INFLUENCE OF STEAM CONCENTRATION ON THE DEGRADATION BEHAVIOR OF REVERSIBLE SOLID OXIDE FUEL CELLS

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ABSTRACT

The degradation behavior of reversible SOFCs was investigated under various steam concentration atmospheres in the power generation and electrolysis processes. In the power generation process at high steam concentration, a sudden drop in terminal voltage was observed and cell performance degraded. After H₂ treatment to the degraded cell, performance recovered but not to the initial level. This result indicated that the irreversible degradation proceeded only partially. On the other hand, during electrolysis, terminal voltage increased continuously while applying a constant current under low steam concentration. This behavior brought about irreversible degradation at both electrodes and suggested interfacial reaction and microstructural destruction.

INTRODUCTION

Solid oxide fuel cells (SOFCs) have great potential as energy conversion devices because of their high efficiency and low emissions. Many studies have been conducted on materials and system development (1-3). However, the long-term stability of stacked SOFCs is the most important requirement for practical use and needs the most improvement. Degradation of SOFCs occurs over time. Many studies have focused on interfacial reactions among components and the deterioration of material properties (4,5).

Generally, SOFCs are operated at high fuel utilization in actual conditions, and the downstream part of the cell is exposed to severe conditions because of the depletion of fuel and high steam concentration, resulting in degradation of the cell. However, this degradation behavior has not been elucidated sufficiently.

In addition, SOFCs can be operated as electrolysis cells called solid oxide electrolysis cells (SOECs), by reverse operation (6,7). A reversible fuel cell can take advantage of off-peak electricity to produce hydrogen, which can be used as fuel during peak power demand. Because steam electrolysis is an endothermic process, high-temperature operation is advantageous for using waste heat, reducing theoretical electrolysis voltage. Electrode polarization losses are also reduced due to improvement of electrode kinetics. In this application, the cathode is placed in high water vapor conditions, but the downstream part of the cell is exposed to the steam depleted atmosphere. Therefore, clarifying the phenomenon under low humidity conditions is required. In this study, the
degredation behavior of reversible SOFCs was investigated under various steam concentration atmospheres in the power generation and the electrolysis processes.

EXPERIMENTAL

Preparation of a Single Cell

A disk of 8 mol% Y₂O₃-stabilized zirconia (YSZ) (Tosoh Co.) 20 mm in diameter, 500 μm thick, was used as an electrolyte. The Ni-YSZ cermet was prepared from NiO (Wako Pure Chemical Industries) and YSZ powder (Tosoh Co, TZ-8YS). The mixture of NiO and YSZ in a 4:1 weight ratio was mixed with polyethylene glycol (Wako Pure Chemical Industries) to form slurry. The resultant slurry was screen-printed onto the electrolyte and then fired at 1400°C for 5 hr in air. The other electrode material, La₀.₆Sr₀.₄MnO₃ (LSM), was prepared from corresponding metal acetates. Reagents in the required molar ratio were dissolved in water and dried at 120°C. The resulting powder was milled for 24 hr and calcined at 900°C for 10 hr. The other surface of the disk was screen-printed with the slurry consisting of LSM and polyethylene glycol and fired at 1150°C for 5 hr in air. The reference electrode was prepared by painting a platinum paste (N.E. Chemcat Co., U-3402) onto its LSM side. The single cell was sandwiched by alumina tubes with a Pyrex glass seal and heated from room temperature to 1000°C at a constant 200°C/hr. Before the electrochemical measurements, Ni-YSZ cermet was reduced under hydrogen atmosphere at 1000°C for 1 hr.

Electrochemical Measurements

A gaseous mixture of H₂-H₂O-N₂ was supplied to anode and cathode in the power generation and electrolysis processes, respectively, with a total flow rate of 100 mL/min. In this report, the ratio of H₂ was fixed as 5 or 10% and balance N₂. The mixture gas was prepared by bubbling H₂-N₂ through water, which was kept at various temperatures. Oxygen was supplied to the other electrode at a flow rate of 100 mL/min. AC impedance measurements and current-voltage characteristic measurements were conducted using the Solartron 1287 electrochemical interface and the Solartron 1260 frequency response analyzer. The applied frequency was in the range of 0.1 Hz to 1 MHz with a voltage amplitude of 10 mV.

RESULTS AND DISCUSSION

Degradation Behavior in Power Generation Process at High Steam Concentration

In the power generation process, a constant current of 200 mA cm⁻² was applied at 1000°C under a 0.6% H₂O, 10% H₂, and balance N₂ atmosphere. Terminal voltage remained constant and no degradation was observed even after 72000 s. The behavior was different when highly humidified gas was supplied to the anode. The time dependence of terminal voltage at 1000°C while drawing a constant current of 200 mA cm⁻² under a 40% H₂O, 10% H₂, and balance N₂ atmosphere is shown in Figure 1. Terminal voltage decreased gradually with time. A sudden drop was observed at about 6000 s. To clarify this, impedance spectra before and after degradation were compared.
Figure 1. Time dependence of terminal voltage while drawing a constant current of 200 mA cm$^{-2}$ in power generation process at 1000°C. Anode gas composition was 40% H$_2$O, 10% H$_2$, and balance N$_2$.

