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The high temperature proton conductor $BaZr_{0.4}Ce_{0.4}In_{0.2}O_{3-\alpha}$

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Abstract

The oxygen ion conductor yttria-stabilized zirconia (YSZ), which is usually used as the electrolyte of SOFC, operates at high temperatures of about 1000 °C. The recent trend in developing SOFC is to reduce the operating temperature. Proton conducting cerates may allow the intermediate temperature operation for SOFC applications. Rare-earth-doped $BaCeO_3$ electrolytes with the perovskite structure present good protonic conductivities at moderate temperatures but rather poor chemical stability and endurance for moisture. Barium zirconate, in contrast, is a rather stable material but exhibits low protonic conductivity. We then focused on a practical protonic conductor of $BaZr_{0.4}Ce_{0.4}In_{0.2}O_3$ (BZCI) that has a relatively high durability against moisture and good protonic conductivity. However, little is known about its stability and electrochemical properties in reducing hydrogen. In this work, the electrochemical properties of BZCI as SOFC electrolytes were investigated in concentration cell and fuel cell operations. From the results of concentration cell measurements, it was revealed that BZCI has good proton conductivities in hydrogen-rich atmospheres and behaves as a protonic and oxide ionic conductor in oxygen-rich atmospheres, with some extent of electronic conductivity, which lowers its ionic transport number. Open circuit voltage (OCV) measurements in Fuel cell operations showed that OCV value of a Pt| BZCI| Pt cell is about 870 mV at 800 °C and 1020 mV at 600 °C.
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1. Introduction

Several proton conductors with perovskies structure (ABO_3) had been intensively investigated because of their potential for electrolytes of SOFC, hydrogen separation membranes and hydrogen sensors [1]. If B-atoms are partially replaced by trivalent cations, charge neutrality is commonly established by the formation of oxygen vacancies. These materials can dissolve water vapor at elevated temperatures according to the defect reaction:

$$(H_2O)_g + V_O^{\bullet\bullet} + O_O^X \leftrightarrow 2(OH)_O^{\bullet} \tag{1}$$

and consequently may become proton conductors [2–5].

It is well known that rare-earth-doped $BaCeO_3$ electrolytes with the perovskite structure present good protonic conductivities at moderate temperatures. Especially 20% Gd-doped $BaCeO_3$ has remarkably high proton conduc-

tivity. However, barium cerates have rather poor chemical stability and endurance for moisture. In CO_2 (or some extent of H_2O)-containing atmospheres, barium cerates easily react and decompose into barium carbonate (or barium hydroxide) and cerium oxide [6–9]. Barium zirconate, in contrast, is a rather stable material but exhibits low protonic conductivity.

A solid proton conductor that combines the high chemical stability of the zirconates and the high conductivity of the cerates could solve the problems. So, many researchers had investigated barium cerate–zirconate. We then focused on a practical protonic conductor of $BaZr_{0.4}Ce_{0.4}In_{0.2}O_3$ (BZCI) that has a relatively high durability against moisture and good protonic conductivity [10]. However, little is known about its electrochemical properties and they should be investigated.

In this work, the electrochemical properties of BZCI as SOFC electrolytes were investigated in concentration cell and fuel cell operations. And we compare the properties of BZCI with those of BCG ($BaCe_{0.8}Gd_{0.2}O_3$, rare-earth-doped $BaCeO_3$).

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2. Experimental

2.1. Sample preparation

Pellets of BZCI electrolyte (13 mm diameter and 0.45 mm thick) were prepared using a conventional ceramic processing procedure. The structure of BZCI was analyzed by X-ray diffraction. The pellets were ground flat before applying electrodes. Cells of Pt|BZCI|Pt were prepared by screen-printing Pt paste (Tanaka precious metals TR7905) onto both faces of each BZCI electrolyte pellet (electrodes consist of 0.16 cm^2 Pt square area). In order to collect current, the electrodes were connected by Pt mesh sheet and Pt paste. Subsequently the cells were calcined at 1000 °C for 2 h.

2.2. Conductivity measurements

The conductivities of Pt|BZCI|Pt cell were measured by the electrochemical ac impedance spectroscopy in wet H$_2$, air and N$_2$ at 500–750 °C with an ac impedance analyzer (Solartron Schlumberger 1286 and 1255).

