EFFECT OF A SULFUR-CONTAINING IMPURITY ON ELECTROCHEMICAL PROPERTIES OF A Ni-YSZ CERMET ELECTRODE

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ABSTRACT

Poisoning effect of sulfur-containing impurity on the electrochemical oxidation of H$_2$ at the interface between a Ni-YSZ cermet electrode and a YSZ electrolyte has been studied at 1023-1273 K in a gas mixture of H$_2$ and H$_2$O using a complex impedance analysis and a DC polarization method. The polarization impedance and the DC overvoltage of the electrode increased when H$_2$S concentration exceeded 0.05, 0.5, and 2 ppm at 1023, 1173 and 1273 K, respectively. This indicates that high-grade desulfurization will be necessary for reducing the operating temperature. Within the experimental conditions, the performance loss caused by the sulfur poisoning was recoverable when H$_2$S was removed from the fuel. From the dependence of sulfur poisoning on the equilibrium partial pressure of S$_2$, we have reached the conclusion that the sulfur poisoning was governed by the total sulfur content in the fuel. In order to obtain further information for mechanism of the poisoning, an equivalent-circuit analysis of the impedance spectra has been conducted to divide the polarization resistance into charge-transfer resistance and mass-transfer resistance. It was found that H$_2$S even at low concentrations primarily disturbs the mass-transfer process, which includes surface diffusion and dissociative adsorption of active species.

INTRODUCTION

Fuel cells are highly efficient power generating systems with good adaptability to the environment. Among various types of fuel cells, solid oxide fuel cells (SOFCs) have distinguished advantages such as a high electric efficiency, high-quality exhaust heat and system compactness. High operating temperatures of SOFCs ranging from 873 K to 1273 K enable them to use a wide variety of fuels including natural gas. For natural gas fueled SOFCs, however, the effect of sulfur impurities must be taken into account and desulfurization has to be considered since several parts per million (ppm) of sulfur-containing impurities are usually added as odorant to natural gas distributed to customers by pipelines.

Among several types of SOFCs, electrolyte-supported cells using yttria-stabilized zirconia (YSZ) as the electrolyte have many material problems arising from the high...
operating temperature, typically around 1273 K. Reduction in operating temperature leads to many benefits including use of low-cost metallic separators instead of expensive ceramic ones, better long-term performance stability, and system compactness as a result of decreased thickness of heat insulators. Fundamental researches, therefore, have been carried out on manufacturing and testing the cells for reduced-temperature operation using electrode-supported cells with a thin YSZ electrolyte film on thick porous electrodes (1-4) as well as the electrolyte-supported cells in which the oxide-ion conductor of doped LaGaO₃ is used as the electrolyte (5-7).

Although many benefits are expected by reducing the operating temperature, it should be noted that at reduced temperatures, sulfur impurities may easily adsorb on the surface of a fuel electrode to degrade the electrochemical performance of the electrode. Of impurities in fuels, the sulfur-containing compounds, which are present primarily as hydrogen sulfide (H₂S) under the fuel electrode environment, are considered to have the greatest impact on SOFC performance (8).

In previous studies on the poisoning effect of sulfur, a direct-current polarization method and complex impedance analysis were used to evaluate cell performance loss, which showed that even low levels in ppm of H₂S may cause significant performance losses at the fuel electrode. Geyer et al. (9) reported that the polarization resistance of a cermet electrode increased by a factor of 2 by addition of only 5 ppm of H₂S at 1223 K in H₂ with 3% H₂O. If the H₂S content is low, however, the performance recovers upon removing the sulfur impurity from the fuel (10-12). As for the high levels of H₂S concentration, Dees et al. (13) reported that the polarization resistance increased by a factor of 2 by addition of 105 ppm H₂S at 1273 K in H₂ with 3% H₂O and the poisoning effect was irreversible. Several possible mechanisms may account for the decrease in the performance of the electrode due to the presence of H₂S in the fuel. The exact mechanism responsible for the performance loss, however, is not clearly defined because of a lack of detailed experimental data. In this study, we have investigated the time-constant of sulfur saturation and removal, and the dependence of the poisoning effect on the operating temperature, the sulfur contaminant concentration and the equilibrium partial pressure of S₂ produced in fuels containing H₂S. In addition, an equivalent circuit analysis of the impedance spectra has been conducted to divide the polarization resistance into charge-transfer resistance and mass-transfer resistance.

