SOFC USING CUBIC STABILIZED ZIRCONIA IN A ZrO2·Sc2O3·Al2O3 SYSTEM AS AN ELECTROLYTE

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ABSTRACT

We examined the possibility of low temperature operation of solid oxide fuel cells using cubic stabilized zirconia in a ZrO2·Sc2O3·Al2O3 system as an electrolyte. The single cell was fabricated using La0.8Sr0.2MnO3 as a cathode and Ni-YSZ as an anode. The maximum power density is 0.63 W/cm² at 800 °C and 1.0 W/cm² at 880 °C. This suggests that the present electrolyte is a good candidate for fuel cells operating in the temperature range 800 °C and 900 °C.

INTRODUCTION

In recent years, much attention has been paid to solid oxide fuel cells (SOFC) because they offer a highly efficient and environmentally benign technology for energy conversion. An SOFC generally operates at about 1000 °C due to the low ionic conductivity of electrolyte such as yttria-stabilized zirconia (YSZ). This high operating temperature causes material problems including electrode sintering, interfacial diffusion between electrolyte and electrode, and mechanical stress arising from different thermal expansion coefficients. Therefore, it is desirable to operate a fuel cell at as low a temperature as possible. Lowering the operation temperature requires a reduction in the ohmic loss of cell components, especially electrolyte material. Since the electrolyte resistance is equal to the product of resistivity and thickness, it can be reduced by developing materials with low resistivities or by fabricating thinner layers. The most promising material with much greater ionic conductivities than YSZ is Gd2O3-doped CeO2. Ceria is thermodynamically stable in the air, but becomes a mixed conductor at low oxygen partial pressure. Considerable effort is being focused on suppressing mixed conductivity by cladding the Gd2O3-doped CeO2 with a thin layer of YSZ. On the other hand, it is difficult to fabricate a dense thin layer of electrolyte on a porous substrate of electrode other than by the electrochemical vapor deposition (EVD) method. Therefore it is necessary to find a new solid electrolyte with high oxygen-ion conductivity.

The ZrO2·Sc2O3 system exhibits the highest ionic conductivity of the zirconia solid solutions [1-4] but the phase diagram shows complex phase relationships [5-8]. We carefully investigated the relationship between ionic conductivity and crystal structure in the ZrO2·Sc2O3 system and found that the 0.88ZrO2·0.12Sc2O3 (β-phase) undergoes a discontinuous change in ionic conductivity at around 660 °C with the structural phase transition from rhombohedral to cubic symmetry. We examined the ionic conductivity and crystal structure of this compound by adding second dopant and found that a small amount of Al2O3 is effective in stabilizing the high temperature cubic phase with high ionic conductivity [9]. The ionic conductivity of cubic stabilized zirconia...
0.89ZrO$_2$-0.105Sc$_2$O$_3$-0.005Al$_2$O$_3$ is about 0.1S/cm at 800 °C. We reported the basic properties of single cell operation in the temperature range between 800 °C and 900 °C using the cubic stabilized zirconia in ZrO$_2$-Sc$_2$O$_3$-Al$_2$O$_3$ system as an electrolyte[10].

On the other hand, Yamamoto and coworkers reported work on the composite of ZrO$_2$-Sc$_2$O$_3$ and Al$_2$O$_3$ with a view to obtaining an electrolyte with higher ionic conductivity and higher mechanical strength than YSZ[11,12]. In this paper, we examined the possibility of low temperature operation on the basis of the current density (I)-terminal voltage (V) characteristic of this fuel cell.

**EXPERIMENTAL**

The thin plate electrolyte used in the present study was fabricated using the doctor blade technique. Its composition was 0.89ZrO$_2$-0.10Sc$_2$O$_3$-0.01Al$_2$O$_3$ and the thin plates were fired at 1600 °C for 2 hours. On the other hand, the sintered bulk specimen was prepared under conditions described in Ref.9. The crystal structure of the specimen was characterized by an X-ray diffraction measurement using nickel-filtered Cu Kα radiation. The ionic conductivity of specimen was evaluated by a four probe dc measurement and a two probe complex impedance measurement at temperatures from 500 °C to 1000 °C. The sample used in the four probe dc measurement was 2.5mm x 18mm x 0.2mm and platinum wires were attached to the corner of the thin plate with platinum paste. The sample used in the complex impedance measurement was cut from a sintered specimen to a size of 2.9mm x 2.7mm x 5.7mm. The ionic conductivity of the sample was evaluated from its complex impedance in the 10$^{-10}$ Hz frequency range with an impedance analyzer (Schlumberger Technologies model SI 1260).

The fuel cell was fabricated using La$_{0.8}$Sr$_{0.2}$MnO$_3$ as the cathode material and Ni-YSZ as the anode material. The thickness of the electrolyte plate was 0.2mm. The fuel electrode (anode), composed of NiO/YSZ, was painted on the electrolyte and fired at 1400 °C in air. The air electrode (cathode), composed of Sr-doped lanthanum manganite (La$_{0.8}$Sr$_{0.2}$MnO$_3$), was painted on the other side of the electrolyte and fired at 1100 °C in air. Each electrode had a thickness of 30-40 μm. To collect current from the fuel cell, a Pt mesh (50 mesh) was attached to each electrode. Pure hydrogen gas was supplied to the anode compartment at 300cc/min after passing through a humidifier at room temperature and pure oxygen gas was supplied to the cathode compartment at 150cc/min. The power generation measurements were carried out at temperatures from 800 °C to 900 °C.

