OXIDATION OF CH₄ ON Ni AND Fe ANODES IN SOLID OXIDE FUEL CELLS

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ABSTRACT

Oxidation and steam reforming of CH₄ on Ni/YSZ and Fe/YSZ anodes were examined, especially under the condition of O₂:Steam/Carbon ≤ 1. In CH₄+H₂O fuel system, steam reforming occurred on anodes to generate CO and H₂. CH₄ consumption rate on Ni was remarkably higher than that on Fe at open circuit. Anodic polarization curve of Ni was divided into two parts: one was oxidation of C at low oxygen potential region, the other was oxidation of H₂ and/or CO at higher oxygen potential region. Anodic polarization curve of Fe was a single slope with low current density. In dry CH₄ fuel system, anodic polarization curves implied both C and H₂ oxidation on both anodes. If enough O²⁻ was supplied on the anode, dry CH₄ was completely consumed to CO+2H₂.

1. INTRODUCTION

In solid oxide fuel cells (SOFCs), natural gas can be reformed internally because of its high operation temperature. Steam reforming, which is one of the common ways for utilizing CH₄, can be written as follows:

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

The produced gases are electrochemically oxidized as follows:

\[
\begin{align*}
\text{CO} + \text{O}^{2-} &= \text{CO}_2 + 2e^- \\
\text{H}_2 + \text{O}^{2-} &= \text{H}_2\text{O} + 2e^-
\end{align*}
\]  

Several authors have reported about the kinetics of steam reforming and the possibilities of internal steam reforming on Ni/Yttria Stabilized Zirconia (Ni/YSZ) cermet[1-5]. Another way to utilize CH₄ is oxidation by O²⁻ through the electrolyte instead of H₂O as follows:

\[
\text{CH}_4 + \text{O}^{2-} = \text{CO} + 2\text{H}_2 + 2e^-
\]
This concept is more attractive than the steam reforming because it can be expected to provide higher fuel cell efficiency and generate both electrical power and synthesis gases (H_2 and CO) as products[6]. To realize this system, it needs an anode which can activate CH_4 under dry condition. In other words, this anode should oxidize deposited carbon and/or show no degradation under carbon deposition. Doped LaCrO_3 perovskites[7,8], CeO_2[9,10] and Fe[11] have been examined for this purpose. We have investigated several metals and carbides as anodes for dry CH_4 oxidation[12]. Among them, Fe showed relatively high catalytic activities without degradation, while Ni showed quick degradation due to coking. However, quite recently, some authors reported the possibility of dry CH_4 oxidation on Ni/YSZ cermet[13,14].

In order to clarify the catalytic activity of Ni and Fe as anode, oxidation and steam reforming of CH_4 on Ni/YSZ and Fe/YSZ anodes were examined under dry CH_4 and low humidity (0≤S/C≤1) condition. The possibility of Ni and Fe anode for dry CH_4 direct introduction and optimal conditions for operations will be also discussed.

2. EXPERIMENTAL

Anode Materials

Ni/YSZ cermet powder (Ni:40 vol%) was prepared by mixing proper amounts of nickel carbonate and 8 mol% YSZ powders (TOSOH, TZ-8Y). This powder was dried and calcined at 1673 K for 5 hours in air. Fe/YSZ cermet powder (Fe:35 vol%) was prepared by mixing proper amounts of Fe_3O_4 (magnetite) and 8 mol% YSZ powders (TOSOH TZ-8Y). Fe_3O_4/YSZ mixture was not calcined in order to prevent making a solid solution of Fe-YSZ. These metal cermet powders were dispersed in 2-propanol solution with a Polyvinyl Butyral (PVB) binder and were painted on YSZ pellets (diameter :1 cm, thickness: 1-1.5 mm) in an area of 0.785cm^2. The painted anode-YSZ pellets were fired at 1673 K for 5 hours.

