ELECTROCHEMICAL OXIDATION OF CH₄ AT THE INTERFACE OF Pt ELECTRODE AND Y₂O₃-STABILIZED ZrO₂ ELECTROLYTE

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ABSTRACT

In order to elucidate the electrochemical reaction of CH₄-H₂O at the interface of a porous Pt electrode / Y₂O₃-stabilized ZrO₂ electrolyte, measurements were made on the gas composition before and after the reaction under direct current polarization. H₂ and C were found to be generated by decomposition of CH₄ at the open circuit condition in a dry CH₄ system. H₂ and CO were generated by the steam reforming in a CH₄-H₂O system. The polarization current was interpreted by electrochemical oxidation of CH₄, H₂, C and CO in a dry CH₄ system and oxidation of H₂ in a CH₄-H₂O system. The rate of each electrochemical oxidation was calculated from the mass balance.

INTRODUCTION

Among various types of fuel cells, solid oxide fuel cell (SOFC) is expected to be the most promising energy conversion system for utilizing fossil fuel resources. One of the advantages of SOFC is its high operation temperature which enables to feed variety of fuel gases without external reforming reactors. In order to design the internal reforming SOFC system, it is necessary to understand the kinetics of electrochemical oxidation of hydrocarbon fuels. This is, however, a difficult task because many chemical and electrochemical reactions are involved simultaneously even if the simplest hydrocarbon, CH₄, is used as the fuel.

When CH₄ is fed together with H₂O, steam reforming reaction occurs:

\[ \text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2 \]  \[1\]

It can be rewritten as the combination of the thermal decomposition of methane and the reaction of the deposited carbon with H₂O

\[ \text{CH}_4 = \text{C} + 2\text{H}_2 \]  \[2\]
\[ \text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2 \]  \[3\]

The amount of CO, CO₂, H₂ and H₂O are variable via shift reaction:

\[ \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \]  \[4\]
Under the existence of CO₂, the following reaction may take place

\[ C + CO_2 = 2CO \]  

[5].

The reforming reaction may occur also with CO₂ as follows

\[ CH_4 + CO_2 = 2CO + 2H_2 \]  

[6].

When the eqs. [4] and [6] occur in series, it gives the same result as the reaction [1].

The possible electrochemical reactions in the anodic direction are listed below

\[ C + O^2- \rightarrow CO + 2e^- \]  

[7]

\[ CO + O^2- \rightarrow CO_2 + 2e^- \]  

[8]

\[ CH_4 + O^2- \rightarrow CO + 2H_2 + 2e^- \]  

[9]

\[ H_2 + O^2- \rightarrow H_2O + 2e^- \]  

[10]

The first step in understanding the kinetics is to make clear what kind of species are reactive and how the total oxidation reaction proceeds. Gas composition analysis is one of the tools to determine the active reactants and the products. Several studies have been reported on oxidation of CH₄ using gas chromatography(1-4, 8-19). Kawada et al. reported that oxidation of hydrogen is the main reaction on Ni-YSZ cermet electrode when \( P(H_2O) / P(CH_4) \) ratio (steam / carbon, S/C) is higher than 1(1). Horita et al. investigated the behavior under a lower S/C condition, and found that the dominant reaction is dependent on the electrode materials(2).

The second step in this study is to assign the Faraday current to the electrochemical reactions [7] to [10] in order to carry out the quantitative analysis. It is difficult because the electrochemical reactions and the chemical reactions are combined with each other, and several combinations of the reactions give the same gaseous composition. However, the present authors found that the quantitative analysis is possible to some extent if the gaseous composition under current flow is compared carefully with those under the open circuit condition. In this study, attempts are made to analyze the electrochemical kinetics of CH₄-H₂O system quantitatively. In order to establish an analytical method, a simple electrode / electrolyte system; i.e. Pt electrode on YSZ, and diluted fuel gases were chosen for this study. The results will be compared with the kinetic models for H₂-H₂O(5) and CO-CO₂(6) reported by Mizusaki et al.

