ABSTRACT

Power generation characteristics of SOFC with internal steam reforming of methane were investigated. Supply of pre-reforming gas to the anode always gave rise to lower generation characteristics than that of post-reforming gas. Although H2-H2O and CO-CO2 fuel systems led to almost the same open circuit voltage at the same reductant / oxidant ratio, the output voltage during power generation was always higher for the H2-H2O at every current density. Response of partial pressure of fuels (H2 or CO) in Ni-YSZ porous electrode was measured by using fuel electrode supported SOFC and oxygen sensor. The diffusion rates of the fuels influenced the concentration of the fuel in the pores of the Ni-YSZ anode. This indicates that the concentration overvoltage controlled by the diffusion process of fuel gases in the electrode pores significantly affects the overall electrode reaction at the triple phase boundary. Response to partial pressure change was faster for the H2-H2O fuel than for the CO-CO2 fuel.

INTRODUCTION

One of the advantages of SOFC system is its fuel flexibility, especially possibility of internal reforming of methane and other hydrocarbons during power generation. During internal reforming of methane, for example, the fuel electrode was exposed to gaseous mixtures of CH4, H2, H2O, CO, and CO2. The reactivity of these gas species and diffusion in the micropores are of significant importance in determining the cell performance (1). The reactivity of CO and H2 has been previously discussed. Dominant contribution of concentration overvoltage has been stressed for the H2-H2O mixture in both extremely concentrated and dilute fuel conditions. We have previously reported basic behavior of internal reforming methane for SOFC (2). Carbon deposition is one of the factors deteriorating the power generation characteristics. For the internal reforming of methane, not only the reactivity of H2 and CO at the triple phase boundary of the electrode-electrolyte-gas phase, but also the reforming reaction and gas diffusion in the pores of the Ni-YSZ electrode to the triple phase boundary are expected to influence the reaction rate. Ni-YSZ cermet is generally used as electrode and reforming catalyst. The purpose of the present study is to analyze the reactivity of gas species in the reformate in relation to the gas diffusion in pores. The influence of the gas species was analyzed from power generation characteristics and transient response.
EXPERIMENTAL

A planar cell was prepared by the slip casting process. The Ni-YSZ cermet electrode was prepared by mixing Ni (80wt%) and YSZ (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 have been described previously (3).

Tubular fuel cells were prepared on electrode substrate by the wet processing procedure as reported previously (3). A Ni-YSZ cermet tube, which was prepared by slip casting of a NiO and YSZ (weight ratio = 4:6) powder mixture, was supplied by Saibu Gas Co., Ltd. and Totsu Co., Ltd. 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 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 internal and external reforming type fuel cell operation was carried out by the system illustrated in Fig 1. A fixed bed catalytic reactor for steam reforming of methane was connected at the upstream of the cell. Two three-way valve enabled supply of pre- and post-reforming gas to the fuel cell. The effect of reforming was investigated by comparing the power generation characteristics.

The tubular cell was used to analyze the response of the cell and the gas supply through porous electrode. A zirconia oxygen sensor was located close to the cell to detect the change in gas composition. With a change in gas composition, the oxygen sensor detected the gas phase change in composition as a rapid change in output voltage, whereas the fuel cell responded slowly after a short induction period due to diffusion of gas in the pore of the electrode. Thus the effect of diffusion of gas in the pore of the electrode was analyzed.

RESULTS AND DISCUSSION

Internal Reforming Type SOFC

SOFC tests with internal reforming of methane were carried out as shown in Fig. 3. In every experiment, the ratio H2O / CH4 (S/C ratio) was fixed at 3, whereas the concentration of the CH4 and H2O was varied by diluting with N2. Since the S/C ratio was equal in every condition the equilibrium partial pressure of oxygen in the mixture was the same, but the measured open circuit voltage was lower as the fuel gas mixture was diluted. This means that the gas mixture was not in equilibrium for the dilute gas mixture condition. Because the electrode Ni-YSZ layer is only about 100 mm thick, the contact time is insufficient for the
complete conversion of CH$_4$ into the equilibrium state. Especially, in a dilute fuel mixture, the conversion to H$_2$ is low because of the low concentrations of both reactants. This result indicates that the H$_2$ / H$_2$O ratio in the vicinity of the triple phase boundary is lower than the equilibrium as the fuel mixture concentration is lowered. This also implies that methane molecules are not directly participating in the electrode reaction, but H$_2$ or CO molecules formed in the reformate determine the open circuit voltage. The current derived from the concentrated mixture was higher than with the dilute fuel.

External and internal reforming was investigated by supplying pre- and post-reformed gas to the cell. It was confirmed that the catalytic reformer completely converted CH$_4$-H$_2$O mixture to the equilibrium gas mixture. The V-I characteristics of the SOFC supplied with pre- and post-reformed gas are compared in Fig. 4. The open circuit voltage for the post-reformed gas was equal to that expected from the equilibrium. The open circuit voltage of SOFC supplied with pre-reformed gas was always lower than that with of the post-reformed gas. The voltage drop with increasing current was also steeper for case of the pre-reformed gas. This also implies that the electrode layer is insufficient to convert CH$_4$ completely, thus the amount of H$_2$ is apt to be deficient as compared with the equilibrated gas after reforming.

