REACTION KINETICS OF CH₄-H₂O GAS-MIXTURES ON Pt/YSZ SYSTEM

Shigenori Onuma, Junichiro Mizusaki*, Atsushi Kaimai, Kenichi Kawamura, Yutaka Nigara, Tatsuya Kawada and Hiroaki Tagawa
Research Institute for Scientific Measurements, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, 980-8577 Japan

ABSTRACT

As a fundamental research on the internal reforming type SOFC anode reaction, a study was made on the reaction kinetics of the CH₄-H₂O gas mixtures at the interface of a porous Pt electrode / Y₂O₃-stabilized ZrO₂ (YSZ) electrolyte at 873--1173 K. The rate of electrochemical oxidation of CH₄ and that of the reforming products, H₂, CO, and C, were determined as a function of the electrode potential and temperature. It was found that the dominant electrochemical reaction is the oxidation of H₂. The rate of the electrochemical oxidation of CO in a CH₄-H₂O system was found larger than that in a CO-CO₂-inert gas system at temperatures below 1073 K. It was suggested that the electrochemical CO oxidation rate is enhanced by the co-existing H₂-H₂O.

INTRODUCTION

Due to the high operation temperature of SOFC, reforming reaction of fossil fuels is considered to take place easily in SOFCs and no large reforming apparatus is necessary for fuel processing. This is generally accepted as one of the merits of SOFC systems compared with other fuel cells, such as PEFC and PEMFC. Recently, it has been pointed out that SOFC is suitable not only for large-scale power stations but also for varieties of small-scale domestic and portable applications. For the latter, the operation temperature is desired to be below 800 °C, considerably lower as compared with 1000°C for the large-scale application. However, the lower temperature operation may be a demerit for reforming reaction to proceed smoothly.

So far, many studies have been made on the anode reaction of SOFC. However, most of the previous researches focused on the relationship between the anode performance and the electrode materials or their microstructures, and little is revealed about the reaction kinetics. The present study aims to clarify the outline of the kinetics of anode reaction and its variation with temperature when the hydrocarbon gas is directly supplied to the anode. Porous Pt on stabilized zirconia electrolyte is selected as a typical model electrode, and CH₄ is selected as model hydrocarbon gas.
EXPERIMENTAL

The electrolyte was a tube-shaped 8 m/o Y2O3 doped ZrO2 (YSZ tube, Nikkato Co., Ltd. 8 mm φ x 300mm L). Using Pt paste, 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. They were heated at 1373 K for 1 h in air, and Pt mesh was used as current collectors.

RE and CE were exposed to air. The test gas mixtures, the mixtures of CH₄, H₂O and He in appropriate ratios, were let flow over WE at 100 to 200 ml/min under atmospheric pressure. The water vapor pressure, P(H₂O), was controlled using a water bubbler and a temperature controlled cold trap. The compositions of the inlet and outlet gas of the cell were analyzed by an on-line gas chromatograph (Chrompack, MicroGC CP2002). Using a molecular sieve column (Chrompack, Molsieve-5A), N₂, O₂, H₂, CH₄, and CO were detected, and CO₂ was detected with a Porapak column (Chrompack, Haysep-A). In this study, the amounts of C₂H₂, C₂H₄, and C₂H₆ were found negligible. The variation of N₂ and O₂ due to gas leakage was also negligible. The standard deviation in the gas analysis for CO, CO₂, CH₄, and H₂ was 1.1, 1.1, 0.52, and 3.4%, respectively.

The three-terminal ac impedance and the dc polarization measurements were made at 873 – 1173 K by a potentiogalvanostat (Toho Technical Research Co., Type-2000) and a frequency response analyzer (NF Co., Type-5720). Ohmic resistance was estimated from the high frequency intercept of the impedance arc over the frequency of 1 mHz to 100 kHz, keeping the ac potential between WE and RE less than 5 mV. To avoid the carbon deposition as much as we could, the cell on stand-by was kept under the anodic polarization condition. Further details are described elsewhere (1).