2.3. Concentration cell measurements and fuel cell operations

Electrochemical concentration cell measurements (including fuel cell operations) were performed in a Pt|BZCI|Pt unit where both sides of BZCI pellet were sealed by a Pyrex glass ring. On either side, humid Ar, O$_2$ and H$_2$ could be selected and mixed with precisely known flow rates (1–200 ml/min) and the partial pressure of water vapor was controlled by adjusting the temperature of water that a carrier gas passed through with taking water vapor.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the X-ray diffraction patterns of BZCI (BaZr$_{0.4}$Ce$_{0.4}$In$_{0.2}$O$_3$) and BCG (BaCe$_{0.8}$Gd$_{0.2}$O$_3$) after sintering. The specimens showed single phase and had cubic perovskite structures.

3.2. Conductivities

The resistances were determined from the high frequency intercept of the spectrum with the real axis. The conductivities of BZCI in various atmospheres at several temperatures are shown in Fig. 2. In each atmosphere, BZCI shows high conductivities.

3.3. Concentration cell measurements

3.3.1. Concentration cell with water vapor and oxygen

To investigate the ionic conduction in oxygen-rich atmosphere, the EMF values of oxygen concentration cell were
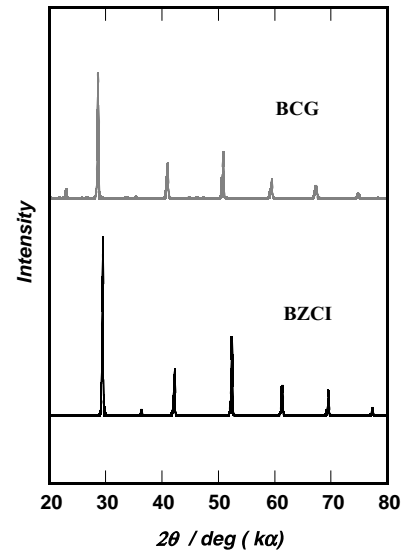

Fig. 1. X-ray diffraction patterns of BZCI and BCG.

measured. In this experiment, oxygen and a mixture of oxygen and argon were supplied to each side of electrodes. The water vapor pressures in both gases were kept constant (p$_{H_2O}$ = 2.98 KPa). Fig. 3 depicts the EMF values of BZCI and BCG obtained at 600–800 °C. Considering the theoretical equation:

$$\text{High p}_{O_2} : U = (t_O + t_H)\frac{RT}{4F} \ln \frac{p'_{O_2}}{p''_{O_2}} - t_H \frac{RT}{2F} \ln \frac{p'_{H_2O}}{p''_{H_2O}} \quad (2)$$

lines for $t_i = 1$ are also shown in Fig. 3. Here, t_H is the transport number for protons, t_O is the transport number for oxygen and t_i ($= t_H + t_O$) is the ionic transport number. BZCI exhibits smaller EMF values than theoretical values ($t_i = 1$) and those values of BCG were close to theoretical line. The ionic transport numbers of BZCI calculated from
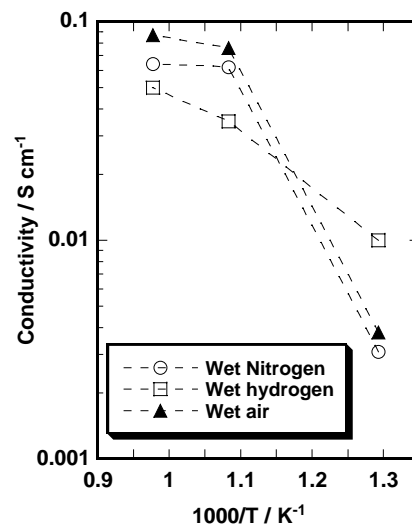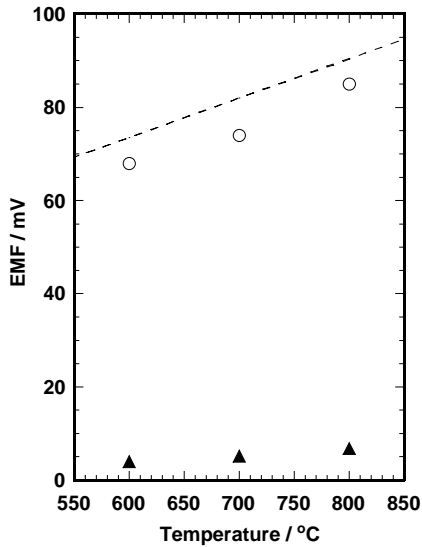

Fig. 2. Conductivities of BZCI in various atmospheres.

