FABRICATION OF POROUS ELECTRODE SUPPORTED SOFC
BY WET PROCESS

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ABSTRACT

Slip casting and slurry dipping methods have been developed as
collection techniques for tubular SOFC. The most important factor for
these wet processes is preparation of slip and slurry. The slip casting
process was successfully employed for fabrication of a Ni-YSZ support
tube with a rib for the deposition of interconnector strip. The YSZ,
interconnector and counter electrode layers were fabricated by the slurry
dipping method. A fuel cell with a porous cathode support could be
fabricated by the co-firing process. The fuel cell fabricated by the wet
process attained 1.09 V of open circuit voltage. These techniques are
promising as an inexpensive and reliable fabrication process for solid oxide
fuel cells.

INTRODUCTION

Solid oxide fuel cells (SOFCs) have been actively investigated as a highly efficient
and clean power generation system. For the practical application of SOFCs, it is important
to improve the reliability of the cell with low fabrication cost. The tubular SOFCs have
been generally fabricated by CVD, EVD (1), and plasma splaying methods (2), though
these methods require relatively expensive fabrication facilities, and complicated masking
process during deposition of the electrolyte, electrode, and interconnector layers. Low
utilization of raw material sometimes becomes the reason for the high cell cost. We have
been developing wet processing technique for fabrication of SOFC to eliminate above-
mentioned problems (3). An electrode porous tube, prepared by the slip casting process,
serves as a support for thin YSZ and other cell component layers. The electrolyte layer
was slurry-dipped onto the support tube to form a dense layer before counter electrode is
coated on to the electrolyte layer. The three layered structure was fabricated by deposition-sintering cycle or by co-sintering process. A dense interconnector layer was also deposited on the electrode support tube by slurry dipping and sintering process.

**EXPERIMENTAL**

Two cell types are considered, i.e., the cells with an anode support and a cathode support tube. The structures of the cells investigated in the present study are shown in Fig.1. The cell with an anode support is basically tubular, but a rib (0.2 mm in height and 5 mm in width) is placed in the longitudinal direction for deposition of an interconnector strip (Fig.1 (a)). This rib is helpful for simplifying the masking process for depositing electrolyte, interconnector, and counter electrode on the electrode substrate. The cell consisted of the electrode support, the electrolyte and outer electrode layers, and interconnector strip on the rib. The cell with a cathode support is also tubular without the interconnector strip at the present stage (Fig.1 (b)).

**Preparation of fuel cells with a porous Ni-YSZ cermet support**

The fabrication procedure for the anode-supported cell is shown in Fig.2. The porous anode support was prepared from NiO and 8 mol % yttria-stabilized zirconia powders. The NiO powder was ground in an alumina pot mill to the average particle size of 1-2 μm. The average particle size of the YSZ powder was controlled to 40-50 μm by a spray dryer. The weight ratio of NiO and YSZ was set at 4 : 6 to adjust its thermal expansion coefficient to that of YSZ. The slip was prepared by mixing NiO-YSZ, water, dispersant, and binder at a volume ratio of 100 : 12-15 : 0.2-0.4 : 0.3-0.6. Polyacrylate and polyvinyl alcohol were used as dispersant and binder, respectively. The slip prepared by this procedure was poured and kept in the gypsum mold until the NiO-YSZ layer developed to the predetermined thickness. After excessive slip was drained from the casted layer on the mold, the green tube of NiO-YSZ was removed from the mold, dried, and finally sintered at 1300 °C for 1h. The sintered anode tube was 15 mm in outer diameter and 2 mm in thickness with a rib (5 mm x 0.2 mm x length).

The YSZ thin film was deposited on the anode support by slurry dipping. Fine YSZ powders were obtained from Tosoh or Daiichi Kigenso. The YSZ slurry, which was prepared by dispersing the powder (6 wt%) in ethanol, was coated on the anode support by repeated dipping process (ca. 10 times) prior to heating at 1300 °C. The dipping-heating cycle was repeated several times until the dense coating with a thickness of 40-80 μm could be obtained. The sample was finally sintered at 1550 °C for 5h.