THEORETICAL

Scheme of Reaction Process on Porous Electrodes

CH₄-H₂O gas mixtures are considered to undergo two types of reactions. One is the “chemical reactions” or the reforming process which takes place without electric current. The other is the “electrochemical reactions” or the reactions which directly involve the electrons in the Pt electrode and the oxide ions in the electrolyte and take place around the triple phase boundary (TPB) of the gas / electrode / electrolyte. The rates of the chemical reactions can be calculated from the mass balance under the open circuit conditions. The rates of the electrochemical reactions can be calculated from the variation in the mass balance with the electrolytic current.

Expected Chemical and Electrochemical Reactions

When CH₄ is fed together with H₂O, not only the steam reforming reaction [1] but also several other reactions may take place. They are:

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + 3\text{H}_2 \\
\text{CH}_4 & \rightarrow \text{C} + 2\text{H}_2 \\
\text{C} + \text{H}_2\text{O} & \rightarrow \text{CO} + \text{H}_2
\end{align*}
\]

[1] [2] [3]
The possible electrochemical reactions in the anodic direction are listed below:

\[ \text{C} + \text{O}_2^{-} \rightarrow \text{CO} + 2e^- \]  
[7]

\[ \text{CO} + \text{O}_2^{-} \rightarrow \text{CO}_2 + 2e^- \]  
[8]

\[ \text{CH}_4 + \text{O}_2^{-} \rightarrow \text{CO} + 2\text{H}_2 + 2e^- \]  
[9]

\[ \text{H}_2 + \text{O}_2^{-} \rightarrow \text{H}_2\text{O} + 2e^- \]  
[10]

### Calculation of Mass Balance

The flux of each gaseous species at WE is calculated from the volume concentration of each species in the inlet and the outlet gas and the gas flow rate. The carbon deposition rate is calculated from the mass balance of carbon and the formation rate of H\(_2\text{O}\) is calculated both from the mass balance of H and O by the following equations:

\[ \nu(\text{C})_{\text{dep}} = \nu(\text{CH}_4)_{\text{in}} - \nu(\text{CH}_4)_{\text{out}} - \nu(\text{CO})_{\text{out}} - \nu(\text{CO}_2)_{\text{out}} \]  
[11]

\[ \nu(\text{H}_2\text{O})_{\text{out from O}} = \nu(\text{H}_2\text{O})_{\text{in}} + \nu(\text{O}_2^{-}) - \nu(\text{CO})_{\text{out}} - 2\nu(\text{CO}_2)_{\text{out}} \]  
[12]

\[ \nu(\text{H}_2\text{O})_{\text{out from H}} = 2\{\nu(\text{CH}_4)_{\text{in}} - \nu(\text{CH}_4)_{\text{out}}\} + \nu(\text{H}_2\text{O})_{\text{in}} - \nu(\text{H}_2)_{\text{out}} \]  
[13]

where \(\nu(\text{C})_{\text{dep}}\) is the flux of the deposited carbon per second, \(\nu(X)_{\text{in}}\) is the inlet flux of the species \(X\) and \(\nu(X)_{\text{out}}\) is the outlet fluxes of \(X\) from the cell. The flux of H\(_2\text{O}\), \(\nu(\text{H}_2\text{O})_{\text{out from O}}\) or \(\nu(\text{H}_2\text{O})_{\text{out from H}}\), is calculated from the mass balance of O or H, respectively. \(\nu(\text{O}_2^{-})\) is the \(\text{O}_2^{-}\) flux calculated from the current passed through the cell, \(i\), by the equation:

\[ \nu(\text{O}_2^{-}) = \frac{i}{2F} \]  
[14]

where \(F\) is Faraday constant.

