ABSTRACT

The Sc$_2$O$_3$-ZrO$_2$ (ScSZ) system, which has a higher electrical conductivity than Y$_2$O$_3$-ZrO$_2$ (YSZ), was investigated as the electrolyte for planar SOFC. The electrical conductivity of 8mol% Sc$_2$O$_3$-ZrO$_2$ (also 8YSZ) showed a significant decrease by annealing at high temperature. However, the high temperature annealing of 11mol% Sc$_2$O$_3$-ZrO$_2$ (11ScSZ) showed good stability over 5000hrs. The cell performance with 11ScSZ as the electrolyte was investigated. High power densities of 0.75W/cm$^2$ (output was 212W) have been achieved with a three layer 13cm x 13cm cell stack.

INTRODUCTION

Planar type SOFCs are still at the fundamental research stage, and improvement of the power density is very important to develop cost effective and compact size fuel cell systems. Yttria stabilized cubic zirconia (c-ZrO$_2$), and yttria stabilized tetragonal zirconia (t-ZrO$_2$), are widely used as the electrolyte in SOFC. Also, alternative electrolytes such as doped CeO$_2$ have been examined by many researchers to operate at a reduced temperature. However, alternative materials still have many problems as SOFC electrolytes. These include; mechanical properties, thermal expansion, phase stability etc. Scandia (Sc$_2$O$_3$) doped zirconia system has the highest conductivity of all the zirconia based systems [1-3]. Toho Gas and Mie University have investigated the Sc$_2$O$_3$-ZrO$_2$ system (ScSZ) as the electrolyte in the planar SOFC. ScSZ shows a electrical conductivity twice as high as YSZ (0.3S/cm), has enough mechanical strength (>200MPa), and almost same thermal expansion coefficient as YSZ (10 x 10$^{-6}$/K) [4]. Also, in a small cell test, the maximum power density of 2.1W/cm$^2$ was obtained at 1273K [5]. Even when the operating temperature was reduced to 1073K, this cell showed a maximum power density of 0.6W/cm$^2$. However, large scale cell and multiple cell stacks using ScSZ have not been developed nor examined. Also, degradation of electrical conductivity in zirconia electrolytes with high temperature annealing is one of
the important problems for the durability of the SOFC, but degradation mechanisms are not yet clear.

In this paper, the aging effect of electrical conductivity in ScSZ system for 5000hrs was measured, and the phase stability was investigated. Also, a three layer cell stack of planar SOFCs was fabricated by using ScSZ electrolyte, and the cell performance is reported.

EXPERIMENTAL

The ScSZ powder was prepared by mechanical mixing of ZrO₂ (99.9%, Tosoh co., Japan) and Sc₂O₃ (99.9%, Sausville chemical co., USA). The ScSZ-Å₂O₃ composites were prepared by wet ball milling ɣ-Å₂O₃ (99.99%, Taimei chemical co., Japan) in ethanol using zirconia balls. 8YSZ (Tosoh co. TZ-8Y) was used as a reference material. The powders were pressed under a pressure of 200MPa using a cold isostatic press and fired at 1873K-1973K for 5-15h. Electrical conductivity was measured by an AC impedance method using sintered rectangular bar of 3mm(B) x 4mm(W) x 40mm(L) with fired platinum paste electrodes and platinum lead wires. The frequency range was 0.1Hz-100kHz. The specimens were annealed in an electric furnace at 1273K in air for 0 to 5000 hrs.

The sintered 11mol% Sc₂O₃ (11ScSZ) with 1wt% Å₂O₃ was used as the electrolyte in the test cells. The dimensions of the electrolyte were 17mm in diameter and 0.25mm thick (small cell), 8cm x 8cm x 0.3mm thick (small stack), and 13cm x 13cm x 0.4mm thick (large stack). Ni/YSZ cermet (Ni:YSZ = 4: 6 wt.) was used for the anode and the composite of LaₓSrₓMnO₃ (X=0.2) with 20wt% YSZ for the cathode. The electrode materials were screen printed using a polymer binder, on the electrolyte plates and fired at 1423K for the cathode and 1573K for the anode. In the stack test, LaₓCaₓCrₓYNiO₃ (X=0.2, Y=0.05) and Ni-alloy (Inconel 600) were used for the bipolar separator plate.

RESULTS AND DISCUSSION

Aging effect of electrical conductivity in ScSZ

Fig.1 shows the changes in electrical conductivity of 8YSZ, 8ScSZ, 11ScSZ and 11ScSZ10Å as a function of annealing period at 1273K. In the initial period of several hundred hours, 8ScSZ showed a significant conductivity decrease. Also, 8YSZ showed the conductivity decrease up to 2000hrs. The electrical conductivity of these materials annealed for 5000hrs, recovered compared to those of the as-sintered samples by re-
sintering at 1873K for 10hrs. On the other hand, 11ScSZ and 11ScSZ10A showed no significant decrease of conductivity with annealing at 1273K, and they seemed to be a suitable material for SOFC usage. It is well known that stabilized zirconia has an aging effect in electrical conductivity, and many aging mechanisms such as phase stability, ordering of the crystal lattice, and the segregation of the impurities at the grain boundaries have been proposed. The changes in the Raman spectra of 8YSZ, 8ScSZ and 11ScSZ with annealing period are shown in Fig 2-1 to Fig 2-3, respectively. The Raman spectra of 8YSZ corresponds to that of the cubic zirconia, and of 8ScSZ to those of a mixture of cubic and tetragonal zirconia [7-8]. In the case of 8YSZ and 8ScSZ, the shifts of the Raman spectra at 250cm\(^{-1}\) increase with annealing period, which suggests the formation of the tetragonal phase of zirconia. In addition, this shift disappeared with re-sintering. No significant changes of the Raman spectra, however, are observed in 11ScSZ. These results indicate that the conductivity decreases with annealing, and is caused by cubic to tetragonal phase change, and 11ScSZ has long term phase stability at 1273K.