Calcia-doped LaCrO₃ (LCC) was prepared by the citrate process. La(NO₃)₃ 6H₂O (0.7 mol), Ca(NO₃)₂ 4H₂O (0.3 mol), and Cr(NO₃)₃ (1.02 mol) were dissolved in water. Then, citric acid (2 mol) and ethylene glycol (4 mol) were added to the solution. The solution was stirred at 90 °C and then heated at around 200 °C to obtain a solid precursor.
The sample was pulverized and heated at 1200 °C for 1h to decompose the precursor into LCC. The particle size of the LCC powder was controlled to 2 μm. The LCC powder (28 wt%) was dispersed in ethanol and coated on to the anode support tube by repeated dipping process (ca. 10 times). Then, the sample with the LCC layer was heated at 1400 °C for 1h. The dipping process was further repeated before the interconnector layer with 50 μm in thickness was finally sintered at 1550 °C for 5h.

The air electrode, La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSM), was prepared by thermal decomposition of the mixture of corresponding acetates. The LSM powder was dispersed in water together with dispersant and binder. The volume ratio of LSM : water : dispersant : binder was 100 : 40 : 0.65 : 3.7. Ammonium polycarboxylate and crystalline cellulose were used as dispersant and binder, respectively. The fuel cell tube was dipped in the LSM slurry after masking the interconnector part. The slurry-dipped sample was dried and heated at 1350 °C for 1h. The resultant air electrode was 200 μm in thickness.

**Preparation of fuel cells with a porous LSM support**

The repeated thermal cycles above 1300 °C inevitably lead to solid state reaction between LSM and YSZ. Therefore, the sequential deposition-sintering process could not be adopted for the cell with the cathode support. Thus, Two types of co-sintering processes for the tubular cell have been developed using the cathode support (Fig.3). The cell by process 1 consisted of the air electrode and electrolyte fabricated by co-sintering process, and the fuel electrode coated by dipping-sintering process. The cell by process 2 consisted of the air electrode, electrolyte, and fuel electrode deposited layer by layer and sintered simultaneously (4). It is important for the co-sintering process to adjust the shrinkage curves for the components during sintering process. The shrinkage curves for the cell components are shown in Fig.4. Thermal shrinkage curve could be modified by the pre-heating treatment for the prepared powder. Then, the green tube of LSM was prepared by the slip casting process using similar procedure to that employed for the preparation of Ni-YSZ. The green tube was then subjected to heating at 1000 °C for 1h to improve its strength. The YSZ slurry was then coated on the LSM support by dipping (3 times) and subsequently heated at 1000 °C for 1h. The fuel electrode was prepared by mixing the NiO (1 μm) and YSZ (6 μm) powder at the weight ratio of 4 : 6. The volume ratio of NiO-YSZ powder : water : dispersant : binder in the slurry was set at 100 : 30 : 0.5-1 : 0.5-1. The dispersant and binder were the same as those used for the preparation of cathode electrode. The cathode support coated with a YSZ thin layer was dipped into the slurry prior to the co-sintering process at 1300 °C for 6h.

**Measurement of properties of electrode supports and I-V characteristics for the fuel cells**

The support tubes were evaluated from its permeation coefficient of gaseous N$_2$, electrical conductivity, thermal expansion coefficient, and diametral ring compression
strength (as mechanical strength). The fuel electrode tube was reduced at 1000 °C in a H₂ stream prior to the measurements. The air electrode tube underwent the same thermal history as the co-sintering process. The I-V characteristics of the fuel cell were measured in a flow system (Fig.5). Humidified hydrogen and oxygen were supplied to the fuel and air electrodes, respectively. The test piece of the cell was supported by two mullite tubes. Two pyrex glass o-rings were located at upper and bottom ends of the tubular cell to ensure gas tightness at high temperatures.

