An Effect of Anodic Reaction on the Current-Voltage Characteristics of Solid Oxide Fuel Cells

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The anodic concentration overvoltage was dominant in the low current density region when high concentration of CH_4 or H_2 was supplied to a Ni-YSZ anode of a solid oxide fuel cell. For a dilute fuel condition, the concentration overvoltage was small at low current densities, but a limiting current appeared due to depletion of fuel at high current densities. In extremely high P_{O_2} region, the anodic polarization became large due to surface oxidation of Ni metal particles.

Solid oxide fuel cells, SOFC, have been actively investigated as an efficient power generation system for the future application. The electrode materials as well as a solid electrolyte have to be developed to derive sufficient power from the single cell. Ni-zirconia cermet has been most popularly employed as a fuel electrode material, because of the high activity for internal reforming of methane. The relation between the anodic electrochemical reaction, generation characteristics, and reforming reaction has not sufficiently investigated. Several kinetic studies on anodic reaction have been done at the open circuit condition using H_2 as a fuel.[1,2] Iwahara et al. [3] stressed a dominant contribution of concentration overvoltage for fuel cell operation in H_2-H_2O atmosphere. The present investigation deals with the effect of the anodic reaction and internal reforming on the power generation experiment.

The Ni- $(ZrO_2)_{0.85}(YO_{1.5})_{0.15}$ (YSZ) cermet anode was prepared by mixing of NiO and YSZ and heating in air at 1400°C. For preparation of a planar cell, the powder mixture of NiO and YSZ (weight ratio = 4:1) was coated on a YSZ pellet (500 µm thick and 18 mm in diameter) and heated at 1100°C prior to reduction with H_2 at 1000°C.[4] In every case, $La_{0.6}Sr_{0.4}MnO_3$ (abbreviated as LSM) was used as a counter electrode and a Pt reference electrode was attached on the YSZ electrolyte. Tubular fuel cells were prepared on a NiO-YSZ (weight ratio = 2:3) substrate by the wet processing procedure as reported previously.[5] 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 SOFC were measured by using a conventional flow system using the following cell components as reported previously:[4]

$$H_2\text{-}H_2O \text{ (or } CH_4\text{-}H_2O\text{)}, \text{ Ni-YSZ / YSZ / LSM, } O_2 \qquad (1)$$

A gaseous mixture of H_2-H_2O or CH_4-H_2O was supplied to the fuel electrode and pure oxygen or air was supplied to the counter electrode. A polarization conductivity of the anode was obtained from the AC impedance analysis (amplitude = 7 mV). Although both tubular and planar cells were tested, the dependence of V-I curve and polarization conductivity on the fuel composition was qualitatively similar to each other.

The effect of CH_4 concentration on the V-I characteristics of the tubular solid oxide fuel cell was measured at a fixed H_2O concentration (25%) and overall flow rate (200 cm³/min) as shown in Fig. 1. High concentration of CH_4 resulted in high open circuit voltage because of the low oxygen partial pressure in the fuel. The shape of the curve also changed systematically with the CH_4 concentration. The curve with high CH_4 concentration is characterized by a significant concave bending in a small current density region followed by a linear decrease in voltage with increasing current density. The curve for low fuel concentration started from a straight decrease and subsequent sharp drop in voltage in high current density region. This sharp voltage drop has known as limiting current due to depletion of the fuel in the mixture. The polarization resistance tended to increase as the concentration of the CH_4 increased.[4]

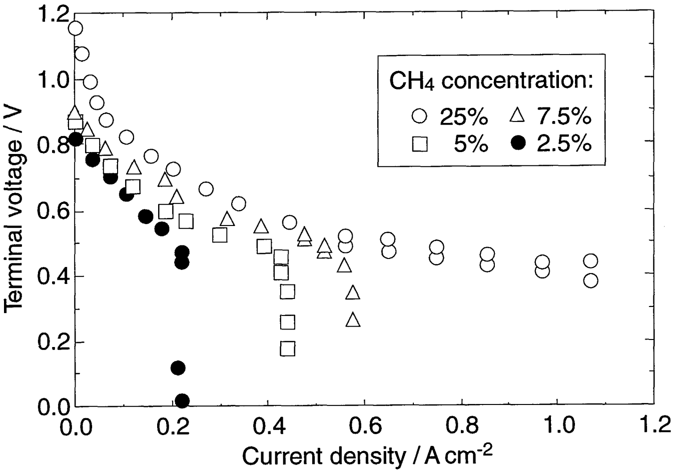

Figure 1. Influence of CH_4 concentration on I-V characteristics at 1273K. Fuel: CH_4-H_2O, Oxidant: Air
Flow rate of fuel gas: 200 cm^3 min^{-1}, H_2O concentration: 25%

To analyze the V-I characteristics, it is important to evaluate the equilibrium partial pressure of oxygen in the fuel gas mixtures. The partial pressure of oxygen (P_{O_2}) in the H_2-H_2O system can be given from the thermodynamic data of the combustion of hydrogen;[6] $H_2 + 1/2\ O_2 \rightarrow H_2O$. Similarly, the partial pressure of oxygen in the CO-CO_2 system can be obtained from the equilibrium of $CO + 1/2\ O_2 \rightarrow CO_2$. As for the CH_4-H_2O system, the gas phase composition after reaction of steam and methane is determined by equilibria of steam reforming and shift reactions;

$$CH_4 + H_2O \rightarrow 3\ H_2 + CO \qquad (2)$$
$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (3)$$

From the thermodynamic data, the equilibrium composition of gaseous mixture containing CH_4, H_2, H_2O, CO, and CO_2 could be obtained.[6] The equilibrium partial pressure of oxygen can be estimated from the ratios of H_2/H_2O and CO/CO_2 in the gaseous mixture. These P_{O_2} values calculated from two gaseous ratios agreed with each other. In other words, the shift reaction connects the

