The Fuel Electrode Material Using Fe-YSZ Cermet

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ABSTRACT

The steam reforming reaction of the lower hydrocarbons on the fuel electrode proceeds rapidly in the neighborhood of the inlet of fuel gas because of the high catalytic activity of Ni-YSZ cermet. Thus, we feel some apprehension for the damage of SOFC which reforms the lower hydrocarbons on the fuel electrode. It is supposed that the steam reforming reaction on the fuel electrode can be controlled by masking it with the Fe-YSZ cermet. It has high electrical conductivity in a reducing atmosphere and the low catalytic activity for the above mentioned reaction. The thermal expansion coefficient of Fe2O3-YSZ mixtures can be adjusted to match the YSZ at 50-1400°C.

1. INTRODUCTION

It is generally known that the order of catalytic activity of a metal for the steam reforming reaction of the lower hydrocarbons (ex. methane, methanol, ethanol) is Ru, Rh > Ni, Pd > Pt > Fe, Co (1, 2, 3). The steam reforming reaction of the lower hydrocarbons on the fuel electrode proceeds rapidly in the neighborhood of the inlet of fuel gas because of the high catalytic activity of the Ni-YSZ cermet (4, 5). Thus, there is some apprehension about damage to the SOFC which reforms the lower hydrocarbons on the fuel electrode. It is supposed that the steam reforming reaction on the fuel electrode can be controlled by masking it with the Fe-YSZ cermet. It has high electrical conductivity in a reducing atmosphere and the low catalytic activity for the above mentioned reaction.

The NiO-YSZ mixtures that is used as the fuel electrode material has a large thermal expansion coefficient. The thermal expansion coefficient (50-1000°C) of NiO56wt%-YSZ mixture that contains 40vol% Ni in a reducing atmosphere and YSZ is $12.5 \times 10^{-6}/\text{C}$, and $10.5 \times 10^{-6}/\text{C}$ respectively. The thermal expansion coefficient of Fe2O3-YSZ mixture can be adjusted to match the YSZ at 50-1400°C. In generally, a slight variation of the thermal expansion coefficient of SOFC components is allowed at 1000°C. Care must be taken to adjust
the thermal expansion coefficient of all SOFC components, when a large SOFC stack is made.

2. EXPERIMENTAL

2.1 Preparation of Fe₂O₃-YSZ Mixture

The raw materials of the Fe₂O₃-YSZ mixture are 8mol%-Y₂O₃ stabilized ZrO₂ (denoted as YSZ) and Fe₂O₃. The compositions of the Fe₂O₃-YSZ mixtures which were prepared in this work are Fe₂O₃ : YSZ = X : (20-X) [wt ratio, X = 6,7,8,9]. These specimens are denoted as FY6/14, FY7/13, FY8/12 and FY9/11 respectively. The raw materials powders were mixed and pre-sintered at 1200°C for 5hr in air. The pre-sintered one was powdered fine and pressed at 2ton/cm² into tablets of 80mm in diameter and 10-15mm in thickness. The final sintering was made at 1500°C for 10hr in air. The final sintered pellets were cut and used for some measurements. In a reducing atmosphere at 700-1000°C, the Fe₂O₃-YSZ mixture is reduced and changed to the Fe-YSZ cermet.

2.2 Fabrication of Cell Type Catalyzer

The Ni40vol%-YSZ cermet, the Ni27vol%-NiAl₂O₄ cermet and the Fe-YSZ cermet containing Al₂O₃ were used as the catalyzer. The catalyzer's raw materials were listed in Table I. The raw materials powders were mixed and sintered at 1200°C for 5hr in air and were finely powdered. A slurry of the catalyzer was smeared on the both surface of a YSZ plate (25mm×100mm×0.5mm). The smeared area was 40cm² and baked at 1400-1450°C for 3hr in air. These YSZ plates were used as the cell type catalyzer.

The construction of the test cell is shown in Fig.1. The cell type catalyzer was set in the reactor which made of Al₂O₃ and examined the catalytic activity for the steam reforming reaction of methane. The steam/carbon ratio of methane was controlled by adjusting the water flow at the pre-heater.

