Title

Physicochemical properties of proton-conductive $\text{Ba}(\text{Zr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1})\text{O}_{3-\delta}$ solid electrolyte in terms of electrochemical performance of solid oxide fuel cells

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Abstract

Previously, most studies of proton-conductive electrolytes for SOFCs were conducted to achieve lower-temperature operation. In this study, we investigate a proton-conductive electrolyte to realize high-efficiency SOFCs. To this end, the dependencies of the total conductivity of $\text{Ba}(\text{Zr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1})\text{O}_{3-\delta}$ on the oxygen partial pressure and temperature under wet and dry conditions were measured. Based on the measurement data, we analyzed the ratio of ionic current density to electronic current density in the temperature range of 550-900°C. Assuming that the area-specific resistance of the electrolyte and the external current density were $0.383 \text{ } \Omega\text{cm}^2$ and 0.25 Acm^{-2} , respectively, the leakage current densities caused by the minority carriers were calculated to be 5.7% and 10.2% of the external current density at 550°C and 600°C, respectively. This study developed a method to evaluate proton-conductive electrolyte materials and established guidelines for the development of new materials for high-efficiency SOFCs.

Keywords

Proton conductor, Solid oxide fuel cell, Efficiency, Perovskite oxide, Potential profile.

Main text

1. Introduction

Currently, there is a strong demand for the development of highly efficient energy-conversion devices to make efficient use of the finite amount of available fossil fuels. Fuel cells can directly convert the chemical energy of the fossil fuels into electric energy and are expected to realize the highest power generation efficiencies among all fossil fuel-based energy-conversion devices. Solid oxide fuel cells (SOFCs) have the potential to achieve the highest power generation efficiency of all fuel cell types, and thus, they are inspiring active ongoing research and development efforts to enable the widespread use of SOFCs.

Although oxide-ion-conductive yttria-stabilized zirconia (YSZ) is the most frequently used electrolyte material in current SOFC-related research and development studies, it was recently reported that an solid electrolyte with adequate proton conductivity and a ionic transport number of 1 could realize very high power generation efficiencies of up

to as high as 85% [1]. The development of such ideal proton-conductive electrolyte materials is the most serious challenge facing the realization of such high efficiencies. Unfortunately, to date, such ideal materials have not been found.

Perovskite-type oxides are known to exhibit proton conductivity at high temperatures, such as the temperatures of SOFC operation, and many proton-conductive, perovskite-type oxides have been studied [2-7]. Among these, doped BaCeO₃ and doped BaZrO₃ are very popular. Although doped BaCeO₃ in the polycrystalline pellet form has been reported to have high ionic conductivity [8-12], these pellets react with the CO₂ and H₂O generated during SOFC operation and decomposed to BaCO₃ and CeO₂ and to Ba(OH)₂ and CeO₂, respectively. Thus, chemical stability is an important challenge for the use of doped BaCeO₃ materials [13-15]. Currently, these challenges remain unresolved. By contrast, doped BaZrO₃ materials have been shown to be highly resistant to reactions with CO₂ and H₂O [13, 14]; however, these materials exhibit lower ion conductivities because of their high electrical resistance, especially at the grain boundaries [16-19]. Similar to BaCeO₃ materials, this challenge has not been

satisfactorily addressed. Therefore, the use of a solid solution of doped BaZrO₃ and doped BaCeO₃ has been reported as a way to obtain both high conductivity and high chemical stability [15, 16, 20-26]. Among these solid solutions, Yang et al. reported the use of Ba(Zr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1})O_{3-δ} (BZCYYb) in a laboratory SOFC and found both high conductivity and chemical stability [27, 28].

However, the conductive behavior under SOFC operation conditions remains poorly understood; thus, gaining a detailed understanding of the conductivity behavior is very important for the practical use of these materials. Additionally, to date, proton-conductive electrolytes have mainly been studied to achieve lower-temperature SOFC operation, and to the best of our knowledge, little research has focused on the evaluation and analysis of proton-conductive electrolytes to improve SOFC efficiency.

In this study, we investigated the Ba(Zr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1})O₃ (BZCYYb) solid solution of doped BaCeO₃ and doped BaZrO₃, which has the potential to achieve both high conductivity and chemical stability and conducted material evaluation studies to determine the material's potential to increase the power-generation efficiency. The

dependencies of the total electrical conductivity on the oxygen pressure and temperature were measured, and the leakage current density was estimated based on the obtained results.

