A STUDY ON FUEL ELECTRODE MATERIALS FOR
SOLID OXIDE FUEL CELLS

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ABSTRACT

Fuel electrode materials for solid oxide fuel cell were investigated from their activities for the electrode reaction and for steam reforming of methane. Mixing of metal oxide with Ni significantly modified the activity for the anodic reaction. Ni-CeOx was effective in promoting anodic reaction, and possessed high activity for steam reforming reaction. Gas phase analysis during power generation of SOFC indicated that steam reforming reaction easily proceeded to supply hydrogen for the electrode reaction for the Ni-based cermets. Extremely low and high steam content resulted in deterioration of the electrode performance. Mixing of large YSZ powder with Ni resulted in fast sintering of Ni, but fine YSZ or CeOx powder with Ni was effective in suppressing sintering of Ni in the cermet.

INTRODUCTION

Solid oxide fuel cells has been actively investigated as an efficient power generation system for the future application. However, fabrication of the single cell and materials selection have still covered important part in the research and development of SOFC. The electrode materials as well as a solid electrolyte have to be developed to derive sufficient power from the single cell. The present investigation focused on the investigation of fuel electrode materials and the chemical reaction occurring at the fuel side of SOFC. Ni-YSZ cermet has been most popularly employed as a fuel electrode material (1). We have previously reported that the oxide material which is mixed with Ni influenced the electrode reaction (2). Mixing of ceria with Ni is effective in reducing polarization, giving rise to a high power density of SOFC. Thus, it implies that the investigation of additives for Ni is one approach in developing fuel electrode material. Another special interest for the SOFC system is the possibility of internal reforming of methane and other hydrocarbons on the fuel electrode. The present investigation deals with the effect of oxide which is mixed with Ni or other metals on the electrode reaction and internal reforming reaction. Information on internal reforming was obtained from the gas phase analysis during the power generation experiment.
EXPERIMENTAL

The Ni-based electrode materials with additives were prepared by mixing of NiO (80wt%) and metal oxides (20wt%) and heating in air at 1100°C. The cermet powder thus obtained was coated on a YSZ pellet (500 μm thick and 18 mm in diameter) which was prepared by the slip casting process. In every case, a La0.6Sr0.4MnO3 (abbreviated as LSM) counter electrode and a Pt reference electrode were attached on the YSZ electrolyte disk. The electrode materials were mixed with turpentine oil before applying onto the electrolyte pellet. The details of the cell configuration was described previously (3).

Tubular fuel cells were prepared on electrode substrate by the wet processing procedure as reported previously (4). A Ni-YSZ cermet tube, which was prepared by slip casting of a NiO and YSZ (weight ratio = 4:2) powder mixture, was supplied from Saibu Gas and Totsu and used as a support for the fuel cell experiment with internal reforming of methane. The size and weight of the Ni-YSZ tube used in the series of experiments were 30 mm long, o.d. = 14 mm, i.d. = 10 mm, and W = 13.4 g. A thin film of YSZ (ca. 40 μm) and a LSM counter electrode were prepared by slurry coating onto the Ni-YSZ support.

Power generation characteristics of SOFCs with different fuel electrode materials were measured by using a conventional flow system as reported previously (3). The planar or tubular cell was attached to a mullite tube which was connected to the flow line by Pyrex glass ring by melting. A gaseous mixture of H2-H2O, CO-CO2, or CH4-H2O was supplied to the fuel electrode and pure oxygen was supplied to the counter electrode. The gas phase composition after steam reforming reaction was analyzed by gas chromatography. The column used for separation of CO2 and N2 was porapak Q and that for separation of H2, N2, CH4, and CO was active carbon. The selectivities to CO and CO2 were defined as ratios of produced CO and CO2 to reacted CH4.

Temperature programmed desorption of H2 and other gases was carried out by using a flow system. Ni-alumina and Ni-YSZ samples were prepared by impregnation of the support oxides in Ni(NO3)2 solution and reduced in a H2 stream prior to the adsorption treatment. Hydrogen was introduced to the samples at a specified temperature and cooled down to room temperature. Then the desorption curve was recorded during the programmed heating schedule (10°C/min).