Measurement of anode characteristics

Cell configuration used in this study is schematically drawn in Fig. 1. A mixture of the fuel and Ar gas was supplied to the anode surface at the rate of about 70-90 ml/min under 1×10^5 Pa. The mixing ratio of fuel (H_2, CH_4) and Ar was controlled by mass flow controllers from 0 (pure Ar) to 20 vol% fuel. Water content of feed gas was controlled from 0 to 20 % by the saturation temperature of water. The anode side was sealed by the Pyrex glass to avoid gas leakage. Platinum counter and reference electrodes were made from platinum paste and exposed to air.

Electrochemical measurements were made with a potenio/galvano stat (TOHO-Giken 2020) and an impedance analyzer (NF5090). The gas compositions both before and after the cell were analyzed with an in-line TCD-type gas chromatograph (M-200, NIPPON TYRAN).

3. RESULTS AND DISCUSSION
3.1 Characteristics of Fe anode at open circuit condition

Figure 2 shows $P(\text{CH}_4)$ effect on open circuit voltage (OCV) and outlet gas evolution rate at constant $P(\text{H}_2\text{O})=3.0$ kPa. In Fig.2a, OCV of Fe anode is shown by open circle symbol. The OCV changed from -834.4 to -849.0 mV vs air in the $P(\text{CH}_4)$ range from 3.6 to 19.3 kPa. The broken line indicates the OCV determined by the $P(\text{H}_2\text{O})/P(\text{H}_2)$ equilibrium. $P(\text{H}_2)$ and $P(\text{H}_2\text{O})$ were obtained from the $\text{H}_2$ and $\text{H}_2\text{O}$ ratio in the outlet gas from the cell. In Fig.2b, $\text{H}_2$ and CO evolution rates from Fe anode cell are shown by open square and diamond symbols, respectively. CH$_4$ consumption rate (open circle symbol) was estimated from the difference between inlet and outlet CH$_4$. The evolution rate was normalized by the geometrical electrode surface area (0.785 cm$^2$). About 12.0 % of inlet CH$_4$ was converted to CO and $\text{H}_2$ at $P(\text{CH}_4)=3.6$ kPa. This value decreased to 3.3 % at $P(\text{CH}_4)=19.3$ kPa. H$_2$ evolution rate and CH$_4$ consumption rate slightly increased as $P(\text{CH}_4)$ was changed from 3.6 to 19.3 kPa. CO evolution rate was kept almost constant in this range. This is due to the limitation of the water amount in the feed gas. Carbon deposition rate, the difference between CH$_4$ consumption rate and CO evolution rate, increased from 0.052 to 0.236 $\mu$mol s$^{-1}$ cm$^{-2}$.

Figure 3 shows temperature dependence of OCV and outlet gas evolution rate at constant $P(\text{CH}_4)=3.6$ kPa and $P(\text{H}_2\text{O})=3.0$ kPa. In Fig.3a, OCV of Fe anode is shown by open circle symbol. The OCV changed from -845.2 to -834.4 mV vs air in the temperature range from 1073 K to 1273 K. The broken line indicates OCV estimated from the $P(\text{H}_2\text{O})/P(\text{H}_2)$ equilibrium. In Fig.3b, $\text{H}_2$ and CO evolution rates and CH$_4$ consumption rate are shown by the same symbols as in Fig.2b. H$_2$ evolution rate and CH$_4$ consumption rate slightly increased as temperature was elevated. Carbon deposition rate was small in this temperature range.

In any $P(\text{CH}_4)$ and temperatures examined, the OCV of Fe agreed well with the oxygen partial pressure determined by the $P(\text{H}_2\text{O})/P(\text{H}_2)$ equilibrium. Fe was oxidized to FeO in this condition because oxygen partial pressure determined by the FeO/Fe equilibrium (~898.6 mV vs air, at 1273 K) was lower than that of the OCV. Strong O or OH adsorption on Fe occurred in CH$_4$-H$_2$O fuel system. In the case of dry CH$_4$ fuel system, the OCV showed very low oxygen partial pressure of about -1400 mV vs air as reported before[12]. The presence of H$_2$O in CH$_4$ fuel can influence the surface status of Fe and OCV drastically.