2. Experimental

2.1. Sample preparation

In this study, $\text{Ba}(\text{Zr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1})\text{O}_3$ (Kusaka Rare Metal Products Co., Ltd.: D50=0.63 μm , BET=8.7 m^2/g) powder was used as the solid solution for the doped BaZrO_3 and BaCeO_3 . First, 1.8 g of the powder was pressed uniaxially into rectangular pellets with dimensions of 45 mm $\times$ 5 mm $\times$ 3 mm at a pressure of 0.5 ton for 30 seconds. The pressed pellets were calcined at 1500°C for 10 h. For the calcination, the powders were inserted between the pellets and the Al_2O_3 base to prevent reaction between the samples and the Al_2O_3 base, as shown in Fig. 1. The relative density of the prepared samples was around 95%, which was estimated from the weight and dimensions measurement. Four Pt wires (diameter=0.3 mm) were connected with Pt

paste to transmit the electric current and monitor the voltage between the terminals; these were calcined at 900°C for 0.5 h.

2.2. Conductivity measurement

Fig. 2 shows the schematic of a conductivity measurement setup. To control the oxygen partial pressure, a mixture of Ar-balanced O₂ gas and Ar-balanced H₂ gas was prepared. The oxygen sensor was placed in the electric furnace, and the oxygen partial pressure was monitored during the measurements to confirm the oxygen concentration. The total conductivity was measured under two different water vapor pressure conditions: the wet condition ($P(\text{H}_2\text{O})=0.023$ bar) and the dry condition ($P(\text{H}_2\text{O})=1.2\times 10^{-6}$ bar). To humidify the gas mixture, the gas was introduced into a bubbler with the temperature controller set to 20°C; to dry the mixed gas, the gas was introduced into a container containing drying agents (DC-A4: NIKKA SEIKO CO., LTD.), and the dew point was maintained under -80°C. The sample was placed in the center of an alumina tube with a diameter and length of 50 mm and 500 mm, respectively. The electric furnace temperature was set between 550°C and 900°C. The

total conductivity of the samples was measured by the conventional four-terminal method using a galvanostat/potentiostat (HAL-3001: Hokuto Denko Corp.). During the measurements, a constant electrical current was applied to the sample, and the voltage between the sample's voltage terminals was monitored. The electrical current was controlled to maintain the voltage between 0.1 and 0.5 V. The total conductivity was calculated using the following equation:

$$\sigma = \frac{I}{\Delta E} \bullet \frac{L}{S} \quad (1)$$

where L is the distance between the voltage terminals, S is the cross-sectional area of the sample, I is the applied electrical current and ΔE represents the voltage between the voltage terminals.

3. Results and discussion

3.1. Results

3.1.1. Conductivity measurements

Fig. 3 shows the conductivity dependencies of BZCYYb on the oxygen partial pressure and temperature at $P(\text{H}_2\text{O})=0.023$ bar. The symbols represent the measured data, and the lines represent the fitted curves. The fitting method is discussed in the next section. The conductivities were proportional to the $1/4$ power of the oxygen partial pressure under high oxygen partial pressure ($P(\text{O}_2) > 10^{-6}$ bar) from 550°C to 900°C , similar to the results found for acceptor-doped, perovskite-type, proton-conducting oxides [29-34]. By contrast, under low oxygen partial pressure ($P(\text{O}_2) < 10^{-13}$), the conductivities were not dependent on the oxygen partial pressure and remained almost constant. Figs. 4 and 5 show the total conductivity dependence on the temperature and the calculated activation energies under both the wet and dry conditions, respectively, for high oxygen partial pressure ($P(\text{O}_2)= 10^{-6} \sim 0.1$ bar). For each oxygen partial pressure, the total conductivities of the wet condition tended to be higher than those of the dry conditions, and the calculated activation energies in the dry condition were higher than those in the wet condition. These results are attributed to the fact that both oxygen ions and protons act as the main ion carriers in the wet condition, whereas only oxygen ions function as

the main ion carriers in the dry condition.

