered pellets were polished using a 3 µm diamond paste. To prepare platinum electrodes, a fluxless platinum paste (Tokuriki Chemical Co., No.8103) was painted over a 1.1 cm square area and sintered at 950°C. Gold electrodes were prepared using the above gold paste. This paste contains a small amount of glass frit to improve the adherence of electrodes, but its electrochemical effects on the electrode may be insignificant. The painted gold paste was sintered at 950°C.

Measurement of the Interfacial Area

Micrographs of the electrodes were taken from the top of the electrodes. The contact area was calculated by a usual procedure of image analysis, assuming that the projected area of the top view of the particles is equal to the contact area.

Measurement of the Potential-Step Chronoamperometry

Rectangular potential pulses having a width long enough for the complete decay of current transient were given between the reference and working electrodes by using a potentiostat (Nikko keisoku NPGS-301, nominal rise time 5 µs). The resultant current decay curves were observed on an oscilloscope screen (Iwatsu DS-6411) and current vs. time data were obtained by reading the scale of the screen.

ANALYTICAL PRINCIPLE OF DECAY CURVES

Measurement of oxygen permeability in $\text{Bi}_2\text{O}_3$

Figure 1 shows the schematic cross-section of Au/YSZ electrode covered by a dense $\text{Bi}_2\text{O}_3$ layer. If a potential-step is applied to this electrode, a current decay curve is obtained. The decay curve is theoretically obtained as follows.

Oxygen molecule in gas phase is dissociatively adsorbed on the $\text{Bi}_2\text{O}_3$ layer, diffuses through the bulk of $\text{Bi}_2\text{O}_3$ and is reduced to $\text{O}^{2-}$ ion at the $\text{Bi}_2\text{O}_3$-Au
interface. In this reaction scheme, atomic oxygen is tacitly assumed as the most probable diffusion species. This assumption is, however, not essential in the construction of the theory, because the atomic oxygen may be replaced with any other species, e.g., $O^{2-} + 2h^+$ which is usually assumed, as long as they obey Fick's diffusion law. The diffusion of atomic oxygen (or other equivalent species) in the Bi$_2$O$_3$ layer is expressed by the following diffusion equation (x axis is defined in Fig.1),

$$\frac{\partial \theta}{\partial t} = D \frac{\partial^2 \theta}{\partial x^2} \quad [1]$$

where $\theta$ is the dimensionless form of oxygen concentration in the Bi$_2$O$_3$ bulk, i.e., $C/C_s$ ($C_s$ is the concentration of oxygen sites in Bi$_2$O$_3$). At the moment when the potential step is applied, the concentration is equal to that at equilibrium state,

$$\theta = \theta_e \quad \text{when} \quad t = 0 \quad [2]$$

If the dissociative adsorption onto the surface of Bi$_2$O$_3$ layer is very fast, the oxygen concentration at the surface maintains its equilibrium value,

$$\theta = \theta_e \quad \text{at} \quad x = 0 \quad [3]$$

At the Au–Bi$_2$O$_3$ interface, the diffusional supply is balanced with the electrochemical consumption, so that

$$D \frac{d\theta}{dx} = -\frac{i}{2FC_s} \quad \text{at} \quad x = d \quad [4]$$

The potential step applied ($V_0$) is compensated by the sum of ohmic drop and concentration polarization due to the bulk diffusion, i.e., diffusional loss($\eta_d$),

$$V_0 = \eta_d + iAR_o \quad [5]$$

where $i$, $A$ and $R_o$ are the current density, nominal electrode area and ohmic resistance including the charge transfer resistance, respectively. Since the true capacity of double layer is too small to be discriminated from the ohmic behavior, this expression is justified. The diffusional loss is expressed by the Nernst equation,

$$\eta_d = -\frac{RT}{2F} \ln \frac{\theta_{x=d}}{\theta_e} \quad [6]$$

where $\theta_{x=d}$ is the oxygen concentration at the Au–Bi$_2$O$_3$ interface. Equation [6] is approximated to the following linear function if $\eta_d$ is small,
\[ \eta_d = \frac{RT}{2F} (1 - \frac{\theta_{\text{end}}}{\theta_e}) \quad [7] \]

Substitution of Eqs.[5] and [7] into Eq.[4] gives
\[ D \frac{d\theta}{dx} = -\frac{1}{2FC_s\theta_e A} (V_0 \frac{RT}{2F} + \frac{RT}{2F_\tau} \theta) \quad \text{at} \ x = d \quad [8] \]