**Reactivity of H$_2$-H$_2$O and CO-CO$_2$**

The reformate gas in the equilibrium case is obviously the mixture of H$_2$, H$_2$O, CO and CO$_2$. The reactivity of H$_2$ and CO for the electrode reaction has been sometimes discussed. To clarify the effect of gas species, the power generation characteristics were obtained for CO-CO$_2$ mixture and H$_2$-H$_2$O mixture. A single planar cell was used and supplied with H$_2$-H$_2$O or CO-CO$_2$ with various mixing ratios as shown in Fig. 5. At 1273K, the both mixtures gave almost similar oxygen potential when the mixing ratio of CO/CO$_2$ and H$_2$ / H$_2$O was the same. Thus, the oxygen partial pressure of both mixtures is almost equal to each other when H$_2$ /H$_2$O = CO/ CO$_2$. The power generation characteristics were obtained for the same single cell supplied with different fuel compositions. The open circuit voltage of the cell was almost the same, when the same ratio of H$_2$ /H$_2$O and CO/ CO$_2$ was supplied to the anode as is expected from the equilibrium. The slope of the power generation characteristics, however, was obviously different for two fuel systems. The H$_2$ fuel gave higher voltage than CO at every composition of fuel and every current density. This means that hydrogen is preferentially consumed by the electrode reaction. This tendency is quite important from the viewpoint of internal reforming where four of these components are simultaneously included. The possible reactivity difference is the reactivity of H$_2$ and CO, whereas the diffusivity of the two component is also different.

The concentration overvoltage was also analyzed according to the method described in the previous report. The reactivity of the gas, and therefore the activation overvoltage was neglected in this analysis. From the limiting current observed, the effective diffusion constant was estimated. The curves in Fig. 6 are simulated curves for the concentration overvoltage. The observed anodic polarization roughly agreed with the above mentioned concentration overvoltage, indicating slow diffusion of CO in CO-CO$_2$ mixture significantly contributes to the anodic polarization.

**Transient Response to Fuel Gas Composition**

The anodic concentration overvoltage was evaluated using transient response of the fuel cell. The anode support tube possesses about 40% porosity. The average pore size determined by the mercury porosimeter was 30 nm. Thus, the bulk and Knudsen diffusion
mechanisms were operative. After supply of gas mixture at a given composition, the gaseous mixture with another gas composition was abruptly supplied to the cell in Fig. 2. Then, the zirconia oxygen sensor set next to the cell first responded to detect the oxygen concentration change. The response of anode supported tube was slow due to the diffusion in micropores. The sharp response of the sensor was regarded as time, \( t = 0 \) at which gaseous mixture arrived at the cell. Then the response of oxygen sensor sharply increased to the emf value expected from the new mixing ratio, whereas the response of the fuel cell was sluggish with an induction period. This corresponds to the gas diffusion in the micropores of the porous electrode. The increase of the fuel cell voltage was slower than the oxygen sensor voltage but the final voltage value should be equal to that of the oxygen sensor and that expected from the Nernst equation. The voltage response was converted into the concentration change as shown in Fig. 7. When the gaseous mixture reaches the triple phase boundary, the voltage gradually changes but the voltage change is still slower than for the oxygen sensor. This implies that the diffusion rate of the gaseous mixture influences the response of a change in atmosphere. The response curve for the \( \text{H}_2 \) fuel with different \( \text{H}_2 \) ratios is shown in Fig. 7. The cell was initially exposed to 0.7\% \( \text{H}_2 + 3\% \text{H}_2\text{O} \) (\( \text{N}_2 \) balance). Then the \( \text{H}_2 \) content was suddenly switched to 97\%, 66\%, 33\%, and 7\%, whereas the concentration of \( \text{H}_2\text{O} \) was kept unchanged. The concentration of \( \text{H}_2 \) increased after induction period of ca. 6 sec, then gradually increased with elapsed time. The final concentration depended on the fed \( \text{H}_2 \) concentration.

The response of the fuel cell was also measured at different current densities as shown in Fig. 8. Although the supplied concentration of \( \text{H}_2 \) was same in every run, the increase was more gradual as the current density increased. If the complete mixing in the gas phase was achieved, the increase in partial pressure of \( \text{H}_2 \) should be rapid and same for every current density condition. Therefore, this result indicates that the diffusion in the micropores to the triple phase boundary significantly affects the rate of the electrode reaction.