Theoretically, \(\nu(\text{H}_2\text{O})_{\text{out from H}}\) and \(\nu(\text{H}_2\text{O})_{\text{out from O}}\) agree with each other. If there is a difference among them in the observed values, we apply \(\nu(\text{H}_2\text{O})_{\text{out from O}}\) to the further calculations. It is because the error in analyzing the mass balance of O was always smaller than that of \(\nu(\text{O}_2^{-})\). \(\nu(\text{O}_2^{-})\) is related to the current which can be measured more accurately than the gas analysis. Information we can get from the experiments is the gas composition before and after the cell and the total current.

### Calculation Procedure for the Rates of Chemical and Electrochemical Reactions Taking Place in Parallel

The composition of outlet gas mixtures under zero current condition is determined by the 9 relationships, mass balance of C, O, and H and the rate of chemical reactions in Eqs. [1]-[6], \(r_n(n=1\ldots6)\). However, since we consider six chemical species of C, CO, CO\(_2\), CH\(_4\), H\(_2\), and H\(_2\text{O}\), \(r_n(n=1\ldots6)\) can not be independent of each other. Here, we employ the chemical reactions [2], [3], and [4] as the independent reaction processes.

The flux of above 6 species and the balance of \(\nu(\text{O}_2^{-})\) under steady state polarization can be expressed using the mass balance, \(r_2-r_4\) and \(r_7-r_{10}\) as follows.

\[ \nu(\text{C})_{\text{dep}} = r_2 - r_3 - r_7 \]  
[15]

\[ \nu(\text{CO}_2)_{\text{out}} = r_4 + r_8 \]  
[16]
\[ v(CH_4)_{\text{out}} - v(CH_4)_{\text{in}} = -r_2 - r_9 \]  
\[ v(H_2O)_{\text{out}} - v(H_2O)_{\text{in}} = -r_3 - r_4 + r_9 \]  
\[ v(O^{2-}) = r_7 + r_8 + r_9 + r_{10} \]  
\[ v(CO) = 2r_2 + r_3 + r_4 + 2r_9 - r_{10} \]

In above seven equations, [15]--[21], the flux of seven species are expressed using seven parameters, \( r_n (n=2-4, 7-10) \). However, these equations are not independent of each other because we also have three mass balance relationships. In order to determine \( r_n (n=2-4) \), it is necessary to use the observed flux of the species under the open circuit condition at which \( r_n (n=7-10)=0 \). After we get \( r_n (n=2-4) \) as a function of the gas composition, we can determine \( r_n (n=7-10) \) using eqs. [15]--[21]. Detailed analytical procedures are described elsewhere (2).

**RESULTS AND DISCUSSION**

**Electrode Potential at Open Circuit Condition**

Fig. 1 shows the electrode potential at zero current condition as a function of \( v(H_2O)_{\text{in}} / v(CH_4)_{\text{in}} (= S/C) \) ratio. The closed symbols (a), (b), (c) and (d) indicate the calculated Nernst potential assuming one of the reactions [7]--[10] is predominant;

![Graph showing electrode potential at open circuit condition](image)

**Figure 1.** The open circuit potential as a function of S/C at (A) 873 K, (B) 973 K, (C) 1073 K, and (D) 1173 K; The total gas flow rate was 100 ml min\(^{-1}\) S/C=0: \( P(CH_4) / P(He) = 1.0 \text{ mbar} / 1.0 \text{ bar}, S/C=0.39 \) to 2.3: \( P(H_2O) / P(CH_4) / P(He) = 3.9 \text{ mbar} to 23 \text{ mbar}/10 \text{ mbar}/ 0.99 \text{ bar.} \)
(a): \[ C + O^2^- \rightleftharpoons CO + 2e^- \]  
\[
\frac{P_a(O_2)_{WE}}{(1 \text{ bar})} = K_a \left( \frac{P(CO)/(1\text{bar})}{(a(C))^2} \right)^2 
\]  
[22]

