SOFC USING Dy–DOPED BaCeO₃ CERAMICS
AS A SOLID ELECTROLYTE

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ABSTRACT

Based on BaCe₁₋ₓDyxO₃₋ₐ (x ≤ 0.20) solid electrolytes, hydrogen–air fuel cells have been constructed and operated at temperature above 800 °C. The terminal voltage was 0.65 V at 400 mA cm⁻² with 0.26 W cm⁻² at 1000 °C and 0.67 V at 200 mA cm⁻² with 0.14 W cm⁻² at 800 °C. These values are rather high considering the thickness of the electrolyte (0.5 mm). Both the anodic and cathodic polarizations are sufficiently small, indicating that the voltage drop on discharging the cell is mainly due to the ohmic resistance of the solid electrolyte. From the measurement of water vapor evolution rates in the anode and cathode compartments, respectively, the charge carriers in the solid electrolyte were determined to be protons and oxide ions, the ratio of which depended on operating temperature.

1. INTRODUCTION

Although stabilized zirconias have been mainly used for a solid electrolyte of SOFC (solid oxide fuel cell), it is desirable to develop alternate solid electrolytes which have better characteristics such as high energy efficiency, low polarization, etc. Recently, it has been reported that some kinds of perovskite–type oxides exhibit a good proton conduction or proton–oxide ion mixed conduction under hydrogen–containing atmosphere at high temperature (1,2). Using these ceramics as a solid electrolyte, small scale fuel cell were constructed by way of experiment, and their performances were examined (3–8). For example, we obtained 0.2 A cm⁻² of short-circuit current from the fuel cell based on Yb–doped SrCeO₃ solid electrolyte (thickness: 0.5 mm) at 1000 °C (2). Also, 1.0 and 1.2 A cm⁻² of short-circuit currents were obtained using Sm– and Gd–doped BaCeO₃ solid electrolytes (thickness: 0.5 mm), respectively, at 1000 °C (7,8).

Besides being interesting to the SOFC characteristic, these perovskite solid electrolytes, particularly BaCeO₃ systems, have a unique property regarding the charge carrier during the discharge of cell (2,4,5,8–10). Although doped BaCeO₃ ceramics exhibit the proton conduction in hydrogen atmosphere, they behave as the mixed proton and oxide ion conductor under the SOFC conductions. In addition, this mixed ion conduction is dependent on the species of dopant trivalent cation and...
its content (10), and hence the SOFC characteristic is also affected by the dopant species. If so, one could expect a better BaCeO3 solid electrolyte by choosing the optimum dopant cation. In view of the above, we investigated various dopant for BaCeO3 and have found that Dy3+ is the best one. Accordingly, we adopted Dy3+ as dopant cation and evaluated the performance of hydrogen–air fuel cell based on BaCe1-xDyxCb-a.

2. EXPERIMENTAL

Dy-doped BaCeO3 ceramics were prepared by a solid state reaction of Ba(CH3COO)2, CeO2 and Dy2O3. The required amounts of raw materials were mixed and then calcined in air at 1300 °C for 10 h. The calcined oxides were ground in a ball mill, followed by hydrostatic pressing into cylindrical pellets at 2 ton cm-2. The pellets were sintered in air at 1650 °C. The porosity of the obtained ceramics was less than 5 %. The crystalline phase was confirmed by X–ray diffraction method.

Electrical conductivity was measured in wet hydrogen atmosphere by complex impedance method. The wet hydrogen was prepared by passing it through water bubbler at room temperature. For the estimation of the SOFC characteristics, we constructed the test cell, the schematic structure of which is shown in Fig. 1. Dy-doped BaCeO3 ceramic was sliced into a disk of 0.5 mm thickness. Porous platinum electrodes were attached to both faces of the disk (electrode area: 0.5 cm2). In order to eliminate the IR drop of lead from the cell, each electrode was connected to two platinum lead wires, i.e., current lead and potential lead. The cell was discharged under the hydrogen–air condition in the range 800–1000 °C. The polarization characteristic of each electrode was measured by current interruption method. In this case, a platinum wire was wound around the side of the ceramic disk as a reference electrode. The amounts of water vapor evolved at the anode and cathode during the discharge were measured with a humidity sensor in order to clarify the contribution of proton and oxide ion conductions in the electrolyte.

3. RESULTS AND DISCUSSION

Total conductivity in hydrogen atmosphere

From X–ray diffraction measurement, it was found that BaCe1-xDyxCb-a system consisted of a single phase of orthorhombic perovskite-type structure in the compositional range studied (0 < x < 0.2). Arrhenius plots of the conductivity in hydrogen atmosphere for this system are plotted in Fig. 2. The maximum conductivity lay in a 20 mol % Dy composition, and the activation energy for the conduction was 0.41 eV above 750 °C. Figure 3 shows a comparison of Dy-doped BaCeO3 with other BaCeO3 systems. The conductivity of BaCeO3 systems depended strongly on the ionic radius of the dopant cations. A cation with slightly larger ionic radius than that of Ce3+ ion (0.087 nm for Schanone's value) might be
preferable as a dopant for good conduction.