RESULTS AND DISCUSSION

Properties of porous electrode supports

Porosity, gas permeation coefficient of N₂, electrical conductivity, thermal expansion coefficient, and mechanical strength of the porous electrode support tubes are summarized in Table 1. The porosity, N₂ gas permeation coefficient, and electrical conductivity of the cathode support were 32.6 %, 6.01 mm² g⁻¹ sec⁻¹, 1.49x10² S cm⁻¹, respectively. These values are suitable for the porous electrode support. Although the porosity and gas permeation coefficient of the anode support before reduction (21.5 % and 3.0 mm² g⁻¹ sec⁻¹, respectively), were insufficient for gas supply, reduction with H₂ significantly improved its porous microstructure. The resultant porosity and gas permeation coefficient for Ni-YSZ support were 33.0 % and 11.4 mm² g⁻¹ sec⁻¹. The mechanical strengths of the supports, i.e., 25.5 MPa for cathode and 27.5 MPa for anode, were also satisfactory for the fuel cell experiment.

Fuel cells with the porous Ni-YSZ cermet support

The SEM photograph of the cross section of the anode supported cell is shown in Fig.6 a). The electrolyte layer was 80 μm in thickness. Although this layer contained a small number of closed pores, gas leakage was scarcely observed. The porous microstructure of air and fuel electrodes was also obvious in the photograph. The interconnector layer is required to possess enough density to ensure gas seal, high electronic conductivity, stability against both reducing and oxidizing atmospheres, and the same thermal expansion coefficient as that of the electrode support. Lanthanum chromite, which is doped with Ca to improve sinterability, has been most popularly used as an interconnector (5). A dense sintered film could be prepared by using the citric acid process which attained very uniform composition of the precursor. Figure 6 b) shows the SEM photograph of the cross section of interconnector film prepared on the rib of the anode support. The interconnector layer was very thin (50 μm) but crack free and dense. The I-V characteristics of the anode-supported cells with and without an interconnector are shown in Fig.7. The open circuit voltage of the cell (1.08 V) was quite close to the theoretical value (1.10 V). This means that the leakage across the electrolyte and interconnector layers was negligible. The cell without an interconnector (cell (b)) attained 0.51 A/cm² at 0.7 V with active electrode area of 8.8 cm². The thickness of the YSZ film
for cell (b) was 50 μm, whereas that of the cell with an interconnector (cell (a)) was 80 μm to improve the stability of film during sintering process for interconnector. However, cell (a) attained 0.36 A/cm² at 0.7 V with active electrode area of 7.4 cm² because of an increase in resistance by the interconnector and thicker YSZ film than cell (b).

Fuel cells with tubular porous LSM support

The cross sectional view of the microstructure of the cell with the cathode support is shown in Fig.8. The electrolyte layer (30 μm) by this preparation was also very dense though the microstructure of the electrodes was porous. The I-V characteristics of the cell is depicted in Fig.9. The open circuit voltage of the cell (1.09 V) indicates that the co-sintered electrolyte layer was dense which is sandwiched by the porous electrodes. The cells by preparation process 1 and process 2 attained 0.44 A/cm² at 0.7 V with the active electrode area of 9.9 cm² and 0.32 A/cm² at 0.7 V with the active electrode area of 14.8 cm², respectively. The difference in current density between two processes appears to result from the porosity of Ni-YSZ anode and the microstructure of anode/electrolyte interface due to different thermal treatment.

CONCLUSIONS

The slip casting and slurry dipping methods were successfully employed in the present study for the fabrication of SOFC with a tubular electrode support. The electrolyte and interconnector of the cells fabricated by the wet process are dense enough to attain the theoretical open circuit voltage. Currently, the tube prepared by deposition-sintering cycle on the anode support achieved better power generation characteristics than the cell by co-sintering with the cathode support probably because of better microstructure. Further optimization of the preparation condition may lead to better power generation results of cells by the co-sintering process.