3. RESULTS AND DISCUSSION

3.1 Thermal Expansion Coefficient

The thermal expansion coefficients of specimens were measured at 50-1400°C in air. The warm-up rate and the cool-down rate was 5°C/min. The size of the specimens used here was 3mm × 4mm × 17mm. All specimens were measured three times and the average value at warm-up was used as its thermal expansion coefficient value. The thermal expansion coefficients of these specimens are shown in Fig.2. The dependence of the coefficients on the
Fe₂O₃ content was slight. The thermal expansion coefficients of YSZ, NiO56wt%-YSZ mixture and FY7/13 in air are shown in Fig.3. The thermal expansion coefficient of FY7/13 matches YSZ better than that of NiO56wt%-YSZ mixture. The thermal expansion coefficient difference between YSZ and FY7/13 was < 1 x 10⁻⁶/°C at 50-1400°C.

If the solid state reaction does not occur between Fe₂O₃ and YSZ, the theoretical value of thermal expansion coefficient of Fe₂O₃-YSZ mixtures rises linearly as that of NiO-YSZ mixtures. Fig.4 shows the calculated results under this assumption. The thermal expansion coefficient of Fe₂O₃ sintered at 1500°C for 10hr in air is 11.6 x 10⁻⁶/°C (50-1000°C). The thermal expansion coefficients of Fe₂O₃-YSZ mixtures change as expected at 1000°C.

In Ar, we measured the thermal expansion coefficient of Ni40vol%-YSZ cermet and FY7/13 which was reduced in H₂ at 1000°C, but we were not sure of the accuracy of the data. Basically, the thermal expansion coefficient of FY7/13 (reductant) matches YSZ better than that of Ni40vol%-YSZ cermet because of the metal content (vol%) of FY7/13 is lower than that of Ni40vol%-YSZ cermet.

3.2 Electrical Conductivity

When the Fe-YSZ cermet is used as the fuel electrode material, it requires a high electrical conductivity, >2 x 10⁻⁶ S/cm, in a reducing atmosphere(6). The electrical conductivity of the specimens were measured in a reducing atmosphere (P₀₂=10⁻¹⁸-10⁻¹⁹ torr) by 4-probe method using direct current at 700-1000°C. The electrical conductivities of Fe-YSZ cermets in a reducing atmosphere are shown in Fig.5. In Fig.5, the broken line shows electrical conductivities of Ni-YSZ cermet(6). The electrical conductivity rises with the increase of metal content. If the Fe-YSZ cermet contains more than 36-38wt% of Fe₂O₃ in the raw materials, it has enough electrical conductivity. In the case of Ni-YSZ cermet, the required content of metal is more than 34-36vol% to keep enough electrical conductivity, but the Fe-YSZ cermet can keep it with lower metal content, 22-24vol%. It is desirable that the content of a metal component in the fuel electrode is as low as possible, because the volume of a metal component changes with P₀₂ and links an increase in the internal resistance of the cell.

The results of X-ray analysis of Fe-YSZ cermets which were reduced in H₂ at 1000°C are shown in Fig.6. Only the peaks of Fe, YSZ were observed.

3.3 Chemical Stability Between YSZ and Fe-YSZ Cermet

One of the merits of SOFC is that it has a high power generation efficiency. Therefore, the ion transference number (tᵢ) of YSZ must be maintained about 1(7). It is calculated using equation [1].
\[ t_i = \frac{E_o}{E_{th}} \]  \[ \text{[1]} \]

\[ E_o : \text{observed open circuit voltage (V)} \]
\[ E_{th} : \text{theoretical open circuit voltage (V)} \]

where \( E_{th} \) is calculated from Nernst's equation [2]

\[ E_{th} = \frac{RT}{2F} \left( \ln K + \ln \frac{PH_{2(a)} \cdot PO_{2(c)}^{1/2}}{PH_{2O(a)}} \right) \]  \[ \text{[2]} \]
\[ H_2 + \frac{1}{2}O_2 \rightarrow H_2O \]  \[ \text{[3]} \]

\[ K : \text{equilibrium constant of equation [3]} \]
\[ PH_{2(a)} : \text{partial pressure of } H_2 \text{ at the fuel electrode} \]
\[ PO_{2(c)} : \text{partial pressure of } O_2 \text{ at the air electrode} \]
\[ PH_{2O(a)} : \text{partial pressure of } H_2O \text{ at the fuel electrode} \]