**EXPERIMENTAL**

**Cell Construction**

The experimental apparatus is shown schematically in Fig.1. The electrolyte was 8 mole percent (m/o) Y₂O₃-stabilized ZrO₂ (YSZ) tube (NIKKATO Co., Ltd.) with 7.5 mm in outer and 4.5 mm in inner diameters and 280 mm in length. The working electrode (WE) with an area of 2.5 cm² was deposited on the outer side of the YSZ tube. The reference and the counter electrodes (RE and CE) were deposited on the inner side of the YSZ tube. The three electrodes were prepared using Pt paste com-
posed of Pt powder (TOKURIKI-KAGAKU, TP-1) and n-butyl acetic acid. They were heated at 1373 K for 1h in air after being painted on the tube, and then Pt mesh was attached on the porous Pt electrodes as current collectors.

Preparation of Gas

RE and CE were exposed to air. The feed fuel gas, CH₄ mixed with H₂O and He was let flow over WE at 100 to 200 ml min⁻¹ under an atmospheric pressure. The water vapor pressure, P(H₂O), in the gas mixtures was fixed by saturating in a cold trap of controlled temperature.

The gas composition both before and after the cell was analyzed by TCD-type on-line gas chromatography (CHROMPACK, MicroGC CP2002).

Electrochemical Measurements

The electrode interface impedance and the DC polarization current were measured using a three-terminal method at 1073 K. The impedance measurements were made over the frequency of 1 mHz to 100 kHz, keeping the ac potential between WE and RE less than 5 mV using a potentiostat/galvanostat (TOHO TECHNOLOGY Co., Type-2000) and a frequency response analyzer (NF CIRCUIT DESIGN BLOCK Co. Ltd., Type-5720). The DC polarization behavior was measured potentiostatically by changing the applied overvoltage. Ohmic resistance was estimated from the high frequency intercept of the impedance arc in the Cole-Cole plot.

Calculation of Mass Balance

The amount of each gas generated at WE was calculated from the volume concentration of each gas and the gas flow rate. From the mass balance of carbon, the carbon deposition rate was calculated by the following equation

$$v(C)_{dep} = (v(CH_4)_{in} - v(CH_4)_{out}) - v(CO)_{out} - v(CO_2)_{out}$$  \[11\]

where $v(C)_{dep}$ is the flux of the deposited carbon per second, $v(CH_4)_{in}$ is the inlet flux of CH₄, $v(CH_4)_{out}$, $v(CO)_{out}$ and $v(CO_2)_{out}$ are the outlet fluxes of CH₄, CO and CO₂ from the cell, respectively. Since detection of H₂O is not possible with our present system, the mole flux of H₂O, $v(H₂O)_{out \text{from-O}}$, was calculated from the mass balance of total O by the following equation

$$v(H₂O)_{out \text{from-O}} = v(H₂O)_{in} + v(O²) - v(CO)_{out} - 2v(CO₂)_{out}$$  \[12\]

where $v(O²)$ is the O²⁻ flux calculated by the following equation

$$v(O²⁻) = i / 2F$$  \[13\]

where $i$ is the current and $F$ is the Faraday constant.

The mole flux of H₂O, $v(H₂O)_{out \text{from-H}}$, can be calculated also from the mass balance of total H by the following equation

$$v(H₂O)_{out \text{from-H}} = 2(v(CH_4)_{in} - v(CH_4)_{out}) + v(H₂O)_{in} - v(H₂)_{out}$$  \[14\]

where $v(H₂O)_{in}$ is the inlet flux of H₂O and $v(H₂)_{out}$ is the outlet flux of H₂. Comparing $v(H₂O)_{out \text{from-H}}$ and $v(H₂O)_{out \text{from-O}}$, the consistency of the mass balance was confirmed.
firmed. If there was a difference between \( v(H_2O)_{out \text{ from-O}} \) and \( v(H_2O)_{out \text{ from-H}} \) due to the measurement error, we applied \( v(H_2O)_{out \text{ from-O}} \) in the further calculation. It is because the current, \( i.e. v(O^2^+) \), can be measured more accurately than gas analysis, and the error of analyzing \( v(CO)_{out} \) and \( v(CO_2)_{out} \) is smaller than that of analyzing \( v(CH_4)_{out} \) and \( v(H_2)_{out} \).