Solution of Eq.[1] under the boundary conditions [2],[3] and [8] is [5]
\[ I = I_{t=0} \left\{ \frac{1}{1+L} + 2L \sum_{n=1}^{\infty} \frac{(L^2 + \beta_n^2) \sin^2 \beta_n}{\beta_n^2(L^2 + L + \beta_n^2)} \exp\left( -\frac{L}{\beta_n^2} \right) \right\} \quad [9] \]

where \( I_{t=0} \) is the current at \( t=0 \), \( \beta_n \) is the positive roots of \( \beta \cot \beta = -L \), and
\[ L = \frac{RTd}{4F^2C_s\theta_e A D} \quad [10] \]

and
\[ t_d = \frac{d^2}{D} \quad [11] \]

This is the decay equation to be compared with the experimental current decay curves. The oxygen permeability, defined by \( C_s \theta_e D \), is calculated from Eq.[10] using the best-fit value of \( L \).

**Extension of the bulk diffusion model to oxygen electrodes incorporating EDB electrolyte**

Figure 2 shows the schematic cross section of the electrode–electrolyte interface of a noble metal electrode incorporating EDB electrolyte. Suppose that oxygen molecule in gas phase is dissociatively adsorbed at three phase boundary (tpb) and dissolved into the EDB electrolyte as atomic oxygen or its equivalent species and is reduced to \( \text{O}^{2-} \) ions at the metal–EDB interface. In comparison between the two electrode structures shown in Figs.1 and 2, the three phase boundary, EDB electrolyte and metal–EDB interface in the latter can correspond to the Bi\(_2\)O\(_3\) surface, Bi\(_2\)O\(_3\) layer and Au–Bi\(_2\)O\(_3\) interface in the former, respectively. An essential difference between the two is in the diffusion distance; the former has a uniform distance while that of the latter is varied with the diffusion path from 0 (at tpb) to 2l (at the center of interface), as indicated in the figure. If \( x=1 \) is taken as an average diffusion distance, that is, the uniform current density equal to that at \( x=1 \) is generated over the entire interface, the above two models are completely equivalent to each other. The
decay equation for Fig.2 model is therefore expressed by the same form as Eq.[9], apart from that the layer thickness d is replaced with half the particle radius r in the definition of L and \( t_d \).

**Curve-Fitting Procedure**

Experimental decay data are given as discrete values of \( I \) vs. t. Equation[9] is expected to deviate from the experimental data at a long time region because of an appreciable lowering in the concentration at tpb from the equilibrium value, so that data near the steady state were abandoned. Calculation of Eq.[9] was repeated for every combination of given values of \( t_d \), L and \( I_{0d} \) until the error function \( \sum |\log I_{exp} - \log I_{cal}| \) is minimized. The best fit values thus obtained were taken as the values of these parameters.

**RESULTS AND DISCUSSION**

Table I gives the best-fit parameter values of Au/YSZ electrodes covered by Bi_2O_3 dense layers as a function of thickness. The time constant \( t_d \) and thickness are in a square relationship as predicted from the definition of \( t_d \) (Eq.[11]). The oxygen permeability calculated from the L values and that measured by Bouwmeester, et.al., are given in the same table. They are in the same order of magnitude, suggesting that the bulk diffusion described here really occurs in the electrode.

One can expect that the similar bulk diffusion takes place in the SOFC electrodes. The current decay curves of an Au/EDB electrode were measured and analyzed by the bulk diffusion model. Figure 3 shows an example of the current decay curve in comparison between the experimental and theoretical ones. The agreement between the two values is good. On the other hand, the decay curve calculated from the adsorption model(6) gives only poor fitting, as shown by a broken line in the same figure. Further, the adsorption model predicts the pseudocapacitance \( C_p \) expressed by the following equation(6),

\[
C_p = \frac{4F^2C_sA}{RT}
\]  

The \( C_p \) value calculated from the slope of the decay curve for Pt/EDB electrode at 700°C is 210 mF per 1 cm² of actual contact area, which is 25 times as high as that estimated from oxygen monolayer, i.e., 8.3 mF/cm². To explain this large capacitance, one must assume a 25 layers of adsorbed oxygen. However, such the thick oxygen layer is unrealistic.

Table II gives the comparison of best-fit parameter values calculated from Eq.[9] between Pt/EDB and Au/EDB electrodes. There is no significant difference in the \( t_d \) value between these two electrodes. This is to be expected from the definition of \( t_d \) (Eq.[11]), which depends only on the electrolyte used, not on the electrode material, if the particle size is the same. (The particle sizes of the Au and
Pt electrodes used are not very different, as seen in Fig.4).