Fig. 3. EMF of the oxygen concentration cell. Broken line indicates the theoretical value ($t_i = 1$) of EMF, and (▲) represents experimental value of BZCI, (○) those of BCG.

Fig. 4. EMF of the hydrogen concentration cel of BZCI. Broken line indicates the theoretical value ($t_i = 1$) of EMF at each temperature, and (○) represents experimental value at 800 °C, (▲) 700 °C, (□) 600 °C.

Fig. 3 are very low and the relaxation times of EMF in a BZCI cell were very long at each temperature.

This result suggests that in an oxygen rich atmosphere, BZCI behaves as an oxide ionic conductor, but the electronic contribution is very large and has some extent of hole conductivity.

3.3.2. Concentration cell with water vapor and hydrogen

To investigate the ionic conduction in hydrogen-rich atmosphere, the EMF values of hydrogen concentration cell were measured. In this experiment, hydrogen and a mixture of hydrogen and argon were supplied to each side of electrodes. The water vapor pressures in both gases were kept constant ($p_{H_2O} = $ Pa). Figs. 4 and 5 depict the obtained EMF values of BZCI and BCG, respectively at 600–800 °C. The theoretical EMF values are given by following equation:

$$\text{Low } p_{O_2} : U = -(t_O + t_H)\frac{RT}{4F} \ln \frac{p'_{H_2}}{p''_{H_2}} + t_O \frac{RT}{2F} \ln \frac{p'_{H_2O}}{p''_{H_2O}} \quad (3)$$

The theoretical line ($t_H + t_O = 1$) is also shown in Figs. 4 and 5. Each EMF values obtained from this measurement is very close to the theoretical value calculated from Nernst's equation. The ionic transport numbers of BZCI calculated from Fig. 4 slightly decrease as temperature rises. This result suggests that the specimens exhibit almost pure protonic conduction under hydrogen atmosphere, and electronic contribution increases with the rise of temperature.

3.3.3. Fuel cell operation

To investigate the ionic conduction in fuel cell conditions, the open circuit voltages (OCV) of fuel cell were measured. In this experiment, hydrogen and air were supplied to anode and cathode, respectively. The water vapor pressures in
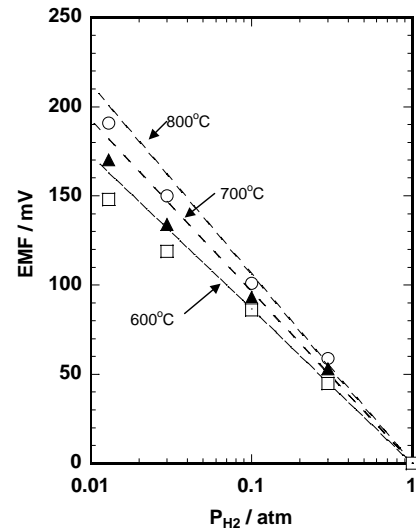
anodic gases were kept constant ($p_{H_2O} = $ Pa) and those of cathode were kept dry. Fig. 6 shows the OCV obtained at 600–800 °C. The line of theoretical OCV values in Fig. 6 were calculated using equation of oxygen concentration cell. Here the ionic transport number $t_i = 1$ and anodic oxygen partial pressures were calculated from the water equilibrium:

$$\frac{p_{H_2O}}{p_{H_2}}\sqrt{p_{O_2}} = \exp\left(-\left(\frac{-247845 + 55.219T}{RT}\right)\right) \quad (4)$$

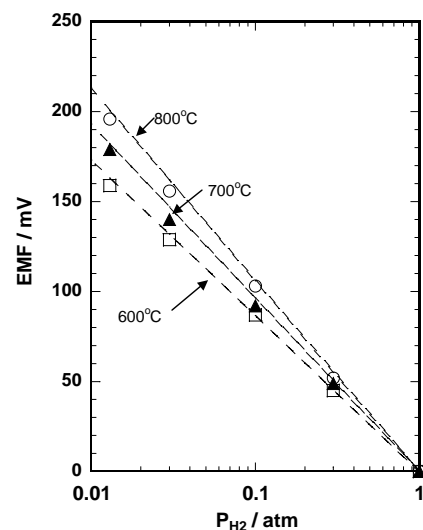The experimental results showed that electronic contribution increases as temperature rises.