Fig. 4 shows that the differences between the total conductivities of the wet and dry conditions were increased at lower oxygen partial pressure and higher temperature. For the higher oxygen partial pressure, this behavior may be ascribable to the increased hole concentration, as indicated by the following equation (2):

The conductivity at higher temperatures in the wet condition was thought to decrease because of the decreased $[OH_o^{\times}]$, as indicated by the following equation (3):

3.2. Discussion

3.2.1. Total conductivity

Many defect chemistry-based explanations of the conductivity of proton-conductive perovskite oxides have been reported [5, 35], and here, the fitting method used in this study is briefly described. In this study, the main reactions of the conductive carriers were assumed to be described by equations (2), (3) and (4) [36].

$$h^{\bullet} + e' = null \quad (4)$$

The equilibrium constants of the reactions described by equations (2)-(4) can be expressed as follows:

$$K_h = \frac{[O_o^{\times}][h^{\bullet}]^2}{[V_o^{\bullet\bullet}](P_{O_2} / P_{O_2}^0)^{1/2}}, \quad (5)$$

$$K_{OH} = \frac{[OH_o^{\bullet}]^2}{[V_o^{\bullet\bullet}][O_o^{\times}](P_{H_2O} / P_{H_2O}^0)}, \quad (6)$$

$$K_{eh} = [h^{\bullet}][e'] \quad (7)$$

The reaction of the trivalent dopant X (X=Y, Yb) substitution into the tetravalent Ce site can be written as follows:

In this measurement, when the concentration of the dopant is written as $[X'_{ce}]$, overall neutrality is preserved, and the equation expressing charge conservation is written as

$$2[V_o^{\bullet\bullet}] + [OH_o^{\bullet}] - [X'_{ce}] + [h^{\bullet}] - [e'] = 0 \quad (9)$$

Within the oxygen partial pressure region used here, the concentrations of both electrons and holes are assumed to be sufficiently small so that equation (9) can be written as

$$2[V_o^{\bullet\bullet}] + [OH_o^{\bullet}] - [X'_{ce}] = 0 \quad (10)$$

The number of oxygen ion sites in BZCYYb is maintained at 3, and the concentration relevant to the oxygen ion site can then be expressed by equation (11).

$$[O_o^\times] + [V_o^{\bullet\bullet}] + [OH_o^\bullet] = 3 \quad (11)$$

When equations (9) and (10) are substituted into equation (6), equation (12), which is quadratic in $[OH_o^\times]$, can be obtained.

$$\left(\frac{4 - K_{OH} P(H_2O)}{K_{OH} P(H_2O)} \right) [OH_o^\times]^2 + 6[OH_o^\times] - [X'_{ce}](6 - [X'_{ce}]) = 0 \quad (12)$$

From equation (12), $[OH_o^\times]$ is expressed by equation (14) by using equation (13) to define A.

$$A = \frac{4 - K_{OH} P(H_2O)}{K_{OH} P(H_2O)} \quad (13)$$

$$[OH_o^\bullet] = \frac{-3 + \sqrt{9 + A[X'_{ce}](6 - [X'_{ce}])}}{A} \quad (14)$$

The hole concentration can be described using equations (5), (10), (11) and (14), resulting equation (15).

$$[h^\bullet] = K_h^{1/2} \left(\frac{[X'_{ce}] - [OH_o^\bullet]}{6 - [X'_{ce}] - [OH_o^\bullet]} \right)^{1/2} P(O_2)^{1/4} \quad (15)$$

In this study, each trivalent dopant, such as Y and Yb, is 10% doped into the tetravalent

B site of ABO_3 -type perovskite oxides, and $[X'_{ce}]$ is 0.2. Thus, the hole concentration

is proportional to the 1/4 power of the oxygen partial pressure at constant temperature and water vapor partial pressure. Here, each electronic charge carrier's mobility is assumed to be independent of the oxygen partial pressure, and the total conductivity can then be expressed by equation (16).

$$\sigma_{Total} = \sigma_{h^{\bullet}} + \sigma_{ion} + \sigma_{e^{\bullet}} = \sigma_{h^{\bullet}}^0 P_{O_2}^{1/4} + \sigma_{ion} + \sigma_{e^{\bullet}}^0 P_{O_2}^{-1/4} \quad (16)$$

where $\sigma_{h^{\bullet}}^0$ and $\sigma_{e^{\bullet}}^0$ represent the conductivity of the holes and the electrons at an oxygen partial pressure of 1 bar, respectively [36]. Table 1 shows the σ_{ion} , the $\sigma_{h^{\bullet}}^0$ and the $\sigma_{e^{\bullet}}^0$ values calculated using equation (16) for temperatures ranging from 550°C to 900°C. Fig. 6 shows the dependences of ion conductivities, hole conductivities and electron conductivities on the oxygen partial pressure at temperature ranging 550°C to 900°C and Fig. 7 shows the calculated ratio of the ion current density to the total current density in terms of the oxygen partial pressure at temperatures from 550°C to 900°C. The results indicate that the ion current density ratio at low temperature is higher than that at high temperature.