**Discharge characteristic of fuel cell**

Figure 4 shows the discharge performance of hydrogen–air fuel cell, in which 20 mol % Dy-doped BaCeO₃ was used as a solid electrolyte and porous platinum as an electrode material. The cell exhibited good and stable performance. The terminal voltage was about 0.65 V at 400 mA cm⁻² with 0.26 W cm⁻² at 1000 °C and 0.67 V at 200 mA cm⁻² with 0.14 W cm⁻² at 800 °C. These values are rather high considering the thickness of the electrolyte (0.5 mm). At any temperature, the relation between terminal voltage and current density was linear, suggesting that ohmic resistance of the solid electrolyte was main cause for voltage drop during discharge. In fact, measured values of both the anodic and cathodic overpotentials were very small as shown in Fig. 5. The open-circuit voltages were somewhat lower than the theoretical values, especially at 1000 °C, due to the contribution of the hole conduction, as described below.

**Proton and oxide ion mixed conduction**

As we pointed out previously (2,5,10), BaCeO₃–based oxides exhibit the proton and oxide ion mixed conductions under the fuel cell conditions. In the present study, the amount of water vapor evolved in each electrode compartment was measured during discharge in order to know which kind of ion is a charge carrier under the fuel cell conditions. The results are shown in Fig. 6 (a) and (b). Water vapor evolution rate at the cathode was higher than that at the anode at 700 °C, while the opposite tendency was observed at 1000 °C. This suggests that the proton conduction is predominant at 700 °C, but the oxide ion conduction becomes significant as the temperature increases. Similar phenomenon was observed in other BaCeO₃ systems (5,8). From a series of studies on proton in the doped perovskite–type oxides, proton might be introduced into the solid according to the following equation (11–15):

\[
\text{H}_2\text{O} + \text{V} \rightarrow 2\text{H}^+ + \text{O}_6
\]  

If the temperature increases, eq. (1) should shift toward the left hand side. This results in a decrease of the proton concentration and in an increase of the oxide ion vacancy concentration. Also, the mobility of oxide ion will increase with temperature. Therefore, the oxide ion conduction becomes significant as the temperature rises.

On the other hand, total amounts of water vapor evolved at the anode and cathode were somewhat less than the values calculated from Faraday's law, indicating the existence of electronic conduction under the present conditions. Since the decrease in oxygen partial pressure at the cathode diminished the departure from the ideal behavior, other mobile carrier was confirmed to be electron hole.
Performance of fuel cell with nickel and $La_{0.6}Ba_{0.4}CoO_3$ electrodes

For the feasibility of the fuel cell application, it is important to use a more stable and cheaper electrode material. Instead of expensive platinum, porous nickel as an anode material and various kinds of oxide electronic conductors as a cathode material were examined. Of the oxide materials examined, $La_{0.6}Ba_{0.4}CoO_3$ showed the best characteristics. The SOFC using this material as a cathode and porous nickel as an anode material and $BaCe_{0.8}Dy_{0.2}O_3-a$ ceramic disk as a solid electrolyte worked stably. The cell performance is shown in Fig. 7. The relation between the terminal voltage and the current density was linear. However, the short-circuit current was somewhat lower compared to that of the cell with platinum electrode. As shown in Fig. 8, the polarization resistances of both nickel anode and $La_{0.6}Ba_{0.4}CoO_3$ cathode were close to that of platinum electrode. It thus seems that the insufficient conductance of nickel or $La_{0.6}Ba_{0.4}CoO_3$ is the main reason for lower power output than that of the cell with platinum electrode.

4. CONCLUSIONS

The Dy-doped $BaCeO_3$ system had a maximum conductivity at 20 mol % Dy which substituted for Ce. The ceramic of this composition had the highest conductivity among the doped $BaCeO_3$ systems. Hydrogen-air fuel cell using 20 mol % Dy-doped $BaCeO_3$ as a solid electrolyte performed satisfactorily above 800 °C, and its power density was high compared to that of the cells with other $BaCeO_3$ systems. Both the anodic and cathodic polarizations were very small under the operation conditions. During the discharge of the cell, $BaCe_{0.8}Dy_{0.2}O_3-a$ ceramic exhibited the proton and oxide ion mixed conduction, which was dependent strongly on the operation temperature: contribution of proton to conduction was significant at 700 °C, whereas oxide ion conduction became predominant as the temperature increased.

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Figure 1  Schematic structure of the fuel cell.
Figure 2 Arrhenius plots of conductivity of BaCe$_{1-x}$Dy$_x$O$_{3-x}$ system in hydrogen atmosphere.

Figure 3 Conductivity of doped BaCeO$_3$ systems in hydrogen atmosphere as a function of ionic radius of dopants.
Figure 4  Discharge performance of the hydrogen-air fuel cell: 
H₂, Pt | BaCe₀.₈Dy₀.₂O₅₋ₓ | Pt, air; 
electrolyte thickness = 0.5 mm.

Figure 5  Polarization characteristics (IR free) of Pt electrodes in the fuel cell: 
H₂, Pt | BaCe₀.₈Dy₀.₂O₅₋ₓ | Pt, air.
Figure 6  Water vapor evolution rate in each electrode compartment during discharge of the cell at 800 and 1000 °C.
Figure 7  Discharge performance of the hydrogen–air fuel cell using porous nickel and perovskite–type oxide as electrode materials: 
\[ \text{H}_2, \text{Ni} \mid \text{BaCe}_{0.8}\text{Dy}_{0.2}\text{O}_3-y \mid \text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_3, \text{air} \]; electrolyte thickness = 0.5 mm.

Figure 8  Polarization characteristics (IR free) of Ni and La_{0.4}Ba_{0.6}CoO_3 electrode in the fuel cell: 
\[ \text{H}_2, \text{Ni} \mid \text{BaCe}_{0.8}\text{Dy}_{0.2}\text{O}_3-y \mid \text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_3, \text{air} \].