Fig. 5. EMF of the hydrogen concentration cel of BCG. Broken line indicates the theoretical value ($t_i = 1$) of EMF at each temperature, and (○) represents experimental value at 800 °C, (▲) 700 °C, (□) 600 °C.
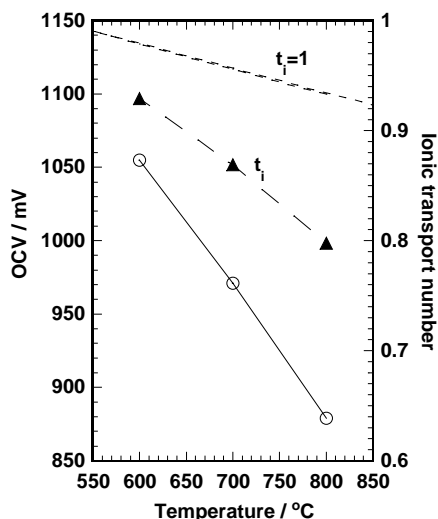
Fig. 6. OCV and ionic transport numbers of a fuel cell with BZCI electrolyte. Broken line indicates the theoretical value ($t_i = 1$) of OCV, and ($\bigcirc$) represents experimental value of OCV, and ($\blacktriangle$) represents ionic transport number of BZCI.

3.4. Dependency of OCV relaxation time on temperature

Through fuel cell operations of BZCI, we found the fact that the relaxation time of OCV pf BZCI severely depends on temperature (Here, 'relaxation time' means the elapsed time between feeding fuel to anode and reaching at the steady state of OCV). Fig. 7 shows the dependency of relaxation time on temperature. In Fig. 7, the OCV values of fuel cell at 500 and 600 °C had become steady state within 1 h, but at 700 and 800 °C, they had not become steady state after 12 h yet. This trend was prominent at 800 °C. OCV measurement at 800 °C indicated that the relaxation time at 800 °C is over 72 h.
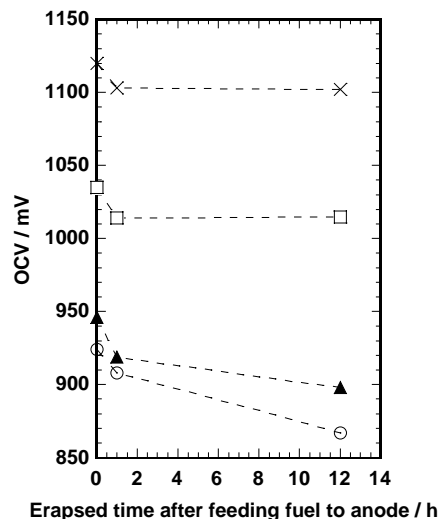

Fig. 7. Dependency of relaxation time of OCV in a Pt|BZCI|Pt cell on temperature. ($\bigcirc$) 800 °C, ($\blacktriangle$) 700 °C, ($\square$) 600 °C, ($\times$) 500 °C.

This severe dependency on temperature was found only in Pt|BZCI|Pt cells, and not in Pt|BCG|Pt cells.

The value of ionic transport number is increased immediately after feeding fuel to anode, because the concentration of hole is decreased by electrons which are generated by following reaction:

$$H_2(gas) + 2h^{\bullet} + 2O_O^X \rightarrow 2OH_O^{\bullet} \tag{5-1}$$

or

$$H_2(gas) + 2O_O^X \rightarrow 2OH_O^{\bullet} + 2e' \tag{5-2}$$
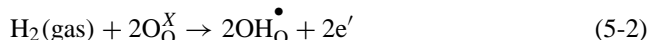
However, at high temperature(700, 800 °C), BZCI has some extent of oxide-ion conductivity, and following cathodic reaction may reprogress very slowly:

$$1/2O_2 + V_O^- \rightarrow O_O^X + 2h^{\bullet} \tag{6}$$

So the concentration of hole in BZCI and electronic transport number increases gradually. Thus, the OCV relaxation time has a dependency on temperature due to above factors. From this result, it is suggested that in fuel cell conditions, hole contribution in BZCI is larger than that in BCG. This results agrees with the those of oxygen concentration cell measurement.

4. Conclusion

Electrochemical properties of $BaZr_{0.4}Ce_{0.4}In_{0.2}O_3$ (BZCI) were measured and compared with those of BCG ($BaCe_{0.8}Gd_{0.2}O_3$). It was revealed that BZCI is a good protonic conductor under hydrogen atmosphere, but under high oxygen partial pressure and fuel cell conditions, it behaves as a protonic, oxide-ionic and electronic mixed conductor. The electronic contribution of BZCI in fuel cell conditions becomes large with the rise of temperature.

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