3.2.2. Leakage current

The charge transport through the electrolyte is discussed based on the well-known Wagner theory. As shown in Fig. 8, we use a one-dimensional model to describe the charge-transport behavior. Here, $x=0$ represents the interface between the anode and the electrolyte extending towards the air side, and the thickness of electrolyte is L . The oxygen potential and charge carrier are assumed to change only along the x -axis, and the direction from the anode to the cathode was defined as the positive direction. In this study, we focused on the protons and holes as charge carriers. The partial current densities of the protons and holes are proportional to the electrochemical potential gradient and are given as follows:

$$J_{H^{\bullet}} = -\frac{\sigma_{H^{\bullet}}}{F} \frac{d\eta_{H^{\bullet}}}{dx} \quad (17)$$

$$J_{h^{\bullet}} = -\frac{\sigma_{h^{\bullet}}}{F} \frac{d\eta_{h^{\bullet}}}{dx} \quad (18)$$

where $\sigma_{H^{\bullet}}$ and $\sigma_{h^{\bullet}}$ are the conductivities of protons and holes, respectively, and $\eta_{H^{\bullet}}$ and $\eta_{h^{\bullet}}$ are the electrochemical potentials of protons and holes, respectively. F is the Faraday constant. The electrochemical potentials can be written as follows:

$$\eta_{H^{\bullet}} = \mu_{H^{\bullet}} + F\phi \quad (19)$$

$$\eta_{h^\bullet} = \mu_{h^\bullet} + F\phi \quad .(20)$$

where $\mu_{H^\bullet}$ and $\mu_{h^\bullet}$ are the chemical potentials of protons and holes, respectively and ϕ is the inner electrostatic potential. Under the steady-state conditions, local equilibria, such as the chemical equilibria described by equations (21) and (22), are assumed to be achieved throughout the electrolyte.

$$\frac{1}{2}H_2 + h^\bullet = H^\bullet \quad (21)$$

$$e' + h^\bullet = null \quad (22)$$

Under the steady-state conditions, the changes of free energy for the reactions described by equations (21) and (22) are equal to zero, and the following equations for the chemical potentials are obtained.

$$\frac{1}{2}\mu_{H_2} + 2\mu_{h^\bullet} = \mu_{H^\bullet} \quad (23)$$

$$\mu_{e'} + \mu_{h^\bullet} = 0 \quad (24)$$

Using equations (19), (20) and (23), $\eta_{H^\bullet}$ can be written as follows:

$$\eta_{H^\bullet} = \frac{1}{2}\mu_{H_2} + \eta_{h^\bullet} \quad (25)$$

Equation (17) represents the electric current density resulting from the protons, and

using equation (25), $J_{H^{\bullet}}$ can be expressed by equation (26).

$$J_{H^{\bullet}} = -\frac{\sigma_{H^{\bullet}}}{F} \left(\frac{1}{2} \frac{d\mu_{H_2}}{dx} + \frac{d\eta_{h^{\bullet}}}{dx} \right) \quad (26)$$

When the proportion of $J_{H^{\bullet}}$ to $J_{h^{\bullet}}$ is defined as r ,

$$r = \frac{J_{H^{\bullet}}}{J_{h^{\bullet}}} \quad (27)$$

$J_{h^{\bullet}}$ can be expressed as

$$J_{h^{\bullet}} = \frac{1}{r} J_{H^{\bullet}} \quad (28)$$

Using equations (18), (26) and (28), we can solve for $\frac{d\eta_{h^{\bullet}}}{dx}$ as follows:

$$\frac{d\eta_{h^{\bullet}}}{dx} = \frac{1}{2} \left(\frac{\sigma_{H^{\bullet}}}{r\sigma_{h^{\bullet}} - \sigma_{H^{\bullet}}} \right) \frac{d\mu_{H_2}}{dx} \quad (29)$$