(b): \[ CO + O^2^- \rightleftharpoons CO_2 + 2e^- \]  
\[
\frac{P_b(O_2)_{WE}}{(1 \text{ bar})} = K_b \left( \frac{P(CO_2)/(1\text{bar})}{P(CO)/(1\text{bar})^2} \right)^2 
\]  
[23]

(c): \[ CH_4 + O^2^- \rightleftharpoons CO + 2H_2 + 2e^- \]  
\[
\frac{P_c(O_2)_{WE}}{(1 \text{ bar})} = K_c \left( \frac{P(CO)/(1\text{bar})^2}{P(H_2)/(1\text{bar})^4} \right)^2 
\]  
[24]

(d): \[ H_2 + O^2^- \rightleftharpoons H_2O + 2e^- \]  
\[
\frac{P_d(O_2)_{WE}}{(1 \text{ bar})} = K_d \left( \frac{P(H_2O)/(1\text{bar})^2}{P(H_2)/(1\text{bar})^2} \right)^2 
\]  
[25]

where \(K_a, K_b, K_c,\) and \(K_d\) are equilibrium constants and \(P_a(O_2)_{WE}, P_b(O_2)_{WE}, P_c(O_2)_{WE},\) and \(P_d(O_2)_{WE}\) are the oxygen partial pressure at \(WE\). The standard state of gases is 1 bar.

The analysis of the outlet gas composition gives \(P(CH_4), P(H_2O), P(H_2), P(CO_2),\) and \(P(CO)\). Since we can not experimentally determine the inlet \(P(H_2O)\) at \(S/C=0\), we estimate \(P_d(O_2)_{WE}\) at \(S/C=0\) assuming the inlet \(P(H_2O)\) is equal to 15 \(\mu\text{bar}\) calculated from the guaranteed value by the gas supplier (Nippon-Sanso Co. Ltd).

As shown by the closed symbols in Fig. 1, the calculated EMF values by the combinations \(CO/CO_2, H_2/H_2O\) and \(CH_4/CO, H_2\) of the outlet gas composition are different from each other. When the gas phase is in equilibrium, these values must be the same. That is, the outlet gas is not in equilibrium.

The open symbols indicate the observed EMF. They show good agreement with those calculated from Eq. [25], suggesting that the rate of redox reaction of \(H_2 / H_2O\) is much faster than those of the others.

**Determination of the Electrochemical Reaction Rates, \(r_n(n=7-10)\)**

Fig. 2 shows the typical outlet gas composition as a function of the electrode potential vs. air. From Fig. 2, we also determine the variable range of \((S/C)_{eff}, v(H_2O)_{out} from-O/ v(CH_4)_{out},\) under polarization as a function of electrode potential, which increases up to 12. Fig. 3 shows the outlet gas composition under the zero current condition at which \(r_n\) \((n=7-10) = 0.\) From Fig. 3, we calculate \(r_4\) under polarization from Eq. [16] as a function of \((S/C)_{eff}.\) Then, using Eqs. [17] and [18], we obtain \(r_2\) and \(r_3.\)

We calculate the electrochemical reaction rates, \(r_n\) \((n=7-10)\) from Fig. 2 using the \(r_n\) \((n=2-4)\) determined above. We obtain \(r_8\) as a function of electrode potential by the use of \(v(CO_2),\) Eq. [16] and \(r_4.\) Using eq. [17], we determine \(r_9\) from the difference between \((v(CH_4)_{in}-v(CH_4)_{out})/ v(CH_4)_{in}\) and \(r_2/ v(CH_4)_{in}.\) \(r_{10}\) is determined using \(r_3/ v(CH_4)_{in}\) in Fig. 2, \(r_4\) and Eq. [18]. After that, we determine \(r_7\) using \(r_8-r_{10}\) and eq. [19]. Fig. 4 shows \(r_7 -- r_{10}\) as a function of the electrode potential. At 973 K and 1073 K, not only the oxidation of \(H_2,\) the reaction [10], but also that of \(CO,\) the reaction [8], takes place simultaneously. At 1173 K and 873 K, only the oxidation of \(H_2\) is shown. At 873 K, the change of \(P(CO)\) and/or \(P(CO_2)\) is very small and is in the range of the experimental error, so that \(r_8\) can not be calculated.
**Electrode Reaction Model in a H₂-H₂O System**