3.2 Characteristics of Ni anode at open circuit condition

In Fig.2a, OCV of Ni anode is shown by closed circle symbol. The OCV changed from -1280.6 to -1156.0 mV vs air in the $P(\text{CH}_4)$ range from 3.8 to 18.9 kPa. In Fig.2b, outlet gas evolution rate is shown by the closed symbol. About 65 % of inlet CH$_4$ was converted to H$_2$ and CO at $P(\text{CH}_4)=3.8$ kPa. This value decreased to 12 % at $P(\text{CH}_4)=18.9$ kPa. H$_2$ and CO evolution rates and CH$_4$ consumption rate slightly decreased as $P(\text{CH}_4)$ was changed from 3.8 to 18.9 kPa. Carbon deposition rate increased from 0.098 to 0.419 $\mu$mol s$^{-1}$ cm$^{-2}$, as $P(\text{CH}_4)$ was raised.

In Fig.3a, OCV of Ni anode is shown by closed circle symbol. The OCV changed from -1146 to -1280 mV vs air in the temperature range from 1073 K to 1273 K. The
broken line indicates the OCV estimated from the $P(H_2O)/P(H_2)$ equilibrium. The dash-dotted line indicates the OCV estimated from the $\alpha(C)/P(CO)$ equilibrium. The $P(CO)$ was estimated from the CO evolution rate. The $\alpha(C)$ was fixed at unity assuming carbon deposition. In Fig.3b, the outlet gas evolution rate was plotted as a function of temperature. With increasing temperature, H$_2$ evolution rate slightly decreased, while CH$_4$ consumption rate and CO evolution rate slightly increased.

In the case of Ni/YSZ anode, OCV indicated the intermediate oxygen partial pressure between the $P(H_2O)/P(H_2)$ and $\alpha(C)/P(CO)$ equilibrium. It was somewhat strange that OCV decreased as $P(CH_4)$ was raised. In accordance with the change of OCV, H$_2$ and CO evolution rates and CH$_4$ consumption rate decreased as $P(CH_4)$ was raised. This is due to the competitive adsorption of C and OH on Ni, which has been reported before\[1,2\]. The deposited C may deactivate the steam reforming and affects the OCV. On the temperature dependence, the OCV drastically changed with increasing the temperature. The OCV at 1073 K was determined by the $P(H_2O)/P(H_2)$ equilibrium, while the OCV at 1273 K was determined by the $\alpha(C)/P(CO)$ equilibrium. From these results, it appears that the surface state of Ni can be easily affected by temperature and $P(CH_4)$.

3.3 Anodic polarization of Ni/YSZ cermet anode

Polarization curves and outlet gas composition analysis under different fuels

Figure 4 shows anodic polarization curves and outlet gas evolution rate from Ni/YSZ cermet anode under different fuels: H$_2$-H$_2$O, CH$_4$-H$_2$O and dry CH$_4$.

In Fig.4(c), polarization curves under different fuels are shown. In H$_2$-H$_2$O fuel system, the polarization curve had the slope of $2F/RT$ ($F$: the Faraday constant, $R$: the gas constant.), as was reported before\[15-17\]. In CH$_4$-H$_2$O and dry CH$_4$ fuel system, the polarization curves were divided into two parts: one was a moderate slope region at low oxygen potential, the other was a steep slope region at higher oxygen potential.

