SIMILARITY AND DIFFERENCE OF DC POLARIZATION CHARACTERISTICS AND ELECTRODE REACTIONS BETWEEN Ni/YSZ ANODES AND Pt/YSZ ANODES IN SOFCs WITH DRY CH₄ FUEL

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ABSTRACT

Characteristics of a Ni/YSZ cermet anode and a Pt/YSZ cermet anode of solid oxide fuel cell (SOFC) were investigated in dry CH₄/Ar fuel for various operating temperatures (750 to 1000°C). The partial pressure of CH₄ was 0.045atm. The DC polarization of the two anodes in CH₄/Ar was measured by using the current interruption method. For comparison, the anode characteristics in H₂ fuel were also evaluated before the experiments in CH₄/Ar. The exhaust gas from the anodes was analyzed by using gas chromatography. The electrochemical and chemical reactions on both anodes were determined by evaluating the composition of exhaust gas and DC polarization curves.

In H₂ fuel, the current density was proportional to the activity of oxygen on both anodes at all operating temperatures studied here. In CH₄ fuel, the current density was relatively proportional to the activity of oxygen on the Ni/YSZ anode at 800°C and on the Pt/YSZ anode at 800°C. However, for both anodes, the reaction order of oxygen activity determined by the relationship between anodic current and oxygen activity decreased with increasing operating temperature. The order was about 1/6 for Ni/YSZ at 1000°C, and about 1/3 for Pt/YSZ at 1000°C. The possible mechanism for the decrease in the reaction order is based on the Langmuir reaction of the carbon with the adsorbed oxygen at the three phase boundary.

INTRODUCTION

Hydrogen (H₂) and hydrocarbons (HCs) are used as fuels for solid oxide fuel cells (SOFCs). HCs have many advantages, including low cost and low storage pressure. However, they have one major disadvantage: the deterioration of the anode due to carbon deposition by thermal decomposition of HCs. An internal steam-reforming system has been suggested for preventing this carbon deposition, but this reduces the power density and the fuel efficiency of SOFCs. Furthermore, a steam-reforming system requires a heat recovery system for heating the steam in the feed gas, thus adding to the complexity of the system. If SOFCs can be operated in dry methane fuels without carbon deposition, their energy efficiency can be increased.

Electrode reactions in diluted dry methane (CH₄) fuel have been reported for a platinum anode [1], a nickel (Ni)/yttria stabilized zirconia (YSZ) anode [2] and an iron...
In a previous study, we found that under high current density and with low concentration (i.e., 4.5%) of dry methane fuels on a Ni/YSZ anode, methane was completely oxidized to carbon dioxide and water without carbon deposition on the three-phase boundary (TPB), where the anodic reaction occurred [3,4]. We also clarified the mechanism that controls the threshold current density for complete oxidation [5, 6]. However, we also found that with high concentration of dry methane fuel, these SOFCs could not stably generate power due to carbon deposition on the anode. Recently, Murray et al. [7] reported the direct oxidation of 97% CH₄ in SOFCs with two-layer structured anodes of Ni/YSZ cermet layer and yttria doped ceria layer. Park et al. [8] reported power generation by SOFC with Cu/ceria cermet anode in dry methane, dry ethane, and dry butane. However, the power densities of SOFCs in these three fuels were not high compared with that of SOFCs in H₂. Therefore, SOFC systems that use dry HC fuels must be further developed and the reaction mechanism in dry HC fuel that guides such development must be clarified. We previously clarified the reaction mechanism based on the complete adsorption of H, H₂O and O, and expressed the current density as a function of partial pressure of H₂ and H₂O in H₂ on Ni/YSZ anode [9, 10]. In the present report, we investigated DC polarization and electrode reactions for a Ni/YSZ anode and a Pt/YSZ anode. We also propose a reaction mechanism in diluted dry CH₄ fuel for both anodes referring to our previously clarified reaction mechanism in H₂ fuel.

**EXPERIMENTAL**

For both Ni/YSZ anode and Pt/YSZ anode, the DC polarizations were measured and the exhaust gases composition from anode were analyzed.