In a H₂-H₂O system at 1073 K, the rate determining step of the electrode reaction is the OH exchange between Pt and the stabilized (SZ) surfaces at the TPB of gas / Pt / SZ.\(^{(3)}\)

The rate determining reaction is represented as follows:

\[
H_{\text{ad}}(\text{Pt}) + \text{OH}_{\text{ad}}(\text{SZ}) \rightarrow H_2O_{\text{ad}}(\text{Pt}) + V_{\text{ad}}(\text{SZ}), \quad a(O) > 10^{-12} \quad \text{[26]}
\]

\[
H_{\text{ad}}(\text{Pt}) + H_2O_{\text{ad}}(\text{SZ}) \rightarrow H_2O_{\text{ad}}(\text{Pt}) + H_{\text{ad}}(\text{SZ}), \quad a(O) < 10^{-12} \quad \text{[27]}
\]

where \(X_{\text{ad}}(\text{Pt})\) and \(X_{\text{ad}}(\text{SZ})\) denote \(X\) species adsorbed on Pt, and on SZ, respectively, \(V\) denotes the surface vacancy site, and \(a(O)\) is oxygen activity on SZ near TPB. Then the rate equation is represented as follows:

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**Figure 2.** The outlet gas composition as a function of the electrode potential at (A) 873 K, (B) 973 K, (C) 1073 K, and (D) 1173 K, under the following inlet gas:

- (A) \(P(H_2O) / P(CH_4) / P(He) = 23 \text{ mbar} / 10 \text{ mbar} / 0.99 \text{ bar}\), under 100 ml min\(^{-1}\).
- (B) \(P(H_2O) / P(CH_4) / P(He) = 6.0 \text{ mbar} / 1.0 \text{ mbar} / 1.0 \text{ bar}\) under 100 ml min\(^{-1}\).
- (C) \(P(H_2O) / P(CH_4) / P(He) = 6.0 \text{ mbar} / 1.0 \text{ mbar} / 1.0 \text{ bar}\) under 200 ml min\(^{-1}\).
- (D) \(P(H_2O) / P(CH_4) / P(He) = 17 \text{ mbar} / 10 \text{ mbar} / 0.99 \text{ bar}\) under 200 ml min\(^{-1}\).
Here, \( i_1 \) is the current density, \( k_1 \) and \( k_2 \) are the rate constants, and \( K_X \) and \( K_Y \) are the equilibrium constants of the reaction between adsorbed species. \( P'(H_2) \) is the equilibrium hydrogen pressure when the probability of the coverage occupancy for the unit area of H atom on SZ is 1/2. \( a^*(O) \) is the oxygen activity on SZ near TPB at the open circuit potential determined by the ratio of \( P(H_2O)/P(H_2) \) and \( K_p \), where \( K_p \) is the equilibrium constant (4) of the reaction below:

\[
2H_2O = 2H_2 + O_2,
\]

\[
P(O_2) = K_p \left( \frac{P(H_2O)}{P(H_2)} \right)^2
\]

[29]
Electrochemical Reaction of $\text{H}_2$-$\text{H}_2\text{O}$ in a $\text{CH}_4$-$\text{H}_2\text{O}$ System

The rate constants, $k_1$ and $k_2$, in Eq. [28] depend on the electrode morphology and temperature. In order to obtain the rate constants for the present electrode, electrochemical measurements were made in a $\text{H}_2$-$\text{H}_2\text{O}$ system with the present cell. The values of the parameters determined for the electrode in this work are listed in Table I. The values of the equilibrium constants, $K_x$, $K_Y$, and $P^0(\text{H}_2)$, at 1073 K are the same to those reported in the preceding paper (3).