Using equations (26) and (29), $J_{H^{\bullet}}$ and the total current density of J_{Total} can be written as follows:

$$J_{H^{\bullet}} = -\frac{1}{2F} \frac{r\sigma_{h^{\bullet}}\sigma_{H^{\bullet}}}{r\sigma_{h^{\bullet}} - \sigma_{H^{\bullet}}} \frac{d\mu_{H_2}}{dx} \quad (30)$$

$$J_{total} = J_{H^{\bullet}} + J_{h^{\bullet}} = \left(1 + \frac{1}{r} \right) J_{H^{\bullet}} = -\frac{1}{2F} \frac{(1+r)\sigma_{h^{\bullet}}\sigma_{H^{\bullet}}}{r\sigma_{h^{\bullet}} - \sigma_{H^{\bullet}}} \frac{d\mu_{H_2}}{dx} \quad (31)$$

Here, the hydrogen chemical potential is expressed by equation (32).

$$\mu_{H_2} = RT \ln P_{H_2} \quad (32)$$

Equation (32) is differentiated with respect to x

$$\frac{d\mu_{H_2}}{dx} = RT \frac{d \ln P_{H_2}}{dx} \quad .(33)$$

Then, using equation (33), the proton and total current densities can be expressed by equations (34) and (35).

$$J_{H^{\bullet}} = -\frac{RT}{2F} \frac{r\sigma_{h^{\bullet}}\sigma_{H^{\bullet}}}{r\sigma_{h^{\bullet}} - \sigma_{H^{\bullet}}} \frac{d \ln P_{H_2}}{dx} \quad (34)$$

$$J_{total} = -\frac{RT}{2F} \frac{(1+r)\sigma_{h^{\bullet}}\sigma_{H^{\bullet}}}{r\sigma_{h^{\bullet}} - \sigma_{H^{\bullet}}} \frac{d \ln P_{H_2}}{dx} \quad (35)$$

Here, considering the H_2O equilibrium, the equilibrium reaction and the equilibrium constant K can be written as

$$K = \frac{P_{H_2O}}{P_{H_2} P_{O_2}^{\frac{1}{2}}} \quad .(37)$$

Additionally, the partial hydrogen pressure is expressed by equation (38).

$$P_{H_2} = \frac{P_{H_2O}}{K P_{O_2}^{\frac{1}{2}}} \quad (38)$$

Assuming that the water vapor partial pressure in anode side is equal to that in cathode side, equation (38) can be differentiated with respect to x and written as follows:

$$\frac{d \ln P_{H_2}}{dx} = -\frac{1}{2} \frac{d \ln P_{O_2}}{dx} \quad .(39)$$

Using equations (34) and (39), the proton and total current densities can be described as

follows:

$$J_{H^{\bullet}} = \frac{RT}{4F} \frac{r\sigma_{h^{\bullet}}\sigma_{H^{\bullet}}}{r\sigma_{h^{\bullet}} - \sigma_{H^{\bullet}}} \frac{d \ln P_{O_2}}{dx} \quad , (40)$$

$$J_{total} = \frac{RT}{4F} \frac{(1+r)\sigma_{h^{\bullet}}\sigma_{H^{\bullet}}}{r\sigma_{h^{\bullet}} - \sigma_{H^{\bullet}}} \frac{d \ln P_{O_2}}{dx} \quad . (41)$$

Under the steady-state conditions, the proton flux is constant throughout, the electrolyte,

and the current densities can be calculated by integrating $\ln P_{O_2}$ with respect to x when

the thickness of the electrolyte is set to be L , as shown in equations (42) and (43).

$$J_{H^{\bullet}} L = \frac{RT}{4F} \int_{\ln P_{O_2}^{Anode}}^{\ln P_{O_2}^{Cathode}} \frac{r\sigma_{h^{\bullet}}\sigma_{H^{\bullet}}}{r\sigma_{h^{\bullet}} - \sigma_{H^{\bullet}}} d \ln P_{O_2} \quad (42)$$

$$J_{Total} L = \frac{RT}{4F} \int_{\ln P_{O_2}^{Anode}}^{\ln P_{O_2}^{Cathode}} \frac{(1+r)\sigma_{h^{\bullet}}\sigma_{H^{\bullet}}}{r\sigma_{h^{\bullet}} - \sigma_{H^{\bullet}}} d \ln P_{O_2} \quad (43)$$