**EXPERIMENTAL**

**Test Cell Preparation**

Dense pellets (20 mm in diameter and 2 mm in thickness) of 8 mol% YSZ were used as the electrolytes for electrochemical cells. NiO powder with an average grain size of 0.9 μm (Nihon-Kagaku-Sangyo) was dispersed in a mixed toluene solution of zirconium octylate (Zr(C₄H₉CH₂CO₂)₄, 99% pure, Nihon-Kagaku-Sangyo) and yttrium octylate (Y(C₄H₉CH₂CO₂)₃, 99% pure, Nihon-Kagaku-Sangyo), the mixing ratio of which was adjusted to the ratio corresponding to the composition of 8 mol% Y₂O₃-92 mol% ZrO₂. The paste thus prepared was screen-printed onto one side of the electrolyte pellet, followed by firing at 1723 K for 7.2 ks to obtain a porous NiO-YSZ cermet electrode.
obtained after reduction of the NiO-YSZ composite were about 25 μm and 45 %, respectively. The YSZ content in the cermet electrode is 10 wt%. For a counter electrode, Pt paste (Tokuriki Kagaku 8103) was painted symmetrically to the Ni-YSZ cermet electrode on the other side of the pellet and fired at 1273 K for 7.2 ks. For a reference electrode, the Pt paste was painted at the perimeter of the pellet and fired at 1273 K for 7.2 ks.

**Electrochemical Measurement**

Figure 1 shows the test geometry used in the electrochemical measurements. Two Sr-doped LaCrO₃ plates with grooves were used as both manifolds and current collectors. Humidified H₂ fuel was fed into the doped LaCrO₃ plates from the top of a furnace and was supplied to the reference, counter and the Ni-YSZ cermet electrodes. H₂S was added to the fuel as the sulfur impurity at the concentration range from 0.02 to 15 ppm. Platinum wires were used as voltage terminals for the working and reference electrodes. The complex impedance measurements were made over the frequency range of 1 mHz-100 kHz with an applied amplitude of 10 mV using the three-terminal method at an equilibrium potential. The system for the impedance measurements was composed of a frequency response analyzer (Solartron 1260), a potentiostat (Solartron 1287) and a personal computer (Compac Armada 1120T). The measured spectra were fitted to the equivalent circuit by using the nonlinear least-square fitting software, EQUIVCRT, developed by Boukamp (15). In order to keep the electrode stable during the complex impedance measurements, the electrode was pretreated under a DC polarization at the current density of 0.3 Acm⁻² in the fuel without H₂S for 180 ks followed by annealing for 180 ks at the equilibrium potential at each temperature. The steady-state polarization was measured by a current interruption method using a current-pulse generator (Hokuto Denko HC-110). Also before the polarization measurements, pretreatment was conducted at a current density of 0.3 Acm⁻² in the fuel without H₂S for 180 ks.