Three gas mixtures, i.e., \( \text{H}_2-\text{H}_2\text{O}, \text{N}_2-\text{H}_2, \) and \( \text{CO-CO}_2 \), were supplied initially at \( t < 0 \); then the gas was switched to \( \text{H}_2-\text{H}_2\text{O} \) mixture with a high \( \text{H}_2 \) concentration at \( t = 0 \) (Fig. 9). The rate of response was different for the three conditions. The response rate was fastest for initial gas supply of \( \text{H}_2-\text{H}_2\text{O} \). The sequence of the response appears to reflect the diffusion rate of the gas mixture and adsorption of these gases on the catalyst surface.

The response curve of the fuel cell was compared for the gas mixtures of \( \text{CO-CO}_2 \) and \( \text{H}_2-\text{H}_2\text{O} \) (Fig. 10). The response curve was obviously different for these two gas mixtures. The response of \( \text{H}_2-\text{H}_2\text{O} \) was obviously faster than that of \( \text{CO-CO}_2 \). This difference is thought to be due to difference in diffusion rate of the gas mixtures. This implies that, even when the reactivity of \( \text{CO} \) and \( \text{H}_2 \) is the same, the concentration overvoltage is larger for the \( \text{CO} \)-based fuel than for the \( \text{H}_2 \)-based fuel.

REFERENCES
1. K. Eguchi, Y. Kunisa, K. Adachi and H. Arai, Journal of the Electrochemical Society, 143, No.11, November (1996).
2. K. Eguchi, Y. Kunisa, M. Kayano, K. Sekizawa, S. Yano and H. Arai, Denki Kagaku, 64(6), 596-601 (1996).
3. K. Eguchi, M. Kayano, K. Kunisa and H. Arai, in Solid Oxide Fuel Cells IV, M. Dokiya, O. Yamamoto, H. Tagawa and S. C. Singhal, Editors, PV95-1, P. 676, The Electrochemical Society Proceedings Series, Pennington, NJ (1995).
Fig.1. Schematic view of experimental apparatus for SOFC with reforming reaction vessel.

Fig.2. Schematic cross section of setup for measurement of response of fuel cell.
Fig. 3. Influence of CH₄ and H₂O concentration on I-V characteristics at 1273K.
Cell: CH₄-H₂O, Ni-YSZ / YSZ / La₀.₆Sr₀.₄MnO₃, O₂
Flow rate of fuel gas: 150ml/min, H₂O/CH₄=3, N₂ balance.

Fig. 4. Influence of CH₄ concentration on I-V characteristics with external or internal reforming of CH₄ at 1273K.
Cell: CH₄-H₂O, Ni-YSZ / YSZ / La₀.₆Sr₀.₄MnO₃, O₂
Flow rate of fuel gas: 100ml/min, H₂O=30ml/min, N₂ balance.
Fig. 5. Influence of the kind and concentration of fuel on I-V characteristics at 1273K.
Cell: CH$_4$-H$_2$O, Ni-YSZ / YSZ / La$_{0.6}$Sr$_{0.4}$MnO$_3$, O$_2$.
Flow rate of fuel gas: 150ml/min, H$_2$O: 0.6%, CO$_2$: 0.5%, N$_2$ balance.

Fig. 6. Comparison of the estimated anodic concentration overvoltage and the anodic polarization at 1273K.
Cell: CH$_4$-H$_2$O, Ni-YSZ / YSZ / La$_{0.6}$Sr$_{0.4}$MnO$_3$, O$_2$.
Flow rate of fuel gas: 150ml/min, H$_2$O: 0.6%, CO$_2$: 0.5%, N$_2$ balance.
Solid line: Anodic concentration overvoltage estimated by calculation.
Plot: Anodic polarization observed by current interruption method.
Fig. 7. Time course of partial pressure of H$_2$ with an abrupt change in $P_{\text{H}_2}$ at $t \geq 0$ into various concentrations of H$_2$ at 1273K. Cell: H$_2$-H$_2$O,Ni-YSZ/YSZ/La$_{0.6}$Sr$_{0.4}$MnO$_3$, O$_2$. Flow rate of fuel gas: 150 ml min$^{-1}$, H$_2$O: 3%, N$_2$ balance.

Fig. 8. Time course of partial pressure of H$_2$ with an abrupt change in $P_{\text{H}_2}$ under different current flow at 1273K. Fuel electrode was exposed at $t \geq 0$ to H$_2$ (97%)-H$_2$O (3%) (N$_2$ balance).
Fig. 9. Time course of partial pressure of H₂ with an abrupt change in $P_{\text{H}_2}$ at 1273K. Fuel electrode was exposed at $t < 0$ to H₂ (0.7%)-H₂O(3%), N₂100%, or CO(0.7%)-CO₂(3%) and at $t \geq 0$ to H₂ (97%)-H₂O (3%) (N₂ balance).

Fig. 10. Time course of partial pressure of H₂ or CO with an abrupt change in $P_{\text{H}_2}$ or $P_{\text{CO}}$ at 1373K. Fuel electrode was exposed at $t \geq 0$ to H₂ (97% or 67%)-H₂O (3%) or CO (97% or 67%)-CO₂ (3%)(N₂ balance).