**Fabrication of the SOFC**

The structure of the SOFC we used is illustrated in detail elsewhere [4]. In this SOFC, the electrolyte was disc of 8-mol%-Y₂O₃-ZrO₂ (8-YSZ; 20 mm diameter, 0.5 mm thickness; manufactured by Toso Co.). The anode was prepared by coating one side of the disc with a mixture of NiO powder or Pt powder (particle diameter was 7μm for NiO and 0.7μm for Pt), 8-YSZ (particle diameter was 0.2μm), ethylcellulose, and α-terpineol. The disc was calcined in air at 1400°C or 1450°C for 3 h for Ni/YSZ and at 1100°C for 4 h for Pt/YSZ. Using a similar calcination method, we coated the opposite side of the disc with La₀.₈5Sr₀.₁₅MnO₃ cathode. The cathode was calcined in air at 1200°C for 4 h.

**Power Generation Experiments in Dry CH₄ Fuel**

The Ni/YSZ anode and the Pt/YSZ anode were used in CH₄/Ar fuel. Various operating temperatures were used, ranging from 750 to 1000°C. The CH₄/Ar mixture gas at atmospheric pressure was used as fuel. The partial pressure of CH₄ was 0.45atm. The characteristics of the Ni/YSZ anodes and the Pt/YSZ anodes in CH₄/Ar were evaluated by using the current interruption method. For comparison with the anode characteristics in H₂ fuel, those for H₂ were also evaluated before the experiments in CH₄/Ar. The exhaust gas from the anodes was analyzed by using gas chromatography. When we use the analysis of the exhaust gas composition to consider the reaction mechanism, we must consider any side reactions of products on anode with other gases. Since our cell was a plug-flow reactor having a short residence time of gas, we can neglect the side reactions.
Details of the gas analysis were described in our previous report [4].

OVERVIEW OF LANGMUIR REACTION MECHANISM ON Ni/YSZ ANODES IN H2 FUEL

Fig. 1 Schematic of our competitive adsorption mechanism on Ni/YSZ anode in H2 fuel

We previously reported the Langmuir reaction mechanism based on competitive adsorption [9, 10]. In this section, we summarize the reaction mechanism in H2 because this reaction mechanism is the basis for constructing our model in dry CH4 fuel. Figure 1 shows a schematic of our previous reaction model. We assumed the following equilibria and reaction scheme. Equilibrium between H2 in the fuel and H on the surface of Ni (H_ad) near the TPB is expressed as

\[
\text{(a)} \quad H_2 + 2V_{ad} \rightleftharpoons K_H 2H_{ad}
\]

where \( K_H \) is the equilibrium constant for H2 and \( V_{ad} \) is the vacant sites for adsorption.

(b) Equilibrium between H2O in the fuel and H2O on the surface of Ni (H2O_ad) near the TPB is expressed as

\[
\text{(b)} \quad H_2O + V_{ad} \rightleftharpoons K_{H2O} H_2O_{ad}
\]

where \( K_{H2O} \) is the equilibrium constant for H2O.

(c) Equilibrium between O in YSZ (O(YSZ)) and adsorbed O (O_ad) is expressed as

\[
\text{(c)} \quad O(YSZ) + V_{ad} \rightleftharpoons K_O O_{ad}
\]

where \( K_O \) is the equilibrium constant for O in YSZ.

The coverage of adatoms, such as H, H2O, and O, is defined as the ratio of the number of adatoms to the total number of sites on the Ni surface available for adsorption. Assuming competitive adsorption on the Ni surface, the vacant coverage is expressed as

\[
\theta_v = (1 - \theta_H - \theta_{H2O} - \theta_O)
\]

where \( \theta_H \), \( \theta_{H2O} \), and \( \theta_O \) represent the coverage of H, H2O, and O, respectively, on the sites for adsorption. The following expressions for the equilibrium constants were obtained from the equilibrium assumptions (a), (b), and (c) above, respectively:

\[
K_H = \frac{\theta_H^2}{\theta_v^2}
\]

\[
K_{H2O} = \frac{\theta_{H2O}}{\theta_v}
\]

\[
K_O = \frac{\theta_O}{a_o \cdot \theta_v}
\]

We assumed the rate-determining step in the production of H2O to be the reaction of H_ad and O_ad on Ni. This reaction can be represented as

\[
2H_{ad} + O_{ad} \rightarrow 2H_2O_{ad} + 2V_{ad}
\]

The current \( i \) flowing in the SOFC can be expressed as the difference of the anodic current density \( i_a \) and cathodic current density \( i_c \):

\[
i = i_a - i_c = k_a \cdot \theta_H^2 \cdot \theta_O - \theta_H \cdot \theta_O^2
\]