**RESULTS AND DISCUSSION**

**Poisoning by Sulfur and Recovery at 1273 K**

Figure 2 shows the complex impedance spectra after full equilibration with the fuels with several concentrations of H₂S. Two arcs seemed to be overlapped in the impedance plots which show depressed semi-circles. As shown in this figure, the addition of H₂S did not change the size of impedance arcs at the concentration of 1 ppm, but increased the size of impedance arcs at 2 ppm and more. These results indicate that the Ni-YSZ cermet electrode was degraded by the sulfur impurity when the H₂S concentration, C(H₂S), exceeded 2 ppm at 1273 K. The steady-state impedance curves became larger with increase of C(H₂S), but no significant difference appeared in the shape of the curves over the whole C(H₂S) range. Figure 3 shows the change in the complex impedance spectrum with time at 1273 K; (a) and (b) are after addition and removal of 15 ppm H₂S, respectively. The impedance measurements were repeated consecutively until the spectra showed no change with time. The figure shows the two selected time-evolution of the impedance spectra. It is found that after the H₂S
addition the size of impedance arcs initially increased with and saturated at time between 3.6 and 4.8 ks. It is also found that after the H₂S removal the size of the impedance arcs decreased with time and recovered to original levels in about 3.6 ks. The complex impedance spectra of the electrode equilibrated in the fuel with 2-10 ppm H₂S were also found to recover to the original size and shape in about 3.6 ks after the H₂S removal. From these results it is concluded that 2-15 ppm H₂S impurity deteriorates the electrode at 1273 K, but this poisoning can be recovered if the H₂S-free fuel is supplied again.

Figure 4 shows the overvoltage (with IR) of the electrode as a function of time at the current density of 0.3 A cm⁻²; (a) and (b) show the overvoltage after H₂S was added to the fuel and H₂S was removed from the fuel, respectively. The overvoltage started to increase with time when H₂S was added to the fuel and saturated after a sufficient time; the steady-state overvoltage was larger than that in the H₂S-free fuel by about 2 mV at C(H₂S) of 2 ppm and 74 mV at C(H₂S) of 15 ppm. The degraded electrode performance fully recovered upon switching to the H₂S-free fuel. These results are consistent with the results in the polarization resistance evaluated by the complex impedance analysis.

**Temperature Dependence of Sulfur Poisoning**

Figures 5 (a) and (b) show the complex impedance spectra after equilibration in the fuels with different H₂S concentrations at 1173 and 1023 K, respectively. At 1173 K the impedance arcs increased when the C(H₂S) exceeded 0.5 ppm, which was lower than the critical concentration (2 ppm) at 1273 K. At 1073 K the impedance arcs began to increase at a much lower concentration of 0.05 ppm. These results suggest that reducing the operating temperature degrades the resistance of the electrode against the sulfur impurities to cause the poisoning at lower sulfur concentrations.

Figure 6 shows typical impedance spectra measured at 1173 K; (a) and (b) indicate the change of impedance spectra after addition and removal of 1 ppm H₂S, respectively. When the H₂S was added to the fuel, the size of the impedance arcs increased with time and saturated after approximately 9 ks which was longer than at 1273 K. When H₂S was removed from the fuel, the size of the impedance arcs decreased with time and finally recovered to its original level before the poisoning. However, a longer time, approximately 90 ks was needed for the recovery at 1173 K as compared with that at 1273 K, which became more remarkable at a lower temperature. At 1023 K, it took approximately 12 ks for the size of the impedance arcs to saturate after the H₂S addition and took approximately 360 ks for the recovery after removing H₂S.

Figure 7 shows the difference between the steady-state overvoltage in the fuel with the H₂S impurity and the initial overvoltage without H₂S impurity as a function of C(H₂S) and the operating temperature at the current density of 0.3 A cm⁻². The minimum concentrations of H₂S which caused the increase of the overvoltage showed good correspondence to those for the polarization resistance evaluated by the the complex impedance analysis, i.e., 2, 0.5 and 0.05 ppm at 1273, 1173 and 1023 K, respectively. Similar to the results in the complex impedance measurements, the increase in the overvoltage recovered at all temperatures when C(H₂S) returns to 0 ppm, i.e., the poisoning effect of sulfur on the overvoltage is also reversible.
over the concentration range studied. The degree of the poisoning caused by sulfur was thus found to have a large dependence on the operating temperature; the critical sulfur level for the performance loss is lower at lower operating temperatures, and at a selected sulfur concentration the overvoltage increases more at lower temperatures. Since it can be presumed that the sulfur impurity adsorbs more easily on the electrode as temperature decreases, these results suggest that an adsorbed impurity inhibits certain electrochemical processes at the interface between the fuel electrode and the electrolyte.