Performance of a single cell with the ScSZ electrolyte

The discharge performance of single cells with ScSZ as the electrolyte was evaluated. Fig.3 shows the discharge characteristics of the small cell using 11ScSZ1A at 1273K and 1073K. The maximum power density of over 2W/cm\(^2\) was obtained at 1273K and 1.0W/cm\(^2\) was obtained at 1073K. The measured ASR (area specific resistance) of this cell, using AC impedance, was 0.15 Ωcm\(^2\) at 1273K, and the high conductivity of ScSZ electrolyte was reflected by the cell performance. Because a small cell has no contact resistance, and has no ohmic losses caused by the bi-polar plate, extremely high power density was achieved. In order to investigate the stacking loss, the cell performance of single cell, 8cm x 8cm (effective electrode area is 25cm\(^2\)), with LaCrO\(_3\) ceramic separators is shown in Fig.4. Even for a large scale single cell, the maximum power density of 1.3W/cm\(^2\) (33W) was obtained at 1273K. From the view point of electric current passage, most of the stacking loss seemed to be caused by the cathode layer in the parallel direction relative to the electrolyte plate. Therefore, geometric design of the separators, and electric conductivity of the cathode materials, are important parameters in improving the power density of planar SOFCs.

Multiple cell stack test

The multiple cell stacks were designed with an internal manifold type construction as shown in Fig.5. Component materials and their specifications are shown in Table 1. Three-layered stack with 8cm x 8cm cells and LaCrO\(_3\) ceramic separators are shown in Fig.6. The maximum power of 83W (power density of 1.1W/cm\(^2\)) was achieved at 1273K. After the end of the test, some visible cracks were observed around the fuel manifold of the separator plate. They seemed to be caused by the lattice expansion of doped LaCrO\(_3\) under reducing atmospheres[6]. In order to ensure the durability of the
planar SOFC with ceramic separator, the LaCrO₃ ceramic material should be improved.

Table 1  Component materials and specifications in stack test

| Materials          | Thickness |
|--------------------|-----------|
| Electrolyte        | 0.3, 0.4mm |
| Cathode            | 50µm      |
| Anode              | 30µm      |
| Separator          | 3.5mm~4mm |

| Specifications                  |
|--------------------------------|
| Electrical conductivity : 0.27S/cm |
| Bending strength 300MPa         |
| Polarization : <100mV at 1A/cm² |
| Polarization : <50mV at 1A/cm²  |
| Electrical conductivity : 46S/cm, Bending strength:250MPa (Ceramics) |

In 1996, enhancement of the cell size progressed. The performance of 13cm x 13cm three-layered stack with effective electrode area of 285cm² is shown in Fig.7. Ni based alloy (Inconel 600) was used as the bi-polar separator plates. Even if the electrolyte thickness was 0.4mm, the maximum power of 212W (Power density of 0.75W/cm²) was obtained with oxygen as the cathode gas at 1273K. Also, when air was used as the oxidizer, the maximum power of 133W (Power density of 0.47W/cm²) was obtained. Voltage drop at high current density was significant under air condition. To obtain higher power density under air, the cathode should be improved.

CONCLUSION

Scandia stabilized zirconia (ScSZ) system was investigated as the electrolyte in a planar SOFC. Single cell and multiple cell stack SOFCs with ScSZ were examined. The following results have been obtained:

(1) Aging effect of the electrical conductivity of ScSZ was observed. 8mol% ScSZ showed a significant conductivity decrease, while 11mol% ScSZ showed good stability in the conductivity.
(2) The conductivity decrease with annealing seemed to be caused by phase instability.
(3) High power densities were obtained for a single cell with a ScSZ electrolyte.
(4) Multiple cell stacks were tested, and the maximum power of 212W (Power density of 0.75W/cm²) was obtained with oxygen at 1273K.

REFERENCES

[1] O.Yamamoto, T.Kawahara, Y.Takeda, N.Imanishi and Y.Sakaki, Science and Technology of Zirconia V, 733-741(1993)
[2] T.Ishii and R.Chiba, Proc. 4th. Int. Symp. Solid Oxide Fuel Cells, eds. M.Dokiya et.al. p295-300 (1995)
Fig. 1 Changes in the electrical conductivity of ScSZ and YSZ as a function of annealing period at 1273K.

Electrochemical Proceedings Volume 97-18
Changes in Raman spectra of annealed samples at 1273K as a function of aging period.
Fig. 3 Discharge characteristics of the small single cell with ScSZ at 1073K and 1273K.

Fig. 4 Discharge characteristics of the 8cm x 8cm single cell with LaCrO$_3$ separators at 1273K.
Tri-layer single cell Separator
Upper: Cathode
Lower: Anode
Separator
Gas manihold

Fig. 5 Construction of a multilayer cell stack.

Fig. 6 View of three layered cell stack.

Fig. 7 Discharge performance of the 13cm x 13cm three layered stack at 1273K.