RESULTS AND DISCUSSION

Electrode Materials for SOFC and Steam Reforming Activity

Nickel has been most popularly employed as a fuel electrode material for Solid oxide fuel cells. Figure 1 shows the power generation characteristics for the cells with Ni-metal oxide cermet electrodes. As we have reported previously, mixing of CeOx with Ni gave rise to higher power generation than Ni-YSZ (2). The mixing with other oxide
materials were not effective in improving I-V characteristics. The microstructures of the Ni-YSZ and Ni-CeOx were almost the same after operation of SOFC in H$_2$ at 1000°C, however the effect of microstructure on the polarization characteristics cannot be excluded. The polarization conductivity of the Ni-ceria electrode was larger than Ni-YSZ (5).

The temperature programmed desorption curve of H$_2$ from Ni-YSZ was compared with that of Ni-Al$_2$O$_3$ (Fig. 2). In both case the loading of Ni was 3.0wt%. Relatively large amount of hydrogen desorption was observed from Ni-Al$_2$O$_3$, whereas the desorption of H$_2$ was very small from Ni-YSZ. The difference in adsorption amounts of H$_2$ primarily reflects the surface area of the supported Ni metal. The nickel particles on Al$_2$O$_3$ are highly dispersed due to large BET surface area of the support (145 m$^2$/g) as compared with that of YSZ (6.6 m$^2$/g). Hydrogen spill-over from Ni to the support also promotes adsorption on Ni-Al$_2$O$_3$. Since the spill-over hydrogen is not abundant and the surface area is small for Ni-YSZ, the adsorption amount at the operation temperature of SOFC is small.

Catalytic activities of Ni-containing catalysts for steam reforming of methane were tested in a conventional fixed bed reactor at H$_2$O/CH$_4$ = 5 (Fig. 3). Commercial NiO (80wt%) was mixed with a ceramic powder (20wt%) and heated in air at 1400°C prior to the reaction. The solid line in the figure is the equilibrium conversion from the thermodynamic data. Ni-YSZ and Ni-SDC almost attained the equilibrium conversion at 500°C or higher temperatures. Although nickel particles for these cerments were expected to be large from the above mentioned data, both Ni-containing catalysts exhibited high activities for methane steam reforming reaction. The activity of Pt, being also listed in the figure, for the reforming reaction was far below the equilibrium line.

We have reported previously that the Ni-based cermet has high activity for internal steam reforming reaction (3). Thus, the I-V characteristics of the H$_2$-H$_2$O system was almost similar to that of CH$_4$-H$_2$O at the same open circuit voltage. Figure 4 compares the I-V characteristics of the fuel cell with a Pt anode at 1000°C in pre- (CH$_4$-H$_2$O) and post-reforming (H$_2$-H$_2$O-CO-CO$_2$) gases. The composition of post-reforming gas was based on the thermodynamic data. The open circuit voltage was fixed at 0.87 V, i.e., Po$_2$ in both gaseous mixtures was set at 10$^{-8}$ Pa. The I-V curve was almost linear in the case of the post-reforming gas. The I-V curve for the pre-reforming gas was almost similar to that of the post-reforming gas near the open circuit condition. However, in the high current density region, the voltage drop was significant for pre-reforming gas. Thus, it is conceivable that the activity of Pt for steam reforming of methane is not so sufficient as to supply enough H$_2$ to the electrode reaction in the high current density region. Figure 4 also contains the result of CeOx-FeOy anode for the pre-reforming gas, but the use of this anode resulted in poor power generation characteristics. Thus, Ni appears to be indispensable for the internal reforming reaction.

Internal Reforming Activity during Power Generation Experiment

A methane and steam mixture (CH$_4$ / H$_2$O = 3) was supplied to the fuel cell fabri-
cated by the slip casting process. I-V curves at different temperatures are shown in Fig. 5. With an increase in temperature, the current density was enhanced at a given voltage because of the decrease in both electrolyte resistance and electrode polarization. A gas phase analysis was carried out during the measurement of the fuel cell experiment (Table 1). Methane conversion and formation rate of H2 at the open circuit condition increased with increasing temperature. The selectivity to CO2 was lowered at high temperatures due to the exothermic nature of the shift reaction.