The oxygen distribution in the electrolyte can then be written as

$$\frac{x}{L} = \int_{\ln P_{O_2}^{Anode}}^{\ln P_{O_2}} \frac{r\sigma_{h^{\bullet}}\sigma_{H^{\bullet}}}{r\sigma_{h^{\bullet}} - \sigma_{H^{\bullet}}} d \ln P_{O_2} \bigg/ \int_{\ln P_{O_2}^{Anode}}^{\ln P_{O_2}^{Cathode}} \frac{r\sigma_{h^{\bullet}}\sigma_{H^{\bullet}}}{r\sigma_{h^{\bullet}} - \sigma_{H^{\bullet}}} d \ln P_{O_2} \quad . (44)$$

Next, when we focused on oxide ions and holes as charge carries, the leakage, oxide ion and total current densities can be described as follows with similar calculations:

$$J_{h^{\bullet}} = \frac{1}{r} J_{O''} \quad (45)$$

$$J_{O''} L = \frac{RT}{4F} \int_{\ln P_{O_2}^{Anode}}^{\ln P_{O_2}^{Cathode}} \frac{r\sigma_{h^{\bullet}}\sigma_{O''}}{r\sigma_{h^{\bullet}} - \sigma_{O''}} d \ln P_{O_2} \quad , (46)$$

$$J_{Total}L = \frac{RT}{4F} \int_{\ln P_{O_2}^{Anode}}^{\ln P_{O_2}^{Cathode}} \frac{(1+r)\sigma_{h\cdot}\sigma_{O''}}{r\sigma_{h\cdot} - \sigma_{O''}} d \ln P_{O_2}, \quad (47)$$

where $\sigma_{O''}$ is the conductivity of oxide ions. These equations (45), (46) and (47)

have the same shapes of (28), (42) and (43). Here, both $\sigma_{H\cdot}$ and $\sigma_{O''}$ can be written

as σ_{ion} and regardless of the ion species types the leakage current density can be

written as follows:

$$J_{h\cdot} = \frac{1}{r} J_{ion}, \quad (48)$$

$$J_{ion}L = \frac{RT}{4F} \int_{\ln P_{O_2}^{Anode}}^{\ln P_{O_2}^{Cathode}} \frac{r\sigma_{h\cdot}\sigma_{ion}}{r\sigma_{h\cdot} - \sigma_{ion}} d \ln P_{O_2}, \quad (49)$$

$$J_{Total}L = \frac{RT}{4F} \int_{\ln P_{O_2}^{Anode}}^{\ln P_{O_2}^{Cathode}} \frac{(1+r)\sigma_{h\cdot}\sigma_{ion}}{r\sigma_{h\cdot} - \sigma_{ion}} d \ln P_{O_2}, \quad (50)$$

where

$$\sigma_{ion} = \sigma_{H\cdot} + \sigma_{O''}. \quad (51)$$

Fig. 9 shows the oxygen and hydrogen potential distributions between the fuel (anode)

side and the air (cathode) side under 20% H₂O-H₂ at temperatures from 550°C to 900°C.

Fig. 10 shows the leakage current density dependence on the external current density

from 550°C to 900°C when the area-specific resistance (ASR) is assumed to be 0.383

Ωcm², which is a typical value for the YSZ electrolyte. Fig. 11 shows the ratio of the

leakage current density to the external current density. Fig. 11 reveals that the leakage

current densities were 5.4% ($r = -19.5$) and 9.7% ($r = -11.3$) of the 0.25 Acm^{-2} external current density at 550°C and 600°C , respectively. These results indicate that the inhibition of the electronic current is necessary during operation at low temperature and high current density to achieve high-efficiency power generation when BZCYYb is used in SOFCs.

The leakage current density causes a consumption of the fuel. Therefore, it is desired to reduce the ratio of leakage current density to the total current density as much as possible. Under certain circumstances, SOFCs can be operated at the fuel utilization ratio of 90%[37]. Under this 90% fuel utilization condition, the leakage current density has to be inhibited less than 10% to the total current density. In terms of enhancement of the robustness of the system, the ratio of the leakage current density to the total current density is desired at least less than 8% (i.e. $r < -11.5$ is desirable) because a flow controller usually controls the gas flows with the accuracy of full scale range to a margin of error of $\pm 1\%$ to $\pm 2\%$. And in terms of the operation under higher fuel utilization condition (e.g. 95%), the ratio of the leakage current density is desired less

than 3% (i.e. $r < -32.3$ is desirable).