**Assignment of Current to Each Electrochemical Reaction**

The eqs. [1] to [10] are not independent of each other. Only 3 independent eqs. for the chemical reactions and 4 eqs. for the electrochemical reactions are necessary in terms of mass balance. The chemical reactions [2] to [4] and the electrochemical reactions [7] to [10] are used in calculations.

The following equations are always valid from the mass balance

\[
\begin{align*}
  v(C)_{dep} &= r_2 - r_3 - r_7 \quad [15] \\
  v(CO_2)_{out} &= r_4 + r_8 \quad [16] \\
  \{v(CH_4)_{out} - v(CH_4)_{in}\} &= -r_2 - r_9 \quad [17] \\
  \{v(H_2O)_{out \text{ from-O}} - v(H_2O)_{in}\} &= -r_3 - r_4 + r_{10} \quad [18] \\
  v(O^2^+) &= r_7 + r_8 + r_9 + r_{10} \quad [19]
\end{align*}
\]

where \( r_n \) is the rate of the \( n \)-th reaction.

It is difficult to assign the electrochemical reaction rate because the result of the gas analysis includes the information from the electrochemical reactions and the chemical reactions. The electrochemical reaction is determined only under the following 2 conditions:

1. The rate of the chemical reaction is much smaller than that of the electrochemical one. In this case, the chemical reaction rate is negligible, and then the electrochemical reaction is calculated directly from eqs. [15] to [18].
2. Dependence of the chemical reaction rate on the gas composition is known. In general, chemical reaction rate is dependent on the composition of the reactants and products. Since gaseous composition varies with the electrochemical reaction, the chemical reaction rate under polarization, \( r_n(\text{polarization}) \) is different from that under open circuit condition, \( r_n(\text{open circuit}) \).

If the composition dependence of the chemical reaction rates are known, \( r_n(\text{polarization}) \) (\( n=2 \) to 4) can be estimated, and the rate of the electrochemical reactions, \( r_n(\text{n=7 to 10}) \), is calculated by eqs. [15] to [18].

The dependence of the chemical reaction rate on the gas composition is obtained experimentally by measuring the outlet gas composition when various gas mixtures are introduced under open circuit conditions. Thus, the assignment of the Faraday current is possible if the results of the gas composition measurements are analyzed carefully.
RESULTS AND DISCUSSION

Case 1: 0.39 ≤ S/C ≤ 3.9

Outlet Gas Composition Fig. 2 shows the typical outlet gas composition as a function of electrode potential, $E$, in a CH$_4$-H$_2$O fuel system. Fig. 2 (a) and (b) correspond to the conditions, S/C=0.39 and 3.9, respectively. In both conditions, only $v$(H$_2$)$_{out}$, $v$(H$_2$O)$_{out from H}$ and $v$(H$_2$O)$_{out from O}$ varied with the current. From this result, it is concluded that the dominant electrochemical reactions are oxidation of H$_2$ to H$_2$O under anodic polarization and reduction of H$_2$O to H$_2$ under cathodic polarization.

Open Circuit Voltage Fig. 3 shows the open circuit voltage (OCV) as a function of S/C. In this figure, lines (a), (b) and (c) indicate OCV calculated assuming that one of the following reaction is predominant

(a): \[ H_2 + O^2- = H_2O + 2e^- , \quad \text{P} \text{(H}_2\text{O)} \text{WE} = (K_a)^2 \left( \frac{\text{P}(\text{H}_2)}{\text{P}(\text{H}_2)} \right)^2 \]  

(b): \[ \text{CO} + O^2- = \text{CO}_2 + 2e^- , \quad \text{P} \text{(CO}_2\text{)} \text{WE} = (K_b)^2 \left( \frac{\text{P}(\text{CO}_2)}{\text{P}(\text{CO})} \right)^2 \]  