**Dependence on S\textsubscript{2}, Partial Pressure**

The partial pressure of S\textsubscript{2}, P(S\textsubscript{2}), in the fuel is determined by the following equilibrium reaction as a function of H\textsubscript{2} partial pressure, P(H\textsubscript{2}), C(H\textsubscript{2}S) and temperature.

\[
2\text{H}_2\text{S} = 2\text{H}_2 + \text{S}_2 \quad [1]
\]

Since P(H\textsubscript{2}) in the fuel is determined by the following equilibrium reaction as a function of the partial pressure of H\textsubscript{2}O, P(H\textsubscript{2}O), and the partial pressure of oxygen, P(S\textsubscript{2}) is also a function of these partial pressures.

\[
2\text{H}_2\text{O} = 2\text{H}_2 + \text{O}_2 \quad [2]
\]

To discuss the influence of P(S\textsubscript{2}) on the sulfur poisoning of the electrode, we measured the steady-state polarization as a function of P(S\textsubscript{2}) which was controlled by changing P(H\textsubscript{2}O) with constant C(H\textsubscript{2}S) or by changing C(H\textsubscript{2}S) with constant P(H\textsubscript{2}O). Figure 8 shows the increase of the overvoltage, \( \Delta V \), by the poisoning as a function of P(S\textsubscript{2}) at a current density of 0.3 A cm\textsuperscript{-2}. The closed circles indicate plots with constant P(H\textsubscript{2}O) of 21\% at all temperatures. With the constant P(H\textsubscript{2}O), \( \Delta V \) increased with P(S\textsubscript{2}), which can be attributed to the increase of P(S\textsubscript{2}) or C(H\textsubscript{2}S). There is no previous study in which the effect of C(H\textsubscript{2}S) on fuel electrodes is separated to that of P(S\textsubscript{2}) to identify the dominant factor of sulfur-poisoning. \( \Delta V \) was, therefore, measured with constant C(H\textsubscript{2}S) in order to separate the influence of C(H\textsubscript{2}S). The open circles indicate plots with constant C(H\textsubscript{2}S). The values of C(H\textsubscript{2}S) in the constant C(H\textsubscript{2}S) conditions at 1023, 1173 and 1273 K were 0.05, 0.5 and 4 ppm, respectively. It can be seen that the P(S\textsubscript{2}) dependence of \( \Delta V \) in the fuel with constant C(H\textsubscript{2}S) is different from that in the fuel with constant P(H\textsubscript{2}O) at all temperatures. With the constant C(H\textsubscript{2}S), \( \Delta V \) showed only negligible dependence on P(S\textsubscript{2}). These results indicate that a factor dominating the poisoning by the sulfur impurity is not P(S\textsubscript{2}) but the total sulfur content in the fuel. In order to obtain further information for investigation of the mechanism of the poisoning, an equivalent circuit analysis of the impedance spectra has been conducted.