![Figure 4](image-url)

**Figure 4.** $[r_2, r_3, v(\text{C})_{\text{obs}}, (v(\text{CH}_4)_{\text{in}} - v(\text{CH}_4)_{\text{out}})]/ v(\text{CH}_4)_{\text{in}}$ under polarization condition in Fig. 2 (A), (B), (C), and (D) as a function of $S/C$, and under open circuit condition. The gas composition is the same as in Fig. 3.

**Table I.** The values of the rate constants and the equilibrium constants for Eq. [28]. The standard state of gases is 1 bar. ( ) means the adjusted values at 873 K as each slope of $-RT \ln(K_x, K_Y, K_Z)$ vs. $T$ and $\log(k_1, k_2)$ vs. $1/T$ among 873--1173 K is the same as that among 973--1173 K. The value of $K_P$ comes from ref. (4).

|                  | $\log[P^0(\text{H}_2)/\text{bar}]$ | $\log(K_x)$ | $\log(K_Y)$ | $\log(K_P)$ | $k_1$     | $k_2$     |
|------------------|-----------------------------------|-------------|-------------|-------------|-----------|-----------|
| ref (3) at 1073K | 1.5                               | 16          | 8.5         | -18.4       | $1.1 \times 10^{-1}$ | $9.0 \times 10^{-3}$ |
| this work at 873K| (-1.5)                            | (18.5)      | (10.5)      | -23.9       | (7.6 $\times 10^{-3}$) | (7.6 $\times 10^{-5}$) |
| this work at 973K| 0.20                              | 17.5        | 9.5         | -20.8       | $2.0 \times 10^{-2}$ | $7.0 \times 10^{-4}$ |
| this work at 1073K| 1.5                               | 16          | 8.5         | -18.4       | $4.0 \times 10^{-2}$ | $3.3 \times 10^{-3}$ |
| this work at 1173K| 2.5                               | 15          | 7.5         | -16.3       | $8.0 \times 10^{-2}$ | $2.0 \times 10^{-2}$ |
Fig. 4 also shows the typical steady state polarization results in a CH₄-H₂O system by \( v(O^2^-) \). The open square symbols, the open triangle symbols, and the closed triangle symbols indicate the observed \( v(O^2^-) \), the calculated H₂ oxidation current from Eq. [28], and \( i_{10} \), respectively. Since \( i_{10} \) is close to \( v(O^2^-) \), \( i_{10} \), the oxidation of H₂, is the predominant electrochemical oxidation reaction in a CH₄-H₂O system independent of S/C and temperature. Good agreement is seen between \( i_{10} \) and the one calculated from Eq. [28]. Therefore, the electrochemical oxidation mechanism of H₂ in the CH₄-H₂O system follows the one proposed in the preceding paper (3).

**Electrochemical Reaction Model in a CO-CO₂ System**

According to a preceding paper (5), the rate determining reaction in a CO-CO₂ system is the O exchange across the TPB between the adsorbed CO and CO₂ molecules on the Pt and the adsorbed oxygen atoms on SZ surface. The rate determining reaction in the CO₂ rich atmosphere and in the CO rich atmosphere, respectively, is as follows:

\[
\begin{align*}
\text{CO}_{\text{ad}}(\text{Pt}) + \text{O}_{\text{ad}}(\text{SZ}) & \rightarrow \text{CO}_{2\text{ad}}(\text{Pt}) \quad \text{(CO₂ rich atmosphere)} \quad [30] \\
2\text{CO}_{\text{ad}}(\text{Pt}) & \rightarrow \text{CO}_{2\text{ad}}(\text{Pt}) + \text{C}_{\text{ad}}(\text{SZ}) \quad \text{(CO rich atmosphere)} \quad [31]
\end{align*}
\]