**RESULTS AND DISCUSSION**

Figure 1 shows the X-ray diffraction pattern of the 0.89ZrO$_2$-0.10Sc$_2$O$_3$-0.01Al$_2$O$_3$ thin plate. The diffraction pattern is completely indexed as cubic symmetry. The lattice constant was estimated to be a=0.5086 nm from the high angle diffraction lines. In comparison with the lattice constant of YSZ (a=0.5138 nm), this value is a little smaller. This is because the ionic radii of the dopant cation Sc$^{3+}$ and Al$^{3+}$ are smaller than that of Y$^{3+}$.

Figure 2 shows the temperature dependence of the ionic conductivity (σ) for the 0.89ZrO$_2$-0.10Sc$_2$O$_3$-0.01Al$_2$O$_3$ thin plate at temperatures ranging from 500 °C to 1000
°C. The dotted line represents the ionic conductivity estimated from the four probe dc measurement and the open circles represent the ionic conductivity estimated from complex impedance analysis. The conductivity of the four probe dc measurement is in good agreement with that of the two probe complex impedance measurement. The open circuit voltage (OCV) obtained from the single cell is 1.15V at 800 °C and this value is almost equal to the theoretical one. This experimental result confirms that the oxygen ion transport number is unity in this electrolyte. The relation between $1/T$ and $\log \sigma$ is not linear and the slope of the Arrhenius plot became less steep with increasing temperature. Badwal et al. reported similar behavior for the temperature dependence of ionic conductivity in the ZrO$_2$-Sc$_2$O$_3$ system[13]. The reason for this behavior is not clear at present. One possible explanation is the vacancy trapping model proposed by Bauerle and Hrizo[14]. A significant number of vacancies are believed to be trapped by the dopant cation and form nonconducting complexes at low temperatures. Since the vacancies become free and mobile with increasing temperature, the conductivity is determined mainly by the migration of oxygen ion vacancies at high temperatures.

Figure 3 shows the I-V characteristic for the fuel cell at 800 °C. The maximum power density is 0.63W/cm$^2$ (0.46V, 1.36A/cm$^2$). The good I-V characteristic implies that both the anode (Ni-YSZ) and cathode (La$_{0.8}$Sr$_{0.2}$MnO$_3$) materials are suitable for use with the cubic stabilized zirconia in ZrO$_2$-Sc$_2$O$_3$-Al$_2$O$_3$ system.

Figure 4 shows the temperature dependence of the current density vs. power density. From this figure, we see that the maximum power density increases linearly with increasing temperature up to 900 °C and a high power density of over 1.0W/cm$^2$ has been achieved at 880 °C. In order to compare the present electrolyte with YSZ (0.92ZrO$_2$-0.08Y$_2$O$_3$), we also measured the temperature dependence of the current density vs. power density of the fuel cell for YSZ as shown in Figure 5. The maximum power density was 0.42W/cm$^2$ at 800 °C and 0.66W/cm$^2$ at 880 °C. These results indicate that the power density of the fuel cell using 0.89ZrO$_2$-0.10Sc$_2$O$_3$-0.01Al$_2$O$_3$ is about 1.5 times larger than that of 0.92ZrO$_2$-0.08Y$_2$O$_3$. Assuming that the temperature dependence of power density is linear, the maximum power density of YSZ at 1000 °C is estimated to be 1.09W/cm$^2$ and this value corresponds to that of present electrolyte at 880 °C. This implies that the operation temperature may be lowered by 120 °C using present electrolyte.

To obtain more information regarding the performance of the fuel cell, we estimated its I-V characteristics at 800 °C and 900 °C as shown in Figure 6. In this figure, the IR drop caused by the electrolyte is also shown as a straight line. Here we assume that the ionic conductivity is 0.1S/cm at 800 °C and 0.2S/cm at 900 °C, the thickness of sample is 0.2mm and the effective electrode area is 1.54cm$^2$. The resistance due to the electrolyte at 800 °C is one half the total resistance. With increasing temperature, the observed overall resistance and the resistance due to the electrolyte both decrease, but the resistance other than the ohmic resistance of the electrolyte remains unchanged. Since the electrode is sufficiently thin and its resistivity is much lower than that of the electrolyte, we believe that not only the overpotential of the electrode but also the contact resistance between the electrode and the Pt mesh contribute to the total resistance.

In conclusion, we examined the performance of a solid oxide fuel cell using cubic
stabilized zirconia in the ZrO$_2$-Sc$_2$O$_3$-Al$_2$O$_3$ system as an electrolyte. The maximum power density was 0.63W/cm$^2$ at 800 °C and 1.0W/cm$^2$ at 880 °C using a thin plate electrolyte (thickness: 0.2mm). The current-voltage performance of the fuel cell suggests that this electrolyte is promising for the low temperature operation in the 800 °C–900 °C temperature range.

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Fig. 1  X-ray diffraction pattern for 0.89ZrO$_2$-0.10Sc$_2$O$_3$-0.01Al$_2$O$_3$.

Fig. 2  Temperature dependence of ionic conductivity for 0.89ZrO$_2$-0.10Sc$_2$O$_3$-0.01Al$_2$O$_3$.

Fig. 3  Relationship between current density (I) and terminal voltage (V) at 800 °C.
Fig. 4 Temperature dependence of current density vs. power density for 0.89ZrO$_2$-0.10Sc$_2$O$_3$-0.01Al$_2$O$_3$.

Fig. 5 Temperature dependence of current density vs. power density for 0.92ZrO$_2$-0.08Y$_2$O$_3$.

Fig. 6 I-V characteristics of the fuel cell at 800 °C and 900 °C.