(c): \[ \text{C} + O^2- = \text{CO} + 2e^- , \quad \text{P} \text{(CO)} \text{WE} = (K_c)^2 \left( \frac{\text{P}(\text{CO})}{\alpha(\text{C})} \right)^2 \]

where $K_a$, $K_b$ and $K_c$ are equilibrium constants and $P_a$(O$_2$)$_{WE}$, $P_b$(O$_2$)$_{WE}$ and $P_c$(O$_2$)$_{WE}$ are equilibrium oxygen partial pressure of the reaction sites near the electrode/YSZ/gas boundary. $P$(H$_2$O), $P$(H$_2$), $P$(CO$_2$) and $P$(CO) are obtained from the outlet gas composition.

If the gas phase were under equilibrium condition, each reaction [21] to [23] would give the same oxygen potential. Therefore the gas phase was not under equilibrium in Fig. 3.

The symbols indicate the observed OCV. They showed good agreement with the equilibrium oxygen partial pressure calculated from $P$(H$_2$O)/$P$(H$_2$). This result suggests the rate of reaction in H$_2$-H$_2$O is much faster than those in others. Horita et al. reported that in the case of Ni/YSZ electrode, OCV is affected by the deposited carbon, and not determined by the reaction [21] of H$_2$-H$_2$O under S/C<1(2), and in the case of Fe/YSZ electrode, OCV is determined by the reaction [21] (2). In this study, OCV was determined by the reaction H$_2$-H$_2$O using Pt electrode. Thus, the catalytic behavior of Pt electrode appears to be similar to Fe/YSZ electrode in a CH$_4$-H$_2$O system under S/C<1.

Case 2: S/C = 0

Estimation of the Chemical Reaction Rate, $r_n$ (n=2,3,4) Fig. 4 shows the outlet gas composition under S/C=0. Carbon deposited slightly at the open circuit.

The rate of conversion of CH$_4$ was about 0.05, i.e. $r_2 = 0.05v$(CH$_4$)$_{out}$ at OCV when S/C=0. With increasing electrode potential from OCV to $E = -700$ mV vs. air, $v$(C)$_{out}$ and $v$(CH$_4$)$_{out}$ decreased and $v$(H$_2$)$_{out}$, $v$(CO)$_{out}$ and $v$(H$_2$O)$_{out}$ increased. From $E = -700$ mV vs. air, $v$(H$_2$)$_{out}$ decreased with increasing electrode potential, and then, $v$(CO$_2$)$_{out}$ increased from $E = -400$ mV vs. air. Though S/C of the inlet gas is zero, it is
higher around the electrode under the polarization condition. From Fig. 4, the effective S/C was estimated to be in the range of 0<S/C<1 in this experiments.

Fig. 5 shows the rate of conversion of CH₄ as a function of S/C of the inlet gas at the open circuit. The rate of conversion of CH₄ varied from 0.05 to 0.10 when S/C varied from 0 to 1. This result showed that 0.05v(CH₄)_in≤r₂≤0.10v(CH₄)_in with 0<S/C<1.

Fig. 6 shows the outlet gas composition as a function of S/C at the open circuit condition in a CH₄-H₂O fuel system. The ratio v(CH₄)_in-v(CH₄)_out/v(CO)_out is equal to 1/1/3, and v(CO₂)_out and v(C)_out were almost zero. Therefore, only chemical reaction [1] proceeded with S/C varying in this region, i.e. r₄=0 (0.39≤S/C≤1).

Assignment of the Current to the Electrochemical Reactions [7] to [10] According to the above discussions, the chemical reaction rates rₙ (n=2,3,4) are determined as follows
1. r₄ equals zero at any condition,
2. the effective S/C is estimated from Fig. 4 for a given electrode potential, and then r₂ is determined from Fig. 5,
3. r₃ is calculated from r₂ and the mass balance of carbon.

Fig. 7 shows assignment of the current to the electrochemical reactions [7] to [10] as a function of electrode potential in a dry CH₄ fuel system. From this figure, the characteristics of each electrochemical reaction is clearly observed. The result of Fig. 7 suggests oxidation of H₂, the reaction[10], was dominant reaction.