The oxygen permeability $C_o \theta D$ is calculated for each $L$ value by inserting the contact area $A$ obtained by image analysis, $R_o$ from $V_o/I_{ac0}$, and $l=2 \mu m$ and $4 \mu m$ for Pt and Au electrodes, respectively, into Eq.[10]. Calculated values are given in Table II in comparison with known experimental data obtained by Bouwmeester, et. al. (4). The same data are also given in the Arrhenius plots (see Fig.5). The values of the present study agree in the slope, i.e., the activation energy for permeation, with the experimental one, but an appreciable discrepancy can be seen in the value, probably being due to the fact that the actual diffusion distance $l$ is longer than expected from the particle size.

Although diffusivity values obtained from $t_d$ may be limited in the accuracy because of difficulty in the precise estimation of diffusion distance, the $D$ value in EDB was tentatively calculated assuming $l=2 \mu m$ and $4 \mu m$ for Pt and Au electrodes, respectively. The results are given in the last column in the table. The order of $1 \times 10^{-5}$ cm$^2$/s at 800°C can be seen, which is reasonable in comparison with conductivity data.

CONCLUSION

The current decay curves of Pt/EDB and Au/EDB electrodes were analyzed assuming an oxygen diffusion through the bulk of EDB electrolyte. While the adsorption model must assume an unreasonably thick oxygen layer in the electrode–electrolyte interface to explain the experimental decay curve, this diffusion model can reproduce the decay curve by assuming two parameter values which are compatible with known permeability data of EDB. We conclude from this finding that, in any electrodes incorporating EDB electrolyte, the bulk diffusion is an essential process for oxygen supply.

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Table I  Best–fit parameter values for a Bi2O3–covered Au/YSZ electrode and oxygen permeability (Cθ0D) in Bi2O3 calculated from the formers. Measured in air at 800°C.

| d(cm) | t_d (s) | L(−) | Cθ0D (g-atom/cm·s) | Exp. value of Cθ0D (g-atom/cm·s)* |
|-------|---------|------|---------------------|----------------------------------|
| 1.06×10⁻² | 0.22    | 1.5  | 1.18×10⁻⁹          | 3.5×10⁻⁹                        |
| 2.8×10⁻²  | 1.70    | 4.5  | 1.16×10⁻⁹          | "                                |
| 3.6×10⁻²  | 2.6     | 5.2  | 1.30×10⁻⁹          | "                                |

* values taken from the raw data of Ref.(4).

Table II  Best–fit parameter values for Pt/EDB and Au/EDB electrodes and oxygen permeability (Cθ0D) calculated from the formers. Measured in air.

| Electrode | Temp t_d (ms) | L(−) | Cθ0D (g-atom/cm·s) | Exp. value of Cθ0D (g-atom/cm·s)* | D(cm²/s)* |
|-----------|---------------|------|--------------------|-----------------------------------|-----------|
| Pt/EDB    | 498           | 1200 | 1.4                | 1.24×10⁻¹¹                        | 3×10⁻⁸    |
|           | 601           | 190  | 1.1                | 7.2×10⁻¹ⁱ                        | 2×10⁻⁷    |
|           | 702           | 39   | 0.37               | 3.0×10⁻¹⁰                        | 1×10⁻⁶    |
|           | 800           | 11   | 0.19               | 7.2×10⁻¹⁰                        | 4×10⁻⁶    |
| Au/EDB    | 500           | 1100 | 0.63               | 1.88×10⁻¹¹                        | 1.5×10⁻⁷  |
|           | 602           | 190  | 3.6                | 1.02×10⁻¹⁰                       | 8×10⁻⁷    |
|           | 699           | 51   | 2.6                | 3.1×10⁻¹⁰                        | 3×10⁻⁶    |
|           | 799           | 20   | 1.2                | 8.6×10⁻¹⁰                        | 8×10⁻⁶    |

* values calculated assuming l=2µm and 4µm for Pt/EDB and Au/EDB, respectively. ** values taken from the raw data of Ref.(4).
Fig. 1 Schematic cross section of a Bi$_2$O$_3$-covered Au–YSZ electrode.

Fig. 2 Mechanism of oxygen diffusion through EDB electrolyte.
Fig. 3 An experimental decay curve in comparison with theoretical ones calculated from two different models.

Fig. 4 Optical micrographs of Au/EDB (left) and Pt/EDB (right) electrodes. Bright parts denote metal particles and dark backgrounds EDB surfaces.
Fig. 5 Oxygen permeability in EDB electrolyte calculated from the best-fit values of $L$. Triangles indicate the value of Au/EDB and circles Pt/EDB. Solid line is the experimental value cited from Ref. (5).