ABSTRACT

The Sc₂O₃-ZrO₂ (ScSZ) system, which has higher electrical conductivity than the Y₂O₃-ZrO₂ system was examined in terms of electrolyte and anode materials of the planar type SOFC. Both electrolyte supported and anode supported type test cells using ScSZ as electrolyte were studied. The electrolyte supported cells were shown to have maximum power density of 2.5W/cm² in H₂-H₂O as fuel and O₂ at 1273K. For anode supported cells power density of 1.0W/cm² in H₂-H₂O as fuel and O₂ at 1023K was registered. This is considered to be sufficient for low temperature operation. Finally, the performance of the Ni/ScSZ cermet anodes was compared to that of conventional Ni/YSZ cermet anodes. The Ni/ScSZ cermet anodes showed lower overpotential than Ni/YSZ cermet anodes in H₂-H₂O as fuel at 1273K. Next, internal methane reforming was tested, the Ni-ScSZ cermet anodes showed a lower overpotential and higher stability than the Ni/YSZ cermet anodes at lower S/C ratio.

INTRODUCTION

SOFCs are expected to be the next-generation fuel cells, because of their high potential energy conversion efficiency. The electrical conductivity of electrolyte is one of the key factors for improving SOFC. Toho Gas has been focusing on the improvement of ScSZ, and our previous studies showed that the ScSZ has good properties as an electrolyte of SOFC (1,2,3,4).

For practical applications, a stable electrical conductivity at the operating temperature is one of the important factors, and 11mol% Sc₂O₃ stabilized zirconia (11ScSZ) obtained from mechanical mixing in the laboratory showed no decrease in electrical conductivity from annealing at several temperatures (5). In this study, the stability of electrical conductivity of ScSZ which is obtained by co-precipitation in quantity lots was studied to examine the effect of preparation process on the properties of ScSZ. Furthermore, internal reforming is also feasible in SOFCs and several such studies have been reported (6,7,8,9,10). The majority of these studies were conducted with a high...
H₂O/CH₄ ratio (exceeding 2). From the perspective of operating cost and efficiency, operation at a low H₂O/CH₄ ratio is advantageous. And some reports indicated the possibility of operation at a low H₂O/CH₄ ratio. In this study, the Ni/ScSZ anodes were tested at a low H₂O/CH₄ ratio and their performance was analyzed. To reduce the cost of SOFC systems, lower operating temperature of the SOFC is important and anode supported cells have been developed (11,12,13,14). We previously reported that anode supported cells using ScSZ as electrolyte show good performance (15). In this study, the anode substrate and interlayer were fabricated, and cell performance was examined.

EXPERIMENTAL

In this study, three types of ScSZ powder obtained in a co-precipitation process of Daiichi Kigenso Kagaku Kogyo Co., Ltd. and having a composition as shown in Table 1 were tested.

| Composition | Abbreviation |
|-------------|--------------|
| (11 mol% Sc₂O₃-89 mol% ZrO₂) 99 wt%-Al₂O₃ 1 wt% | 11ScSZ1A |
| 10 mol% Sc₂O₃-1 mol% Y₂O₃-89 mol% ZrO₂ | 10Sc1YSZ |
| 10 mol% Sc₂O₃-1 mol% CeO₂-89 mol% ZrO₂ | 10Sc1CeSZ |

Aging Study of ScSZ Electrolyte

ScSZ powders as shown in Table 1 were pressed at a low pressure and then pressed at 100MPa using a cold isostatic press. The pressed samples were sintered at 1723K for 5 hours and cut into pillar shapes of 3 x 4 x 30 mm. The samples were placed in an annealing furnace at 1273K for a predetermined time. The electrical conductivity of annealed samples was measured using platinum paint electrodes with the AC impedance method over a frequency range of 1-10⁴ Hz using a frequency analyzer.