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**Fig. 1** The schematic configuration of the fuel cells

| NiO powder | YSZ powder | water | additives |
|------------|------------|-------|-----------|
| mixing     |            |       |           |
| slip casting, sintering at 1300 °C for 1h | YSZ powder | ethanol | additives |
| anode support tube | mixing | | slurry |
| dipping into YSZ slurry | drying | | |
| repeat this process several times | pre-sintering at 1300 °C for 1h | |
| sintering at 1550 °C for 5h | YSZ thin film |
| masking YSZ layer, dipping into LCC slurry | pre-sintering at 1400 °C for 1h, dipping |
| drying, sintering at 1550 °C for 5h | LCC strip |
| masking LCC strip, dipping into LSM slurry | drying, sintering at 1350 °C for 1h |
| LSM layer |
| cell with a porous anode support |

**Fig. 2** Flow chart of the fabrication procedure for anode supported cell
LSM powder | water | additives

- mixing
- slipcasting, drying at room temperature
- pre-heating at 1000 °C for 1h

Cathode support tube
- dipping into YSZ slurry
- drying at room temperature
- pre-heating at 1000 °C for 1h

YSZ thin layer
- dipping into NiO-YSZ slurry
- drying at room temperature
- sintering at 1300 °C for 1h

NiO-YSZ layer
- cell with a porous cathode support

Process 1
- co-sintering at 1300 °C for 6h

YSZ layer
- dipping into NiO-YSZ slurry
- drying at room temperature
- co-sintering at 1300 °C for 6h

NiO-YSZ layer
- cell with a porous cathode support

Process 2

Fig. 3 Flow chart of the fabrication procedure for cathode supported cell

Fig. 4 Sintering curves for LSM cathode and Ni-YSZ cermet anode.
Fig. 5 Gas flow system of tubular fuel cell

Table I Properties of porous electrode tubes

| Property                                  | La$_{0.7}$Sr$_{0.3}$MnO$_3$ | Ni-YSZ cermet |
|-------------------------------------------|----------------------------|---------------|
| Porosity (%)                              | 32.6                       | 21.5 (33.0)   |
| N$_2$ gas permeation coefficient (mm$^4$ g$^{-1}$ sec$^{-1}$) | 6.01                       | 3.0 (11.4)    |
| Conductivity (S cm$^{-1}$)                 | $1.49 \times 10^2$ b)     | $3.10 \times 10^2$ c) |
| Thermal expansion coefficient (x10$^6$ deg$^{-1}$) | 11.3                       | 11.0 e)       |
| Mechanical strength (MPa)                  | 25.5                       | 42.0 (27.5) g) |

a) measured at room temperature. b) measured in O$_2$ at 1000 °C.
c) measured in H$_2$ at 1000 °C.
d) measured in the temperature range between 60-1000 °C.
e) measured in Ar after reduction with H$_2$ at 1000 °C.
f) diametral ring compression strength.
g) measured after reduction in H$_2$ at 1000 °C.
Fig. 6 SEM images of the cross sectional microstructure of the anode supported cell

Fig. 7 I-V characteristics of fuel cells at 1000 °C

(a) \( \text{H}_2 + \text{H}_2\text{O}, \text{Ni-YSZ support/YSZ (80 \( \mu \text{m})/LSM (7.4 \text{ cm}^2), O}_2 \) with an interconnector

(b) \( \text{H}_2 + \text{H}_2\text{O}, \text{Ni-YSZ support/YSZ (50 \( \mu \text{m})/LSM (8.8 \text{ cm}^2), O}_2 \) without an interconnector
a) YSZ thin film on the cathode support tube fabricated by process 1
b) cell with the cathode support fabricated by process 2

Fig. 8 SEM images of the cross sectional microstructure of the cathode supported cell

Fig. 9 I-V characteristics of fuel cells at 1000 °C

- $H_2 + H_2O$, Ni-YSZ (9.9 cm$^2$) / YSZ / LSM support, O$_2$ slurry dipping co-sintering
- $H_2 + H_2O$, Ni-YSZ (14.8 cm$^2$) / YSZ / LSM support, O$_2$ co-sintering

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