The effect of space velocity was measured at 12.5% CH4 and 25% H2O. The open circuit voltage was almost unchanged with the overall flow rate of the reaction gas. The polarization became large with increasing flow rate of the gas. The methane conversion decreased and CO selectivity increased with increasing flow rate.

The relation between CH4 conversion and the current of the fuel cell was measured as shown in Table 2. The passage of current gave rise to the increase in conversion of methane as compared with that of the open circuit condition. The removal of H2 and formation of H2O from the reaction system appears to shift the conversion of the steam reforming reaction. Outlet hydrogen / reacted CH4 ratio was larger than 3 at the open circuit condition, but decreased with an increase in current accompanied with the consumption of H2. The active electrode area of the tubular cell used in the series of experiments was 4.7 cm². The amount of H2 oxidized by passing 1A of current is estimated to be 7.63 cm³/min.

The effect of fuel concentration was measured at a fixed H2O concentration (50%) and overall flow rate (200 cm³/min) as shown in Table 3. High concentration of CH4 resulted in high open circuit voltage because of the low oxygen partial pressure in the fuel. The conversion of methane and selectivity to CO2 was lowered with increasing concentration of CH4. At an extremely low CH4 concentration of 2.5%, the conversion of methane was unstable with time probably due to the deterioration of the Ni electrode with steam.

The effect of water content in the reaction gas was analyzed at a fixed CH4 concentration of 10%. The I-V characteristics are shown in Fig. 6. The open circuit voltage was highest in the case of 2% H2O again due to the low Po2 in the fuel. The voltage at a given current density was higher in the case of 20% H2O than those of 2% and 60% H2O. The low performance of fuel cell at 2% H2O is because of the high polarization resistance and deterioration of electrode with carbon deposition, whereas that at 60% H2O is resulted from the extremely high water content. The anodic polarization at the open circuit condition decreased with increasing content of H2O in agreement with our previous report (3). The methane conversion was enhanced with increasing water content and CO selectivity was lowered. These tendencies with water content are understood by considering the equilibria of reforming and shift reactions.

Control of Sintering of Ni in Cermet Anode

Sintering of Ni at the operating condition is one of the damaging factors for SOFC.
A large surface area of Ni particle is desirable both from the electrode reaction and steam reforming reaction. Thus, the effect of additive on the resistance to sintering of Ni was investigated. Figure 7 shows the microstructures of Ni-YSZ and Ni-CeOx after heating in air at 1100°C and after subsequent heating in H₂ at 1100°C. The YSZ powders used for mixing with Ni were commercial powder (TZ-8YS) without pretreatment and powder after heating at 1300°C in air. The scanning electron micrographs of ceramic without mixing with Ni was observed after heating the powders at 1100°C in H₂ as shown in Fig. 7. The microstructural differences were not obvious after heating the Ni-YSZ in air, but contrasting microstructural difference could be seen between two Ni-YSZ. The Ni grains were developed into large particles of the size of 7 µm in the case of Ni with preheated YSZ, whereas the microstructure of Ni with fine YSZ was maintained to be 1 µm before and after reduction with H₂. The mixing with fine CeOx powder (1 µm) was also effective in suppressing sintering of Ni. It is expected that the resistance to sintering of Ni for Ni-based cerments is related with sinterability of mixed ceramic materials. As previously pointed out by Matsuzaki et al. (6) for the Ni-YSZ system, fine particle of ceramic dispersed on the surface of Ni powder is effective in maintaining the small particle size of Ni.

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Fig. 1 Influence of oxide in Ni-Oxide cermets on I-V characteristics (T = 1000°C).

\[ \text{H}_2 + \text{H}_2\text{O} \text{ (PO}_2\text{=2.94×10}^{13}\text{ Pa) , anode / YSZ/La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3, \text{ O}_2 \text{ (PO}_2\text{=1.0×10}^5\text{ Pa)} } \]

Fig. 2 Hydrogen desorption from Ni-YSZ and Ni-Al\textsubscript{2}O\textsubscript{3}.