In this study, r values of BZCYYb were calculated to be -19.5 and -11.3 at 550°C and 600°C under 0.25Acm^{-2} , respectively. These r values are bigger than the requirement of $r (< -32.3)$. In terms of the leakage current density, materials which has smaller r value than BZCYYb are preferable for the electrolyte material to realize high power generation efficiency. Therefore, the development of new materials is desirable.

4. Conclusion

To achieve high-efficiency SOFCs, we measured the total conductivity dependencies of the BZCYYb material, which is a solid solution of doped BaCeO_3 and BaZrO_3 , on the oxygen partial pressure and temperature under wet and dry condition and obtained the following results:

- The total conductivity was proportional to the $1/4$ power of the oxygen partial pressure under the high oxygen partial pressure, similar to the results obtained previously for acceptor-doped, perovskite-type, proton-conductive oxides.

- At each oxygen partial pressure, the total conductivities under the wet condition tended to be higher than those under the dry condition.

- Using the measurement data, the ratio of the ionic current density to the total current density was calculated for temperatures from 550°C to 900°C.

- When BZCYYb electrolyte is used in SOFCs, the leakage current densities were calculated to be 5.4% (i.e. $r = -19.5$) and 9.7% (i.e. $r = -11.3$) of the external current density of 0.25 Acm^{-2} at 550°C and 600°C, respectively, when the ASR was assumed to be $0.383 \text{ } \Omega\text{cm}^2$.

In preceding studies, proton-conductive electrolytes for SOFCs have been studied to achieve SOFC operation at lower temperatures. In this study, we focused on adapting a proton-conductive electrolyte to realize high-efficiency SOFCs. Additionally, we have elucidated methods to predict physicochemical properties of SOFCs with the solid electrolyte having a mixed conduction of proton, oxide-ion, hole, and electron, and gave guidelines for future material development in terms of electrical efficiency.

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Captions

Fig. 1 Diagram of the pellet sintering configuration.

Fig. 2 Schematic of the conductivity measurement setup.

Fig. 3 Dependence of the total BZCYYb conductivity on the $P(O_2)$ at $P(H_2O)=0.023$ bar.

Fig. 4 Dependence of the total BZCYYb conductivity on temperature at $P(H_2O)=0.023$ bar and 1.2×10^{-6} bar.

Fig. 5 Dependence of the calculated activation energy on $P(O_2)$ at $P(H_2O)=0.023$ bar and 1.2×10^{-6} bar.

Fig. 6 Dependences of ion conductivities, hole conductivities and electron conductivities on the oxygen partial pressure at temperature ranging 550°C to 900°C.

Fig. 7 Dependence of the calculated ratio of the ion current density to the total current density on $P(O_2)$.

Fig. 8 Diagram of $h^\bullet$ and $H^\bullet$ transport through a proton-conductive electrolyte.

Fig. 9 Oxygen and hydrogen potential distributions in BZCYYb electrolyte at temperatures ranging from 550°C to 900°C.

Fig. 10 Dependence of the leakage current density on the external current density when ASR was assumed to be $0.383 \Omega\text{cm}^2$.

Fig. 11 Ratio of the leakage current density to the external current density.

Table 1 Calculated σ_{ion} , $\sigma_{h^\bullet}^0$ and $\sigma_{e^\bullet}^0$ values for temperatures from 550°C to 900°C.

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Parameter	550°C	600°C	700°C	800°C	900°C
σ_{ion}	9.41×10^{-3}	1.20×10^{-2}	1.67×10^{-2}	2.21×10^{-2}	3.01×10^{-2}
$\sigma_{h^{\bullet}}^0$	2.15×10^{-3}	4.05×10^{-3}	1.31×10^{-2}	3.08×10^{-2}	5.86×10^{-2}
$\sigma_{e^{\bullet}}^0$	2.00×10^{-11}	1.00×10^{-10}	1.00×10^{-9}	3.00×10^{-9}	9.00×10^{-9}

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