686 Electrochemical Society Proceedings Volume 2001-16
Using Eqs. 1-4 and Eq. 5, \( i \) can be expressed as a function of \( K_n, K_{H2O}, K_{a_o}, P_{H2}, P_{H2O}, k_n \), and \( k_c \) as

\[
i = i_n - i_c = \frac{K_n \cdot P_{H2} \cdot K_{a_o}}{(1 + K_n \cdot P_{H2} + K_{H2O} \cdot P_{H2O} + K_{a_o} \cdot a_o)} - k_c \cdot \frac{K_{H2O} \cdot P_{H2O}}{(1 + K_{H2O} \cdot P_{H2O} + K_{a_o} \cdot a_o)}
\]

The dependence of \( i_n \) and \( i_c \) on \( P_{H2}, P_{H2O}, \) and \( a_o \) is determined by the terms in the denominator of Eq. 6. The terms \((K_nP_{H2})^{0.5}, K_{H2O}P_{H2O}, \) and \( K_{a_o} \) correspond to \( \theta_n/\theta_n, \theta_{H2O}/\theta_n, \) and \( \theta_{a_o}/\theta_n \), respectively. Near the TPB, these terms represent the ratio of the respective coverages of \( H, H_2O, \) and \( O \) to the coverage of vacant sites on \( Ni. \) For example, if \( K_{H2O}P_{H2O} \gg (1 + (K_nP_{H2})^{0.5} + K_{a_o} \), then Eq. 6 indicates that \( i_n \) is approximately proportional to \( P_{H2}, a_o, \) and \( (P_{H2O})^{0.5} \). However, if \( (K_nP_{H2})^{0.5} \gg (1 + K_{H2O}P_{H2O} + K_{a_o} \), then Eq. 6 indicates that \( i_n \) is approximately proportional to \( P_{H2}^{0.5} \) and \( a_o \). These various dependencies can be derived by changing the functional order of the four terms in the denominator of Eq. 6.

**RESULTS AND DISCUSSION**

**Relationship Between Anodic Current \( i_a \) and Oxygen Activity \( a_o \) in Dry CH₄**

Figures 2 and 3 show the \( i_a \) as a function of \( a_o \) on the Ni/YSZ anode and the Pt/YSZ anode in dry CH₄. For comparison, data also is shown for both anodes in H₂. For both anodes in H₂ at all operating temperatures, \( i_a \) was proportional to the \( a_o \). In dry CH₄ fuel, \( i_a \) was relatively proportional to \( a_o \) on the Ni/YSZ anode at 800°C and on the Pt/YSZ anode at 800°C. However, for both anodes, the reaction order decreased with increasing operating temperature. The reaction order was about 1/6 for the Ni/YSZ anode at 1000°C, and about 1/3 for the Pt/YSZ anode at 1000°C. The possible reaction mechanism based on the Langmuir reaction of carbon with oxygen at the TPB will be discussed later, in the section “Possible reaction mechanism on
the Ni/YSZ anode and Pt/YSZ anode in dry CH₄ fuel”.

**Exhaust Gas Composition From Anodes in Dry CH₄**

Figures 4 ~9 show the production rate of the exhaust gas of the SOFC as a function of \( i_a \) in dry CH₄ fuel for the Ni/YSZ anode and for the Pt/YSZ anode at various operating temperatures. For both anodes, the production rate of CO₂ increased with increasing \( i_a \). CO₂ was detected by the gas chromatograph at \( i_a > 0.55 \text{ A/cm}^2 \) for the Ni/YSZ anode at 1000 °C (Fig. 4) and at \( i_a > 0.38 \text{ A/cm}^2 \) for the Pt/YSZ anode at 964 °C (Fig. 7). The minimum \( i_a \) where CO₂ was detected decreased with decreasing operating temperature. For a given \( i_a \), the production rate of CO₂ on the Pt/YSZ anode was less than that on the Ni/YSZ anode. The production rate of C on the Pt/YSZ anode was greater than that on the Ni/YSZ anode. The production of CO₂ did not affect the reaction order of \( a_0 \) (Figs. 2 and 3).

