SULFUR TOLERANCE OF SOLID OXIDE FUEL CELLS

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ABSTRACT

Influence of H2S fuel impurity on power generation characteristics of SOFCs has been analyzed by measuring cell voltage at a given current density, as a function of operational temperature, H2S concentration, and fuel gas composition. Reversible cell voltage drop was observed around 1000°C, but fatal irreversible degradation occurred at lower operational temperatures, at higher H2S concentrations, and at lower fuel H2/CO ratios. Sulfur tolerance of SOFCs improved by using Sc2O3-doped ZrO2 instead of Y2O3-doped ZrO2 as electrolyte and/or as electrolyte component in the anode cermet. It has been found that H2S poisoning consists of at least two stages, i.e. an initial cell voltage drop within a few minutes to a metastable cell voltage, followed by a gradual larger cell voltage drop associated with the agglomeration of Ni particles.

INTRODUCTION

SOFCs are the most flexible fuel cells with respect to fuel selection, so that various types of fuels such as hydrocarbons, coke oven gas, and biogas may be used (1-3). However, fuel impurities, especially sulfur compounds, can cause degradation of fuel electrodes and thus electrochemical performance (4-8). Sulfur compounds are also added in city gas and LPG gas, so that the understanding of sulfur poisoning and the increase in sulfur tolerance are of technological relevance for SOFC commercialization. Therefore in this study, sulfur tolerance of SOFCs is analyzed by using H2S-containing fuel gases with respect to operation temperature, H2S concentration, fuel composition, anode and electrolyte materials, to develop sulfur-tolerant SOFCs as well as to understand sulfur poisoning mechanism.

EXPERIMENTAL

Two kinds of electrolyte materials were used in this study: 8YSZ (8 mol% Y2O3-92 mol% ZrO2, supplied from Tosoh) and 10SSZ (10 mol% Sc2O3 -1 mol% CeO2-89 mol% ZrO2 or 10 mol% Sc2O3-90 mol% ZrO2 (9), supplied from Daiichi Kigenso Kagaku) with a thickness of 200 µm. Electrode layers were prepared via screen
printing technique, followed by heat-treatments for anodes at 1400°C for 5 h and then for cathodes at 1150°C for 5 h. Electrode area was 5x5 mm². For electrochemical characterizations, fuel gases containing a small amount of H₂S were supplied to the anodes. As H₂S is soluble in water, H₂S (diluted by N₂ gas) was added just after humidifying fuel gases. Fuel impurity tolerance was evaluated by measuring cell voltage at a constant current density (200 mA/cm²). Electrolyte material and electrolyte component in the anode cermet were also modified, and in some cases, additives were impregnated into the porous anode layers. FESEM was used to analyze microstructural changes caused by H₂S. Thermochemical calculations (10,11) were also carried out to derive equilibrium diagrams containing Ni and S.

RESULTS AND DISCUSSION

**H₂S Concentration Dependence of Sulfur Poisoning**

Figure 1 shows cell voltage in the case where H₂-based fuel gases containing H₂S in different concentrations were supplied. Just after mixing H₂S of a few ppm, a decrease in cell voltage was detected. Cell voltage drop became larger with increasing H₂S concentration. However, under these experimental conditions, cell voltage could be recovered to the initial value by supplying the identical fuel gas but without H₂S, as shown in Fig. 2, indicating that such sulfur poisoning is reversible.

**Figure 1. H₂S concentration dependence of cell voltage at 200 mA/cm² (1000°C, H₂:CO = 100:0, Electrolyte: YSZ).**

**Temperature Dependence of Sulfur Poisoning**

Figure 3 shows cell voltage in case H₂-based fuel gas containing 5 ppm H₂S was supplied, at different operational temperatures, to the cells consisting of 8YSZ electrolytes. Figure 4 shows (the absolute values of) cell voltage drop as a function of operational temperature. Cell voltage drop was observed at all cases, but at temperatures higher than 850°C, cell voltage became stable after the initial cell voltage drop within a few minutes. However, at 850°C, cell voltage became unstable and cell voltage drop was not recovered to the initial cell voltage by using the identical fuel gas.
but without H$_2$S, indicating that sulfur poisoning became rather irreversible with decreasing operational temperature (6-8).

**Figure 2.** Cell voltage at 200 mA/cm$^2$ for the H$_2$-based fuel with and without H$_2$S (1000°C, H$_2$S conc. = 5 ppm, H$_2$:CO = 100:0, Electrolyte: YSZ).

**Figure 3.** Temperature dependence of cell voltage at 200 mA/cm$^2$, H$_2$S conc. = 5 ppm (Electrolyte: YSZ).

**Figure 4.** Temperature dependence of cell voltage drop at 200 mA/cm$^2$, H$_2$S conc. = 5 ppm (Electrolyte: YSZ).

**Fuel H$_2$/CO Ratio Dependence of Sulfur Poisoning**

Cell voltage (drop) was measured also as a function of H$_2$/CO ratio of fuel gases. Figure 5 shows cell voltage for mixed H$_2$+CO fuel gases, and Figure 6 shows (the absolute values of) cell voltage drop caused by the H$_2$S addition. In case CO concentration was lower than 90%, cell voltage became stable after the initial voltage drop. However, for CO-rich fuel gases with CO concentration at and above 90%, cell voltage decreased rapidly below zero at the constant current density fixed by the external galvanostat in the experiments. This fatal cell voltage drop could not be recovered even after supplying fuel gas without H$_2$S. These results indicate that sulfur
poisoning is serious for CO-rich fuel gases.