**Equivalent-Circuit Analysis**

The equivalent-circuit analysis was applied to the complex-impedance spectra measured in the fuels with several concentrations of H\textsubscript{2}S at 1023-1273 K to divide the
polarization resistance into the charge-transfer resistance \( (R_e) \) and the mass-transfer resistance \( (R_d) \) which includes surface diffusion and dissociative adsorption of active species. Details of the equivalent-circuit analysis technique have been published elsewhere (16). Figure 9 shows the results of the equivalent-circuit analysis; (a), (b) and (c) indicate \( R_e, R_d, \) and an ohmic resistance \( (R_b) \), respectively, after equilibration in the fuels at 1023 K-1273 K. The influence of the sulfur impurity on the resistances became larger at lower temperatures. Of all the resistances \( R_b \) was most insensitive to the sulfur impurity at all temperatures. It should be noted that at 1173 K and 1273 K the low concentration of \( \text{H}_2\text{S} \) increased \( R_d \) selectively. Figure 10 shows the change of the resistances with time at 1273 K after addition and removal of 4 ppm \( \text{H}_2\text{S} \). Under this condition, \( R_e \) and \( R_b \) remained constant, but \( R_d \) changed with time. These results clearly show that under mild conditions for the sulfur poisoning, i.e. high temperatures and low \( \text{H}_2\text{S} \) concentrations, the sulfur impurity mainly interferes the mass-transfer process which includes surface diffusion and dissociative adsorption of active species.

CONCLUSIONS

The influence of the sulfur impurity on the electrochemical properties of the fuel electrode has been investigated at 1023-1273 K in a gas mixture of \( \text{H}_2 \) and \( \text{H}_2\text{O} \) by using the complex impedance analysis and the DC polarization method. The main results are as follows:

1. The polarization impedance and the DC overvoltage of the electrode increased when \( \text{H}_2\text{S} \) concentration exceeded 0.05, 0.5, and 2 ppm at 1023, 1173 and 1273 K, respectively.

2. The time needed for the influence of the sulfide impurity to saturate was almost independent of the sulfur concentration, and was found to be about 12, 9 and 4 ks at 1023, 1173 and 1273 K, respectively.

3. Within the experimental conditions, the performance loss caused by the sulfur-poisoning was recoverable when \( \text{H}_2\text{S} \) was removed from the fuel; the time needed for the recovery was found to be 360, 90 and 4 ks at 1023, 1173 and 1273 K, respectively.

4. From the dependence of sulfur poisoning on the equilibrium partial pressure of \( \text{S}_2 \), it was found that the sulfur poisoning was governed by the total sulfur content in the fuel.

5. From the equivalent circuit analysis of the impedance spectra, the influences of the sulfur impurity on the charge-transfer resistance, mass-transfer resistance and ohmic resistance were found to be different from one another.

6. At 1173 and 1273 K, the low concentration of \( \text{H}_2\text{S} \) disturbed mass-transfer process selectively, which includes surface diffusion and dissociative adsorption of active species.

REFERENCES

(1) N.Q. Minh, J. Am. Ceram. Soc. 76, 563 (1993).  
(2) S. De Souza, S.J. Visco and L. C. De Jonghe, Solid State Ionics 98, 57 (1997).  
(3) J.W. Kim, A. V. Virkar, K.Z. Fung, K. Mehta and S.C. Singhal, J. Electrochem. Soc. 146, 69 (1999).  
(4) K. Ogasawara, I. Yasuda, Y. Matsuzaki, T. Ogivara and M. Hishinuma, in Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells
(SOFC-V), U. Stimming, S.C. Singhal, H. Tagawa, and W. Lehnert, Editors, PV 97-40, p.143, The Electrochemical Society Proceedings Series, Pennington, NJ (1997).

(5) T. Ishihara, H. Matsuda, M. Azmi and Y. Takita, *Solid State Ionics* **86-88**, 197 (1995).

(6) K. Huang, R.S. Tichy, J. B. Goodenough and C. Milliken, *J. Am. Ceram. Soc.* **81**, 2581 (1998).

(7) I. Yasuda, Y. Matuzakai, T. Yamakawa and T. Koyama, *Solid State Ionics*, **135**, 381 (2000.)

(8) N. Q. Minh, and T. Takahashi, Science and Technology of Ceramic Fuel Cells, Elsevier, Amsterdam, pp. 209-210, 1995.