Figure 2 shows the impedance spectrum of each electrode at OCV. On the anode side, after the degradation, the resistance concerned with IR loss and reaction overvoltage increased drastically. However, after reduction treatment at the anode side under hydrogen atmosphere for 1 hr, the performance was recovered but not to the initial level. These results suggest that the irreversible degradation proceeded only partially. On the other hand, even after the degradation, IR loss at cathode side showed no change, and the reaction resistance slightly decreased; this was caused by the improvement in the surface structure of LSM when applying current. Consequently, the degradation is attributed to partial oxidation of Ni with volume expansion at the anode. Therefore, the increase in IR loss at the anode side was caused by decreasing conductivity and increasing contact resistance. Furthermore, considering that irreversible behavior was observed, agglomeration of Ni particles might occur. The enlargement of semicircles at high and low frequency, assigned to activation and concentration overvoltage, respectively, should be caused by the reduction in active reaction sites at the triple phase boundary and the water rich atmosphere in the vicinity of the electrode. To investigate the degradation behavior under the more severe condition, a similar experiment was conducted.

![Graph](image.png)

Figure 2. Impedance spectra of (a) Ni-YSZ anode and (b) LSM cathode at 1000°C under open circuit condition. Anode gas composition was 40% H$_2$O, 10% H$_2$, and balance N$_2$. 
The time course of the current density when the terminal voltage was held at 0.2 V is shown in Figure 3. Anode gas composition was a 40% H$_2$O, 5% H$_2$, and balance N$_2$ balance. In this condition, the current continuously decreased with time. Impedance spectra before and after degradation at open circuit voltage (OCV) are also shown in Figure 4. After the degradation, resistance at both anode and cathode increased, and sufficient recovery was not observed after the reduction treatment, which was different in Figure 2. This irreversible behavior indicates that the anode degradation may be caused by not only NiO formation but also by microstructural destruction, including Ni agglomeration. The increase in cathode resistance may be explained by the reduction in the anode area. Accordingly, SOFCs should be operated considering these results to avoid irreversible degradation at the downstream part of the cell.

Figure 3. The time dependence of current density when the terminal voltage was held at 0.2 V in the power generation process at 1000°C. Anode gas composition was 40% H$_2$O, 5% H$_2$, and balance N$_2$.

![Figure 3](image)

Figure 4. Impedance spectra of (a) Ni-YSZ anode and (b) LSM cathode at 1000°C under open circuit condition. Anode gas composition was 40% H$_2$O, 5% H$_2$, and balance N$_2$.

![Figure 4](image)

**Degradation Behavior in Electrolysis Process at Low Steam Concentration**

Current-voltage characteristics in the electrolysis process under various steam concentration atmospheres at 1000°C are shown in Figure 5. OCV increased with a decrease in steam concentration, consistent with the theoretical prediction. A sudden increase in
terminal voltage, which was observed at a certain current density under any conditions investigated, depended on steam concentration. Considering that no such behavior was observed in the power generation process, this should be the diffusion limited current behavior. However, the terminal voltage increased not steeply but gradually in the higher voltage region. This result suggests the existence of different hydrogen evolution mechanism, but this is not elucidated yet. Hereafter, we focused on the degradation behavior before and after the electrolysis process at low steam concentration.

A single cell degraded under 0.6% H₂O atmosphere drawing a constant current of 100 mA cm⁻² to the electrolysis direction for 24 hr. The time course of terminal voltage and impedance spectra are shown in Figures 6 and 7, respectively. During electrolysis at constant current, the terminal voltage increased steeply within the first 2 hr, and then gradual increase up to 1.49 V was observed. Momma et al. have reported the similar behavior, which was continued until the LSM electrode was delaminated, and they concluded that direct contact between LSM and YSZ brought about the degradation (7). In our experiment, however, the degradation was observed at both electrodes, especially at Ni-YSZ cathode, whose resistance was about two times larger than that of the anode.

Figure 5. *I-V* characteristics in electrolysis process at various steam concentrations. Cathode gas composition was 0.6-5.0% H₂O, 10% H₂, and balance N₂.

Figure 6. Time dependence of terminal voltage while drawing a constant current of 100 mA cm⁻² in the electrolysis process at 1000°C. Cathode gas composition was 0.6% H₂O, 10% H₂, and balance N₂.
Figure 7. Impedance spectra of (a) Ni-YSZ cathode and (b) LSM anode at 1000°C under open circuit condition. Anode gas composition was 0.6% H₂O, 10% H₂, and balance N₂.

Even after reduction treatment at the cathode under H₂ atmosphere for 1 hr, performance did not recover. Since the decomposition voltage of ZrO₂ calculated from the Gibbs free energy at 1000°C is about 2.3 V, YSZ should be stable in this experiment. The increase in anode resistance could be caused by an interfacial reaction between YSZ and LSM. On the other hand, the drastic increase in cathode resistance may be caused by microstructural destruction because the electrode delaminated easily and no recovery was observed after reduction treatment. Some kind of reaction might occur at the interface or electrode; however, the phenomenon on the cathode side has not been elucidated completely and is under investigation by microstructural analysis.

CONCLUSIONS

The degradation behavior in power generation and electrolysis processes was investigated under various steam concentration atmospheres. In the power generation process at high steam concentration, Ni in the cermet electrode was partially oxidized to NiO, increasing total resistance. This phenomenon may possibly bring about microstructural destruction including Ni agglomeration. Accordingly, SOFCs should be operated to avoid irreversible degradation at the downstream part of the cell. In the electrolysis process at low steam concentration, both anode and cathode degraded, caused by the interfacial reaction at YSZ/LSM and microstructural destruction, respectively. However, further investigation is required to elucidate these phenomena in the electrolysis process.

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