The slurry of FY7/13 was smeared on the surface of the fuel electrode of a cell which fabricated using the co-sintering process and baked at 1500°C for 5hr in air. The smeared area, which corresponds to the fuel electrode area, was 2cm². The electrolyte thickness was 0.5mm and the Ni40vol%-YSZ cermet was used as the fuel electrode material. The \( t_i \) of YSZ was checked using this cell. By loading the electric current, 0.1A/cm², at 1000°C for 2000hr, the terminal voltage dropped from 0.6V to 0.4V, but the \( t_i \) of YSZ was maintained 1 (Fig.7). The electric current was stopped only when the open circuit voltage was measured.

Fig.8-1,-2 shows the EPMA results of the test cell. The aggregation of Fe was not observed in the fuel electrode, as in the case of Ni. The effect on progress of the diffusion of Ni and Fe into the YSZ caused by generation was minimal.

### 3.4 Steam Reforming of Methane

The catalytic activity of Ni27vol%-NiAl₂O₄ cermet, Ni40vol%-YSZ cermet and Fe-YSZ cermet containing Al₂O₃ for the steam reforming reaction of methane was examined using the
cell type catalysts. When the steam/carbon ratio changed from 2 to 5 at 1000°C, the changes of the methane conversion are shown in Fig.9. In Fig.9, the blank line shows the results of the steam reforming of methane without a catalyst. The methane conversion was reduced by the increase of steam/carbon ratio. The catalysts containing Ni show high catalytic activity for the steam reforming reaction of methane at 1000°C, but the catalyst containing Fe shows low catalytic activity. Therefore, it can be supposed that the steam reforming reaction on the fuel electrode can be controlled by masking it with the Fe-YSZ cermet.

4. CONCLUSIONS

1). The thermal expansion coefficient of FY7/13 matches YSZ better than that of Ni56wt%-YSZ cermet in air. The thermal expansion coefficient difference between YSZ and FY7/13 is $< 1 \times 10^{-6}/°C$ at 50-1400°C.
2). In the case of Ni-YSZ cermet, the required content of metal is more than 34-36vol% to keep enough electrical conductivity, but the Fe-YSZ cermet can keep it with lower metal content, 22-24vol%.
3). When the cell which used FY7/13 as the fuel electrode material was operated for 2000hr with loading the electric current, 0.1A/cm², at 1000°C, the ion transference number of YSZ was maintained 1.
4). The catalysts containing Ni show high catalytic activity for the steam reforming reaction of methane at 1000°C, but the catalyst containing Fe shows low catalytic activity.

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Table I  The raw materials of the catalysts.

| Cata. raw material                             | raw material                          |
|------------------------------------------------|---------------------------------------|
| Ni40vol%-YSZ cermet                          | NiO (reagent grade)                   |
|                                               | YSZ (8mol%-Y2O3 stabilized ZrO2)      |
| Ni27vol%-NiAl2O4 cermet                       | NiO (reagent grade)                   |
|                                               | Al2O3 (reagent grade)                 |
| Fe-YSZ cermet containing Al2O3                | Fe2O3 (reagent grade)                 |
|                                               | YSZ (8mol%-Y2O3 stabilized ZrO2)      |
|                                               | Al2O3 (reagent grade)                 |

Fig. 1. Test cell construction.
Fig. 2. Thermal expansion coefficients of Fe$_2$O$_3$–YSZ mixtures.

Fig. 3. Thermal expansion coefficients of fuel electrode materials.

Fig. 4. Thermal expansion coefficients of Fe$_2$O$_3$–YSZ mixtures.

Fig. 5. Electrical conductivities of Fe–YSZ cermets.
Fig. 6. X-ray diffraction of Fe-YSZ cermets.

Fig. 7. Changes of ion transference number of YSZ.

Fig. 9. Methane conversion changes influenced by steam/carbon ratio.
Fig. 8-1. Area analysis of Fe in fuel electrode.
Fig. 8-2. Area analysis of Ni in fuel electrode.