(9) J. Geyer, H. Kohlmueller, H. Landes, and R. Stubner, in *Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells (SOFC-V)*, U. Stimming, S.C. Singhal, H. Tagawa, and W. Lehnert, Editors, PV 97-40, p.585, The Electrochemical Society Proceedings Series, Pennington, NJ (1997).

(10) S. C. Singhal, R. J. Ruka, J. E. Bauerle, and C. J. Spengler, Anode Development for Solid Oxide Fuel Cells, Report No. DOE/MC/22046-2371, U.S. Department of Energy, Washington, DC, 1986.

(11) D. Stolfen, R. Spah and R. Schamm, in *Proceedings of the 5th International Symposium on Solid Oxide Fuel Cells (SOFC-V)*, U. Stimming, S.C. Singhal, H. Tagawa, and W. Lennert, Editors, PV 97-40, p. 88, The Electrochemical Society Proceedings Series, Pennington, NJ (1997).

(12) P. Primdahl and M. Mogensen, in *Proceedings of the 6th International Symposium on Solid Oxide Fuel Cells (SOFC-VI)*, S.C. Singhal and M. Dokiya, Editors, PV 99-19, p.530, The Electrochemical Society Proceedings Series, Pennington, NJ (1999).

(13) D. W. Dees, U. Balachandran, S. E. Dorris, J. J. Heiberger, C. C. McPheeter and J. J. Picciolo, in *Proceedings of the 1st International Symposium on Solid Oxide Fuel Cells (SOFC-I)*, S.C. Singhal, Editor, PV 89-11, p. 317, The Electrochemical Society Proceedings Series, Pennington, NJ (1989).

(14) Y. Matuzakai, M. Hishinuma, T. Kawashima, I. Yasuda, T. Koyama and T. Hikita, in Program and Abstracts of 1992 Fuel Cell Seminar, P. 119 (1992).

(15) B. A. Boukamp, *Solid State Ionics* **20**, 31 (1986).

(16) Y. Matuzakai and I. Yasuda, *J. Electrochem. Soc.* **147**, 1630 (2000).
Fig. 1. Test geometry used in the electrochemical measurements. A: working electrode, B: reference electrode (Pt), C: counter electrode (Pt), D: YSZ pellet, E: Pt mesh for current collection, F: doped LaCrO$_3$ plate for current collection and manifold, G: Al$_2$O$_3$ plate for manifold, H: pushrod.

Fig. 2. The complex impedance spectra measured after equilibration in the fuels with several concentrations of H$_2$S at 1273 K.

Fig. 3. The change of the complex impedance spectra at 1273 K after (a) addition and (b) removal of H$_2$S.
Fig. 4. The overvoltage (with IR) of the electrode as a function of time at a current density of 0.3 Acm\(^2\) after (a) addition and (b) removal of H\(_2\)S.

Fig. 5. The complex impedance spectra measured after equilibration in the fuels with several concentrations of H\(_2\)S at (a) 1173 K and (b) 1023 K.
Fig. 6. Typical complex impedance spectra measured at 1173 K after (a) addition and (b) removal of 1 ppm H₂S.

Fig. 7. The difference between the steady-state overvoltage in the fuel with H₂S and the initial overvoltage in the H₂S-free fuel as a function of C(H₂S) at the current density of 0.3 A cm⁻².

Fig. 8. The increase of the overvoltage as a function of P(S₂); the open and closed circles indicate plots with constant C(H₂S) and with constant P(H₂O), respectively. The values of the constant C(H₂S) are 0.05, 0.5, and 4 ppm for 1023, 1173 and 1273 K, respectively, and the value of the constant P(H₂O) is 21% at all temperatures.
Fig. 10. Change of the resistances with time at 1273 K after addition and removal of 4 ppm H₂S.

Fig. 9. Resistance components after equilibration in the fuels at 1023 K-1273 K; (a), (b) and (c) indicate Re, Rd and Rb, respectively.

Electrochemical Society Proceedings Volume 2001-16