When we express the current density in the CO₂ rich atmosphere and in the CO rich one by \( i_3 \) and \( i_4 \), respectively, the total current density, \( i_3 + i_4 \), can be expressed as follows (5):

\[
i_3 + i_4 = \left\{ k_3 P(\text{CO})^{1/2} a(\text{O})^{1/2} - k_3' P(\text{CO}_2)^{1/2} \right\} + \left\{ k_4 P(\text{CO}) - k_4' P(\text{CO}_2)^{1/2} a(\text{O})^{1/2} \right\} \quad [32]
\]

where, \( k_3, k_3', k_4, \) and \( k_4' \) are rate constants. As to \( k_3 \) and \( k_3' \) as well as \( k_4 \) and \( k_4' \), one of them can be determined when another one is given, because \( i_3 = 0 \) and \( i_4 = 0 \) hold at the equilibrium condition. The closed symbols in Fig. 5 show \( k_3 \) and \( k_4 \) calculated from the reported polarization data (5) and Eq. [32].

![Figure 5](image-url)  
**Figure 5.** Rate constant, \( k_3 \) and \( k_4 \), of the electrode reaction of CO-CO₂ in a pure state (expected) and in a reformed gas (observed)
Electrochemical Reaction of CO-CO$_2$ in a CH$_4$-H$_2$O System

$k_3$ and $k_4$ depend on the electrode morphology and temperature. Those for our electrode are determined by the following procedures.

1. The parameters are determined so that $r_8$ determined from the observed data at 1073 K at $E = -200$ mV vs. air agrees with the calculated $r_8 = (i_3 + i_4) \times 2.5 / 2F$. Here, 2.5 in $(i_3 + i_4) \times 2.5 / 2F$ represents the area of WE. The $k_3/k_4$ ratio at 1073 K is taken as the same value as that obtained in the preceding paper (5).

2. Assuming the activation energies of $k_3$ and $k_4$ for the present electrode to be the same as those in the preceding paper (5), the rate constants at 873 K, 973 K, and 1173 are estimated, which are shown by $k_3$ (expected) and $k_4$ (expected) in Fig. 5.

The electrochemical reaction rate calculated from Eq. [32] with $k_3$ (expected) and $k_4$ (expected) and $r_8$ determined from the observed data are expressed by the closed circles and the closed squares, respectively in Fig. 4. The former is much smaller than the latter one at $T < 1073$ K. Then, we try to determine the values of $k_3$ and $k_4$ which reproduce $r_8$ at about $E = -450$ mV in the study with $S/C = 0$ at 873 K and $E = -500$ mV at 973 K in Fig. 4(B). The $k_3$ and $k_4$ thus determined are shown as $k_3$ (observed) and $k_4$ (observed) in Fig. 5. At 873–973 K, we get $k_4$ (observed) = $k_4$ (expected). In Fig. 4, the calculated $r_8$ by Eq. [32] with $k_3$ (observed) and $k_4$ (observed) is represented by the open circle symbols with the solid curve. As shown in Fig. 5, the relationship between log $k_3$ (observed) and $1/T$ does not follow the Arrhenius type: $k_3$ (observed) increases with decreasing temperature at 873–1073 K. This infers that the component in the CH$_4$-H$_2$O gas mixtures affects the reaction [31]. Since $k_4$, hence the reaction [32], is not affected, the species affected by the CH$_4$-H$_2$O gas mixtures is limited to the one that only appears in Eq. [31]. That is $O_{ad}(SZ)$. In H$_2$-H$_2$O and, therefore, in CH$_4$-H$_2$O gas mixtures, YSZ surface at large $a_0$ is covered by $OH_{ad}$ (3), and the coverage increases with decreasing temperature. It is concluded that $OH_{ad}(SZ)$ shows catalytic effect to enhance the reaction [31].

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