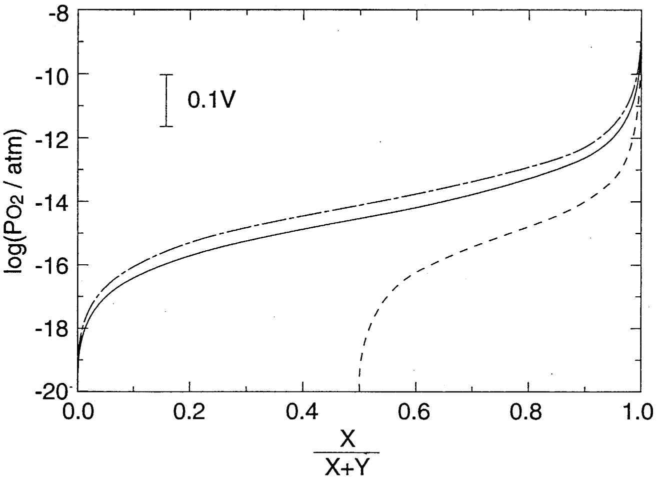

Figure 2. Plots of log(P_{O_2}) vs. fractional concentration of fuel gas at 1273K.
—·—·— X=[CO_2], Y=[CO]
——— X=[H_2O], Y=[H_2]
- - - - - - - X=[H_2O], Y=[CH_4]

equilibria of H_2-H_2O and CO-CO_2 until an unique P_{O_2} value is attained. The equilibrium P_{O_2} estimated from these thermodynamic calculation is shown in Fig. 2 as a function of the reactant gas fraction. In this calculation, the total pressures of the gaseous mixtures were fixed at 1 atm. The three curves are characterized by a steep change in log P_{O_2} in the both ends of the curves and the gradual slope in the intermediate concentration region. It is expected that a small concentration change in the reactant mixture gives rise to orders of P_{O_2} change in the fuel rich region. This means that, in the very concentrated fuel, even a small current passage significantly enhance the P_{O_2} in the vicinity of the triple phase boundary. In the case of the CH_4-H_2O system, for example, a small current and resultant evolution of H_2O and CO_2 lead to large P_{O_2} difference between the triple phase boundary and the flowing gas mixture. Thus, the concentration overvoltage significantly appears in the low current density region of the CH_4-rich condition. On the other hand, the initial power generation was shown by straight line in the low fuel concentration but the limiting current appeared in high current density region due to the depletion of the fuel. The dependence of log P_{O_2} on H_2 concentration was basically the same as in the case of the CH_4-H_2O system. The dominant concentration overvoltage in the discharging condition has been already confirmed by Iwahara et al. [3] by measuring the potential difference between the anode and a supplied gas with a needle-shaped sensor.

The dependence of electrode polarization conductivity, σ_a, which is the inverse of the polarization resistance, was measured for the planar cell as a function of partial pressure of oxygen in the H_2 -H_2O system (Fig. 3). The electrode conductivity showed a maximum at about $P_{O_2}= 10^{-8}$ Pa, while the anodic electrode conductivity decreased either with increasing or decreasing P_{O_2}. The decrease in the higher P_{O_2} region appears to be attributed to the surface oxidation Ni. As the operating P_{O_2} approaches to that for oxidation of bulk Ni (broken line in Fig. 3), the surface is covered with an oxide or hydroxide layer, which is less active for the electrochemical reaction than the metallic surface. On the other hand,

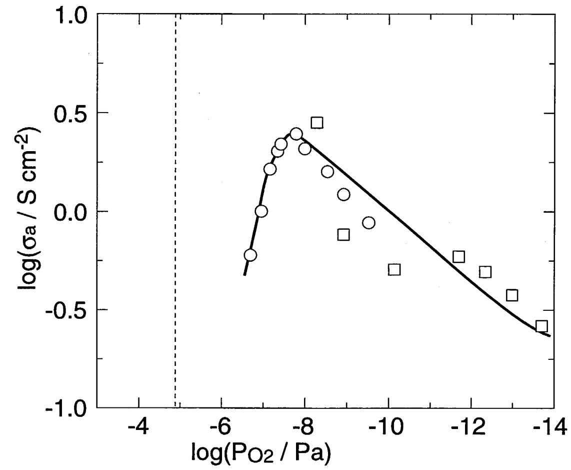

Figure 3. Dependence of polarization conductivity, σ_a on P_{O_2} in the anode atmosphere of the fuel cell at 1273K.
Fuel: ○ H_2-H_2O(present study), Oxidant: O_2 (P_{O_2}=1.01×10^5 Pa); Flow rate of fuel gas: 150 ml min^{-1}, H_2 concentration: 3.3%
-------- P_{O_2} of equilibrium: Ni + 1/2O_2 ⇔ NiO
□ σ_a in H_2-H_2O from ref. 4.

the decrease in polarization conductivity in the low P_{O_2} region was similarly observed for other fuel systems, as has been also reported for the CO-CO_2, and CH_4-H_2O systems.[4] Although it is possible to explain this dependency by the activation polarization, the concentration polarization appears to be most likely explanation. As P_{O_2} is lowered, the difference in P_{O_2} between the triple phase boundary and gas flowing at outer surface is significant even with a small current passage. This situation at low P_{O_2} corresponds to large voltage drop in the small current density region of Fig. 1 and the small polarization conductivity in Fig. 3. The effect of concentration overvoltage may be minimized by using the thin film patterned electrode employed by Mizusaki et al.[1] However, for the practical electrode, the mass transfer in the pores will cause the concentration overvoltage in the fuel rich condition.

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