The following reactions (I~III) for the Ni/YSZ anode in CH₄ were previously reported [3—6]:

\[
\begin{align*}
\text{CH}_4 & \rightarrow 2\text{H}_2 + \text{C} \quad (I) \\
\text{C} + \text{O}_2 & \rightarrow \text{CO} + 2\text{e}^{-} \quad (II) \\
\text{CH}_4 + 4\text{O}_2 & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 8\text{e}^{-} \quad (III)
\end{align*}
\]

Reaction (III) represents the complete oxidation of CH₄ and is therefore important in the development of an anode in pure dry CH₄ fuel. For both anodes at all operating temperatures, the amount of carried electrons, which we calculated by using the value determined from the exhaust gas analysis and assuming the above three reactions [(1)~(3)], agreed well with that calculated by using \( i_a \). Figures 9 and 10 show the relationship on Ni/YSZ at 900 °C and Pt/YSZ at 860 °C, respectively. Accordingly, reaction (III) also occurred on the Pt/YSZ anode at higher \( i_a \) and higher anode potential.

Here, we discuss the justification of reactions (I) and (II) on the Pt/YSZ anode at lower \( i_a \) and lower anode potential. At lower current, the products were H₂ and CO. Two possible reaction schemes can explain our results except for the combination of reaction (I) and (II). One possibility is the
The combination of Reactions (I), (IV), and (V):

\[ \text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} + 2e^- \quad (IV) \]

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad (V) \]

The other is the combination of Reactions (I) and (VI):

\[ \text{CH}_4 + \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 + 2e^- \quad (VI) \]

Figures 7~9 show that steam was not detected in the exhaust gas at the lower current. The carried electrons calculated from \( i_a \) were equivalent to that ([Production rate of CO]x2) calculated assuming the combination of Reactions (I), (IV) and (V).

Accordingly, if CO was produced by Reactions (IV) and (V) (the first possibility described above), all of H\(_2\)O produced by Reaction (IV) should react with CH\(_4\) by Reaction (V). It seems that this did not occur.

If CO was produced by Reactions (I) and (VI) (the second possibility described above), the ratio of the increase of H\(_2\) with increasing current to that of CO would be 2, which is the products ratio of Reaction (VI) because for the combination of Reactions (I) and (VI), Reaction (I) should be constant, independent of \( i_a \). Although the increase of H\(_2\) was larger than twice that of CO for Ni/YSZ, the increase of H\(_2\) was similar to twice that of CO for Pt/YSZ anode as shown in Figs.7~9, which was the ideal value of 2.

If the production rate of CH\(_4\) on TPB by Reaction (I) is the same as that of C on TPB by Reaction (II), then the overall reaction corresponds to (VI). Our experiments involving the Pt/YSZ anode seem to indicate the same production rates of Reaction (I) and (II).

Therefore, the reactions on the Pt/YSZ anode, as well as on the Ni/YSZ anode, in dry CH\(_4\) should be expressed by the combination of Reactions (I) and (II). As shown in Figs.4~9, the production rate of H\(_2\) increased with \( i_a \). This increase indicates that Reaction (I) was enhanced with increasing current. The possible reason for the enhancement will be discussed in the next section.

At operating temperature lower than 900°C, the production rates versus anode potential at 1 atm O\(_2\) on Ni/YSZ and on Pt/YSZ were similar. However, at operating temperature higher than 900°C, the behavior differed.

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Possible Reaction Mechanism For Ni/YSZ and Pt/YSZ Anodes in Dry CH₄ Fuel

Here, we propose a reaction mechanism that explains the different dependence of $i_a$ on $a_o$ at higher temperatures and the increase in the production rate of H₂ by reaction (I) with increasing current. Assuming the adsorption equilibrium (c) between O in YSZ (O(YSZ)) and adsorbed O (Oad) at the TPB, as in our model in H₂ fuel, we obtained equation (4). Based on the rate-determining reaction of Langmuir reaction in H₂ fuel, we assumed the rate-determining step to be the Langmuir reaction of C at the TPB (Reaction (II)) with the Oad at the TPB in dry CH₄ fuel, thus yielding

$$i_a = k_a \cdot \theta_c \cdot \theta_v$$  \hspace{1cm} (7)

where $\theta_c$ is the coverage of the C at TPB or the carburized Ni at TPB, and $\theta_v$ is the coverage of the vacant sites for O.