In Fig. 4(a), outlet gases evolution rates under dry CH$_4$ are shown as a function of oxygen potential versus air. Broken line( CH$_4$(in) ) indicates the inlet CH$_4$ rate, which was kept constant during the experiment. The O$^{2-}$- evolution rate estimated from the gas evolution[ n(O$^{2-}$(meas.)) in Fig.4(a) ] almost agreed with the O$^{2-}$- fluxes calculated from the current density [ n(O$^{2-}$(calc.)) in Fig.4(a) ]. Hence the oxide ion flux through the electrolyte perfectly consumed at the anode. When the anode polarization was below $E=-750$ mV vs. air, H$_2$ and CO evolution rates increased with the relation of H$_2$/CO=2. The reaction of equation (4) occurred in this region. At higher oxygen potential than -750 mV vs. air, H$_2$O and CO$_2$ evolution might start. Carbon deposition was estimated from the difference between the CH$_4$ consumption and CO and CO$_2$ evolution. No carbon deposition was observed at higher oxygen potential than -750 mV vs.air though small carbon deposition occurred at open circuit and low oxygen potential.

In Fig.4(b), outlet gases evolution rates are shown under CH$_4$-H$_2$O fuel condition. Large amounts of H$_2$ and CO were generated by the steam reforming. Up to $E=-850$ mV vs. air, the oxidation seems to proceed with the relation of $\Delta H_2/\Delta CO=2$ ( $\Delta$ :increase of the gas evolution rate from the open circuit ), as was observed in the dry
CH$_4$ fuel condition. In other words, parallel reaction of (1) and (4) occurred in this oxygen potential region. At higher oxygen potential region than $E=-850$ mV vs. air, H$_2$O and CO$_2$ evolution was observed. A small carbon deposition \[ n(\text{C dep.}) = n(\text{CH}_4\text{ con.}) - n(\text{CO}) - n(\text{CO}_2) \] was estimated to be completely eliminated at higher oxygen potential region than this point from the carbon mass balance.

From anodic polarization curves, the reactions for the current generation both in dry CH$_4$ and CH$_4$-H$_2$O fuel system were divided into two parts: 1) direct CH$_4$ oxidation at low oxygen potential, 2) H$_2$ and/or CO oxidation at medium to high oxygen potential.

At low oxygen potential region (from OCV to -900 mV vs. air), the apparent reaction was direct CH$_4$ oxidation (eq.(4)). The possible oxidation paths are: 1) direct oxidation of deposited carbon to generate CO, and 2) oxidation of H$_2$ occur at first, and subsequent formation of H$_2$O enhances the steam reforming to generate CO and H$_2$. At medium oxygen potential region (from -900 to -700 mV vs. air), the current densities of each polarization curve under different fuel system showed the following order: CH$_4$-H$_2$O$>$H$_2$-H$_2$O$>$dry CH$_4$. This order can be determined by the amount of H$_2$ and CO. At high oxygen potential region (higher than -700 mV vs. air), the polarization curves of different fuels showed small differences. In this region, the amount of H$_2$+CO is almost same in the different fuel systems. This suggests that the oxidation and steam reforming was fast enough to generate H$_2$+CO[4] at the high oxygen potential. However, Kawada et al.[5] once reported that CH$_4$ steam reforming was slow process than H$_2$ oxidation on Ni/YSZ cermet. One of the reason of this difference can be the CH$_4$ concentration in the feed gas. They adopted 100 vol% CH$_4$ as a fuel, although only about 4 vol% CH$_4$ was in this study.

Enough O$_2$ supply will make a perfect consumption of the deposited carbon (assuming that all CH$_4$ is converted to CO+2H$_2$) on Ni surface, which corresponds to 184 mA/cm$^2$ in this experimental condition. The highest current density obtained in the dry CH$_4$ condition exceeded this value and complete oxidation occurred at high oxygen potential. Thus operation under dry CH$_4$ fuel on Ni is possible if the oxygen potential is controlled higher than $E=-700$ mV vs. air.