**Figure 5.** $\text{H}_2/\text{CO}$ ratio dependence of cell voltage at 200 mA/cm$^2$ (1000°C, H$_2$S conc. = 5 ppm, Electrolyte: YSZ).

**Figure 6.** $\text{H}_2/\text{CO}$ ratio dependence of cell voltage drop at 200 mA/cm$^2$ (1000°C, H$_2$S conc. = 5 ppm, Electrolyte: YSZ).

**Sulfur Poisoning of Cells with Different Electrolytes**

10SSZ electrolytes instead of 8YSZ electrolytes were also used and cell voltage drop was measured at different operation temperatures. In this case, 8YSZ was used as electrolyte component in the anode cerments. Results are shown in Fig. 7. In case 8YSZ was used as the electrolyte material, a large voltage drop was observed below 875°C. However, in case 10SSZ was used as the electrolyte material, voltage drop was less than 0.2 V even at 800°C (H$_2$S conc. = 5 ppm), and cell voltage became stable after the

**Figure 7.** Temperature dependence of cell voltage drop at 200 mA/cm$^2$, H$_2$S conc. = 5 ppm.

**Figure 8.** H$_2$S concentration dependence of cell voltage drop at 200 mA/cm$^2$, 800°C (Electrolyte: SSZ).
initial voltage drop. Figure 8 shows cell voltage drop at 800°C at different H₂S concentrations in the H₂-based fuel gas. The cells based on 10SSZ electrolytes were relatively sulfur-tolerant, compared to the cells based on 8YSZ electrolytes. However, H₂S concentration of 20 ppm was still too high so that a large (fatal) voltage drop was observed also for 10SSZ-based cells.

**Sulfur Poisoning of Cells with Different Electrolyte Materials in the Anodes**

Cell voltage drop was measured at 800°C for the cells in which 10SSZ was used both for the electrolytes and for the electrolyte components in the anodes. Results are shown in Fig. 9. Sulfur tolerance was further improved by substituting electrolyte components with 10SSZ in the anodes. Even though experiments for much longer time periods are needed to conclude on the long-term stability, no fatal voltage drop was observed even with fuels containing 100 ppm H₂S. These experimental results indicate that sulfur tolerance is in fact improved by using Sc₂O₃-doped ZrO₂ electrolytes. Whereas the reasons for such improvements should be clarified, this experimental fact suggests, at least, that sulfur tolerance depends also on anode and electrolyte materials besides nickel.

**Figure 9. Cell voltage of H₂S-tolerant SOFCs at 200 mA/cm², 800°C**

(Electrolyte: SSZ, Anode: Ni-SSZ or Ni-YSZ).

**Sulfur Poisoning of Cells with Anodes Containing Additives**

As sulfur tolerance may be controlled by modifying anode and electrolyte materials, cell voltage drop was measured with anodes into which various additives were impregnated using acidic solutions, including Ce, Ti, Sc, Y, Zr, Nb, Mg, Ca, La, or Al stable as oxides and Ru or Co stable as metals under operation conditions. The results are shown in Fig. 10. We have found that some oxides were effective to keep cell voltage drop smaller.
Sulfur Poisoning Processes

One possible explanation for sulfur poisoning may be the formation of Ni sulfide (NiSx). In order to examine this possibility, the stability regions of Ni compounds were derived by thermochemical calculations (10,11). The Ni-S-O equilibrium diagram at 800°C calculated is shown in Fig. 11, as a function of $P_{O_2}$ and $P_{S_2}$. At this temperature, Ni sulfide exists in liquid state, so that the formation of Ni sulfide, if any, could cause a rapid and drastic change of porous anode microstructure. However, $P_{H_2S}$ at the phase boundary of $Ni_3S_2(l)$ and Ni(fcc) was ca. 2000 ppm derived from the corresponding $P_{S_2}$ in Fig. 11, indicating that sulfur poisoning especially at $H_2S$ concentrations of several ppm in this study can not be simply explained by Ni sulfide formation.

Microstructural change was also examined by observing the cross section of anodes using FESEM. No obvious microstructural change was found just after the initial cell
voltage drop. This indicates that the initial cell voltage drop may be associated with e.g. the dissociative adsorption of sulfur-based species around three-phase boundaries leading to an increase in anodic polarization. Figure 12 shows the cross section of an anode layer after the large fatal voltage drop. Agglomeration of Ni particles could be distinguished, which leads to an irreversible decrease in three-phase boundaries. In addition, anode layers were often easily detached from the electrolyte plates after H2S poisoning experiments followed by cooling to room temperature. These tendencies suggest that agglomeration of Ni particles accelerated by the presence of sulfur may be one of the reasons for the fatal cell degradation associated with a large voltage drop.

Figure 12. FESEM image of anode cross section after the fatal voltage drop (200 mA/cm^2, 800°C, H2S conc. = 5 ppm, Electrolyte: YSZ).

CONCLUSIONS

It was found that sulfur poisoning becomes serious with increasing H2S concentration, with decreasing operational temperature, and/or with decreasing H2/CO ratio. Sulfur tolerance was improved especially by using Sc2O3-doped ZrO2 as electrolyte materials and as electrolyte components in the anodes. Sulfur poisoning of SOFCs consists of at least two stages, i.e., an initial cell voltage drop within a few minutes to a (meta)stable cell voltage, followed by a gradual but fatal larger cell voltage drop associated with the agglomeration of anode Ni particles.

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