We assumed that oxygen was the only adsorbed species for Vad, yielding

$$\theta_v + \theta_0 = 1$$  \hspace{1cm} (8)

Here, $\theta_c$ was assumed to be constant at a given $i_a$ because of the steady state between Reactions (I) and (II), which are expressed as

\begin{align*}
CH_4 + V_c & \rightarrow k_{CH4} C_{TPB} + 2H_2 \quad \text{(I)} \\
C_{TPB} + O_{ad} & \rightarrow k_a CO + 2V_c \quad \text{(II)}
\end{align*}

where $C_{TPB}$ is the C at TPB or carburized Ni at TPB, $V_c$ is the vacant sites for the C deposition or the carburization of Ni, and $k_{CH4}$ and $k_a$ are the rate constants of Reaction (I) and (II), respectively. Assuming steady state between Reactions (I) and (II) yields

$$k_{CH4} \cdot P_{CH4} \cdot \theta_{vc} = k_a \cdot \theta_c \cdot \theta_v$$  \hspace{1cm} (9)

where $\theta_{vc}$ is the coverage of the vacant sites for the C deposition or the carburization of Ni. In our model, we assumed two types of vacant sites at TPB: vacant site (Vad) for O, and sites (Vc) for the C deposition or the carburization of Ni. In Vad sites for adsorption of O were not affected by the deposition of C and the carburization of Ni. However, in Vc, sites for the C deposition or the carburization of Ni depended on $\theta_c$ and $\theta_v$.

Therefore, in our model, we assumed

$$\theta_{vc} = \theta_v - \theta_c$$  \hspace{1cm} (10)

Using equations (4) and (7)-(10), the $i_a$ can be expressed as a function of $k_a$, $k_{CH4}$, $k_a$, $P_{CH4}$, and $a_0$:

$$i_a = k_a \cdot k_{CH4} \cdot P_{CH4} \cdot \frac{K_o a_o}{(1 + K_o a_o)(k_a K_o a_o + k_{CH4} P_{CH4} (1 + K_o a_o))}$$  \hspace{1cm} (11)

We previously reported that in H₂ fuel [9],

$$1 >> K_o a_o$$  \hspace{1cm} (12)

This relationship indicates that the coverage of the vacant sites for adsorption of O is much larger than the coverage of O because $K_o a_o$ is equal to the ratio of the coverage of
O to the coverage of the vacant sites. Applying relation (12) to equation (11) yields

\[ i_a = k_a \cdot k_{CH_4} \cdot P_{CH_4} \cdot \frac{K_o a_o}{k_a K_o a_o + k_{CH_4} P_{CH_4}} \]  \hspace{1cm} (13)

The dependence of \( i_a \) on \( a_o \) is governed by the terms in the denominator of Eq. 13. For example, if \( k_{CH_4} P_{CH_4} >> k_a K_o a_o \), then Eq. 12 indicates that \( i_a \) is relatively proportional to \( a_o \). However, if \( k_{CH_4} P_{CH_4} << k_a K_o a_o \), then Eq. 12 indicates that \( i_a \) is relatively independent of \( a_o \). Therefore, when the temperature dependence of \( k_a \) is larger than that of \( k_{CH_4} \), the reaction order of \( a_o \) to \( i_a \) decreases with increasing temperature (Figs. 2 and 3). The difference in reaction order between Ni/YSZ and Pt/YSZ can be explained by the difference in the temperature dependence of the rate constants \( k_a \) and \( k_{CH_4} \). Furthermore, the increase in the production rate of \( H_2 \) with increasing \( i_a \) (Figs. 4~9) can be explained by equation (9).

The mechanism discussed in this section is one possible mechanism. Further investigation is needed to clarify the mechanism involved in dry methane fuel.

**SUMMARY**

The characteristics of Ni/YSZ cermet anodes and Pt/YSZ cermet anodes were investigated for dry CH4/Ar fuel. In dry CH4 fuel, the current density was relatively proportional to the oxygen activity on the Ni/YSZ anode at 800°C and on the Pt/YSZ anode at 800°C. However, for both anodes, the reaction order of oxygen activity decreased with increasing operating temperature. The order was about 1/6 for Ni/YSZ at 1000°C, and was about 1/3 for Pt/YSZ at 1000°C. The reactions on both anodes in dry CH4 were reactions (I)~(III):

- \( CH_4 \rightarrow 2H_2 + C \) (I)
- \( C + O_2 \rightarrow CO + 2e^- \) (II)
- \( CH_4 + 4O_2 \rightarrow CO_2 + 2H_2O + 8e^- \) (III)

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