Adsorption of H\textsubscript{2}: 400°C → room temp., heating rate 10°C/min.
Fig. 3  Steam reforming reaction of CH₄ over Ni- and Pt-based cermet catalyst.  
(Reaction condition: S/C=5, SV=7000 h⁻¹)

Fig. 4  I-V characteristics for the fuel cell with 

- Pt and △(CeOₓ)₀.₈(FeOᵧ)₀.₂ anode. 

- fuel: □CH₄ + H₂O \[ \log (P₀₂/P₁) = -8.80 \]
- □H₂ + H₂O + CO + CO₂ \[ \log (P₀₂/P₁) = -8.81 \]
  \( (H₂:CO:CO₂ = 3.5:0.7:0.3) \)
- △CH₄ + H₂O

\[ \log (P₀₂/P₁) = -8.81 \]

Current density / A cm⁻²

Terminal voltage / V
Fig. 5 I-V curves of fuel cell with steam reforming reaction at different temperatures. 

CH₄-H₂O, Ni-YSZ/YSZ/LSM, O₂,

Flow rate in fuel gas, CH₄: 50 cm³/min, H₂O: 150 cm³/min, N₂: 200 cm³/min,

Table 1 Steam reforming of methane at the open circuit condition of Fig.5

| T / °C | V / volt | Conversion | CO selectivity | CO₂ selectivity | H₂ evolution rate / mmol min⁻¹ |
|-------|----------|------------|---------------|----------------|------------------|
| 1000  | 0.88     | 89.9       | 79.5          | 20.5           | 5.65             |
| 900   | 0.91     | 82.9       | 70.0          | 30.0           | 5.27             |
| 800   | 0.92     | 70.9       | 60.1          | 39.9           | 4.58             |

Table 2 Gas phase composition during fuel cell experiment with steam reforming reaction

T = 1000°C

| I / A | V / volt | Conversion | CO selectivity | CO₂ selectivity | Formed H₂ / reacted CH₄ |
|-------|----------|------------|---------------|----------------|-------------------------|
| 0     | 0.96     | 73.4       | 84.5          | 15.5           | 3.54                    |
| 0.5   | 0.71     | 78.2       | 83.8          | 16.2           | 3.30                    |
| 1.0   | 0.62     | 79.5       | 81.7          | 18.3           | 3.21                    |
| 1.5   | 0.56     | 81.2       | 79.8          | 20.2           | 3.09                    |
| 2.0   | 0.51     | 82.0       | 72.8          | 27.2           | 3.03                    |

Flow rate in fuel gas, CH₄: 75 cm³/min, H₂O: 150 cm³/min, N₂: 150 cm³/min,
Table 3  Fuel cell experiment with steam reforming reaction at different CH₄ concentrations (T = 1000°C)

| CH₄ concentration | I/A | V/Volt | Conversion of CH₄/% | CO selectivity / % | CO₂ selectivity / % | Formed H₂ / reacted CH₄ |
|-------------------|-----|--------|---------------------|--------------------|---------------------|------------------------|
| 2.5%              | 0.5 | 0.81   | 100                 | 15.7               | 84.3                | 2.31                   |
|                   | 0   | 0.67   | 100                 | 29.7               | 80.3                | 3.08                   |
| 12.5%             | 1.5 | 0.58   | 98.1                | 61.2               | 38.8                | 2.66                   |
|                   | 0.75| 0.75   | 97.3                | 60.8               | 39.2                | 2.95                   |
|                   | 0   | 0.92   | 100                 | 76.4               | 23.6                | 3.12                   |
| 25%               | 2   | 0.73   | 93.7                | 92.4               | 7.60                | 2.79                   |
|                   | 1   | 0.84   | 98.4                | 96.0               | 4.00                | 2.67                   |
|                   | 0   | 1.06   | 96.0                | 98.3               | 1.70                | 2.98                   |

Overall flow rate: 200cm³/min, H₂O concentration: 50%

Fig.6  Influence of steam concentration on I-V characteristics (1000°C).
H₂O concentration: □ : 2% , ○ : 20% , △ : 60%
flow rate of gas : 250 cm³/min, CH₄ concentration: 10%
Fig. 7  Backscattered electron images of (a)(b) Ni-based cermets (63wt% Ni) and (c) YSZ and CeOx powders without Ni. (a) after heating at 1100°C for 5h in air and (b)(c) after heating at 1100°C for 10h in H2.