Electrolyte Supported Cell Manufacturing Method

The materials of electrolyte supported cells are shown in Table 2. The ScSZ electrolytes were obtained by tape casting. The dimension of the electrolyte was 20mm x 20mm and 0.3mm thick. Ni/YSZ or Ni/ScSZ cermet was used for the anode. NiO (Nacalai-tesuque Inc.), 8 mol% yttria-stabilized zirconia (8YSZ, Tosoh Co.), 10Sc1YSZ and 10Sc1CeSZ were used for anode material. NiO and 8YSZ or ScSZ were mixed with ethanol for 24 hours using ball milling process and then dried to obtain the predetermined mass ratio (Ni:YSZ or Ni:ScSZ = 4:6). La₀₉Sr₀₂MnO₃ (LSM, Seimi Chemical Co.) and 8YSZ were used for the cathode. LSM and 8YSZ were mixed with ethanol for 24 hours using ball milling process and dried to obtain the predetermined mass ratio (LSM:8YSZ = 8:2). The electrode materials were screen printed with polymer binder on electrolyte plates and fired at 1573 to 1623K for anodes and 1423K for cathodes. The electrode surface area for the test cell is 0.2 cm².
Table 2: Component materials of self supported cell

| Component | Material |
|-----------|----------|
| Electrolyte | 11ScSZ1A |
| Anode | Ni++8YSZ, Ni++10Sc1YSZ and Ni++10Sc1CeSZ |
| Cathode | LSM++8YSZ |

**Anode Supported Cell Manufacturing Method**

Fig. 1 shows a schematic diagram of, and Table 3 lists the component materials for the anode supported cells tested in this study. 3mole% yttria-stabilized zirconia (3YSZ, Tosho Co.) and nickel oxide were used to make a porous anode substrate. NiO and 3YSZ powder was ball milled with ethanol for 24h. The mixture was dried and made into suspension by mixing with binder for tape casting. The suspension was tape casted and fired at 1673K. The Ni/ScSZ interlayer and ScSZ electrolyte layer were screen printed on the Ni/3YSZ substrate, dried and fired at 1673K. The cathode was also screen printed, dried and fired at 1423K. The dimension of anode substrate was 20mm x 20mm and 0.3mm thick and cathode surface area for the test cell was 0.2cm².

![Schematic diagram of anode supported cell in this study.](image)

Table 3: The component materials of anode substrate cell

| Component | Material |
|-----------|----------|
| Anode substrate | Ni++3YSZ |
| Anode interlayer | Ni++11ScSZ1A |
| Electrolyte | 11ScSZ1A |
| Cathode | LSM++8YSZ |

**RESULTS AND DISCUSSION**

**The Electrical Conductivity Change of ScSZ**

The changes in electrical conductivity of ScSZ during the annealing period at 1273K are shown in Fig. 2. The conductivity of as-sintered samples of 11ScSZ1A, 10Sc1YSZ and 10Sc1CeSZ were 0.298, 0.307 and 0.322 S/cm, respectively. After 2500 hours annealing, no significant decrease in conductivity could be observed. These results correspond to our previous report of the results from the samples prepared by mechanical mixing. In the case of 10mol% Sc₂O₃ stabilized zirconia (10ScSZ), electrical conductivity was affected by the preparation method, so that, 10ScSZ obtained by co-precipitation displayed better electrical properties than those obtained from mechanical mixing process. On the other hand, 11ScSZ shows good electrical properties irrespective of preparation method.
The comparison of performance at 1273K between the Ni/YSZ and the Ni/ScSZ anodes is shown in Fig.3. The total cell performance was improved slightly by changing the anode material from Ni/YSZ to Ni/ScSZ. To confirm the effect of anode material change on cell performance, anode overpotential for each cell was measured by AC impedance method. The comparison of anode overpotentials of Ni/YSZ and Ni/ScSZ at 1273K in 97%H₂-3%H₂O as fuel and O₂ is shown in Fig.4. The overpotential of Ni/ScSZ is lower than for Ni/YSZ. These results indicate that the influence of ZrO₂ on activity of Ni-ZrO₂ anode is equal to that of catalyst.
Next, internal methane reforming condition was tested. A comparison of the anode overpotential of Ni/YSZ and Ni/ScSZ at 1273K in 97%CH₄-3%H₂O (S/C=0.03) as fuel and O₂ is shown in Fig.5. In this condition, Ni/ScSZ also showed lower overpotential than Ni/YSZ. At current density below about 2A/cm², overpotential of Ni/ScSZ increased, although above this current density it decreased. This phenomenon didn’t occur in Ni/YSZ. These results suggested that steam reforming and partial oxidation of methane simultaneously occur at high current density conditions and high electrical conductivity of ScSZ contributes to partial oxidation of methane.