The slope of the rate of electrochemical oxidation of H₂ decreased at the potential higher than E= -700 mV vs. air. This result is explained by the concentration polarization of H₂ because v(H₂)_out decreased in this potential region in Fig. 4. Therefore the other electrochemical reactions [7] to [9] began to be significant at E= -700 mV vs. air.

The rate of oxidation of CO, reaction [8], is smaller than that of [10] by about 2 orders of magnitude in Fig 7. These results correspond to the report of Mizusaki et al.(5-6). According to their reports, the rate of the electrochemical reaction at 973 to 1073K in H₂-H₂O atmospheres is faster than that in CO-CO₂ by 1 to 2 orders of magnitude.

The rate of oxidation of carbon, the reaction [7], is not supposed to be dependent on the electrode potential.

The direct oxidation of CH₄ was observed when the concentration of H₂ decreased at high electrode potential. The mechanism of this reaction seems to be related to the H₂ concentration because it was not observed in this study under 0.39≤S/C≤3.9 where the concentration of H₂ is high enough to be supplied by steam reforming.
CONCLUSION

1. The current in CH₄ oxidation was assigned to the electrochemical reaction of CH₄, CO, H₂ and C at the interface of Pt electrode / Y₂O₃-stabilized ZrO₂ electrolyte in a CH₄ system at 1073K.
2. The predominant electrochemical reaction is oxidation of H₂ to H₂O.
3. The electrochemical oxidation of CH₄, CO, H₂ and C to CO, H₂O and CO₂ proceeds in a dry CH₄ system where H₂ and C are generated by the decomposition of CH₄.

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Fig. 1. The schematic view of electrochemical reactor.

Fig. 2. The outlet gas composition as a function of electrode potential in a CH₄-H₂O fuel system at 1073K, the total gas flow rate is 200 ml/min.¹; in each condition of (a) S/C=0.39; P(H₂O) / P(CH₄) / P(He) = 0.39 kPa / 1.0 kPa / 0.099 kPa, (b) S/C=3.9; P(H₂O) / P(CH₄) / P(He) = 0.39 kPa / 0.10 kPa / 0.10 MPa.

Fig. 3. The open circuit voltage (OCV) as a function of S/C at 1073K. Symbols indicate observed OCV; P(H₂O)/P(CH₄)/P(He)=0.39 to 2.3 kPa /0.10 to 1.0 kPa/0.099 to 0.10 MPa, the total gas flow rate is 100 ml/min.¹.
Eq. 4. The outlet gas composition as a function of electrode potential under the inlet gas of S/C = 0 at 1073K; 
P(CH₄) / P(He) = 0.10kPa / 0.10MPa, the total gas flow rate: 100ml/min⁻¹.

Fig. 5. The rate of conversion of CH₄ as a function of S/C of the inlet gas at the open circuit at 1073K; P(H₂O) / P(CH₄) / P(He) = 0.39 to 2.3kPa / 0.10 to 1.0kPa / 0.099 to 0.10MPa, the total gas flow rate: 100 ml/min⁻¹.

Fig. 6. The outlet gas composition as a function of S/C at the open circuit condition in a CH₄-H₂O fuel system at 1073K; P(H₂O) / P(CH₄) / P(He) = 0.39 to 2.3kPa / 0.10kPa / 0.099kPa, the total gas flow rate: 100 ml/min⁻¹.

Fig. 7. Assignment of the current to the electrochemical reactions [7] to [10] which mean the following reactions as a function of electrode potential under inlet gas of S/C = 0 at 1073K;
C+O₂→CO+2e⁻ [7]
CO+O₂→CO₂+2e⁻ [8]
CH₄+O₂→CO+2H₂+2e⁻ [9]
H₂+O₂→H₂O+2e⁻ [10]
P(CH₄) / P(He) = 0.10kPa / 0.10MPa, the total gas flow rate: 100 ml/min⁻¹.