Furthermore, the durability of Ni/ScSZ was tested. Fig.6 shows the performance of test cells over a period of 250 hours at 1273K in 97%CH₄-3%H₂O as fuel and O₂. In the case of Ni/YSZ anode, the performance first improved, then degraded to 250 hours. In the case of Ni/ScSZ anode,
the performance also first improved, then maintained an almost constant output voltage. In these performance tests, the change of overpotential against operation time was measured; Fig. 7 and 8 show the data that was obtained. Fig. 7 indicates that overpotential of Ni/YSZ anode first fell, then increased to 250 hours. On the other hand, the overpotential of Ni/ScSZ anode also first fell and then maintained an almost constant value as shown in Fig. 8. A drop in the performance of the test cells using Ni/YSZ anode may be attributable to a drop in the anode performance. To confirm this assumption, the anode materials were analyzed by XRD method. To compare with the XRD pattern of Ni/ScSZ anode before and after performance test, no compositional change was found. In the case of Ni/YSZ anode, there was no compositional change, but the background of XRD pattern obtained after the performance test had increased remarkably. Next, ESCA observation was conducted for the Ni/YSZ anode, and carbon deposition on Ni particles was confirmed. These differences between Ni/YSZ and Ni/ScSZ anodes are due to different electrical conductivity of YSZ and ScSZ.

![Image of performance stability](image_url)

**Fig. 6 Performance stability of test cells using Ni/ScSZ and Ni/YSZ anodes at 1273K in 97%CH₄-3%H₂O as fuel and O₂.**

![Image of overpotential change](image_url)

**Fig. 7 Change of Ni-YSZ anode overpotential against operating period at 1273K in 97%CH₄-3%H₂O as fuel and O₂.**
Fig. 8 Change of Ni-ScSZ anode overpotential against operating period at 1273K in 97%CH₄-3%H₂O as fuel and O₂.

These results indicate that it is possible to operate cells under low humidity conditions using Ni/ScSZ anode.

**Performance of Anode Supported Cells**

Fig. 9 shows a comparison of the performance of the anode substrate cells between this study and the previous one (13). To compare with previous data, the maximum power density was improved from 0.8W/cm² to 1.0W/cm² in H₂-H₂O as fuel and O₂ at 1023K in this study. Improvements in power density are believed to be caused by the thinning of anode substrate and the existence of Ni/ScSZ interlayer.

Fig. 9 i-V and i-P characteristics of anode substrate test cells at 1023K.
CONCLUSIONS

Current status of SOFC development using ScSZ can be summarized as follows:

(1) ScSZ obtained in quantity lots through co-precipitation process showed stable electrical conductivity in annealing.
(2) The Ni/ScSZ cermet anodes showed lower overpotential than Ni/YSZ cermet in H$_2$-H$_2$O as fuel at 1273K.
(3) The Ni/ScSZ cermet showed lower overpotential and better stability than the Ni/YSZ cermet anodes at lower S/C ratio.
(4) The performance of anode substrate cell was improved by thinning anode substrate and the existence of a Ni/ScSZ interlayer.

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