Effect of $P$(CH$_4$) on anodic polarization

Figure 5 shows $P$(CH$_4$) effects on anodic polarization curves at $P$(H$_2$O)$=3.0$ kPa and 1173 K. With increasing $P$(CH$_4$) from 3.6 to 75.0 kPa, the OCV decreased as was observed at 1273 K. The polarization curve at $P$(CH$_4$)$=3.6$ kPa was divided into two parts, as was observed at 1273 K: CH$_4$ direct oxidation at moderate slope region, and H$_2$ and CO oxidation at steep slope region. On the other hand, the polarization curves above $P$(CH$_4$)$=11.7$ kPa showed a single slope. The overall reaction occurred at high $P$(CH$_4$) was eq.(4), which was supported by the outlet gas composition analysis. As stated before, the steam reforming rate slightly decreased as $P$(CH$_4$) was raised at open circuit. At high $P$(CH$_4$), significant amount of carbon deposition occurred because of the insufficient oxygen source. O$_2$ pumping by anodic polarization up to $E=-600$ mV vs. air would not be able to make up this gap. At higher oxygen potential than $E=-600$ mV vs. air, the polarization curves showed the current densities in the order of $P$(CH$_4$). This
means that the steam reforming was fast enough to supply H₂ or CO for oxidation [4],
though the carbon deposition occurred.

3.4 Anodic polarization of Fe/YSZ cermet anode

Figure 6 shows anodic polarization curves of Fe/YSZ cermet under H₂-H₂O,
CH₄-H₂O, and dry CH₄ fuel conditions. In H₂-H₂O fuel system, the slope of the
polarization curve of Fe/YSZ shows similar value to that of the Ni/YSZ anode, although
the current density obtained was small compared with Ni/YSZ. In dry CH₄ fuel
condition, the polarization curve was divided into three parts. The first step of the
polarization curve may be oxidation of deposited carbon up to -900 mV vs. air. The
second step of the polarization curve may be CO oxidation and Fe oxidation from -900
mV to -700 mV. The third step of the polarization curve may be oxidation of FeO to
Fe₃O₄ at higher than -700 mV region.

In CH₄-H₂O fuel system, the polarization curves showed low current density. A
drastic depression of current density was due to strong O or OH adsorption on Fe
surface to form FeO. Formation of FeO deactivates C or H₂ oxidation. However Fe was
not affected by H₂O in the H₂-H₂O fuel system. Hence the presence of H₂O in CH₄
easily makes an inactive Fe-OH or Fe-O surface layer and affects the oxidation of C and
H₂. In dry CH₄ fuel system, Fe anode can remain active because no oxidation happens on
the Fe surface. It should be noted that Fe can remain activated CH₄ under carbon
deposition condition for more than 200 hours[12]. Formation of Fe₃C gave a small
influence on the anode activities.

4. CONCLUSIONS

Ni and Fe were examined as anodes for oxidation of CH₄ under dry and relatively
low humidified conditions. Anodes examined here can be used in the following fuel
conditions:
<Case 1> CH₄+H₂O (S/C<1 condition) and O²⁻ pumping (Anodic polarized condition):
Carbon deposition was eliminated by O²⁻ supply at high oxygen potential and current
density. Ni can be a candidate for this case. Fe is not appropriate for this case due to low
steam reforming activities and surface oxidation.
<Case 2> Dry CH₄ direct-introduction ( O²⁻ is the only oxygen source): Ni and Fe can
be candidate for the anode. In the case of Ni, enough current density is needed to avoid
carbon deposition. In the case of Fe, enough current is better but not necessary.

In this study, the degradation of anode under long term operation was not
discussed because of complicated factors. This will be reported in the future.

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**Figure 1** Schematic representation of the test cell configuration.
(Anode part was Ni/YSZ cermet or Fe/YSZ cermet)
Under open circuit condition, $P(\text{H}_2\text{O})=3.0$ kPa

Fe/YSZ: estimated from $P(\text{H}_2\text{O})/P(\text{H}_2)$

Ni/YSZ: estimated from $P(\text{H}_2\text{O})/P(\text{H}_2)$

Ni/YSZ: estimated from $a(\text{O})/P(\text{CO})$

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Figure 2 CH$_4$ partial pressure effect on open circuit voltage(a) and outlet gas evolution rate(b) at Ni/YSZ and Fe/YSZ cermet anodes at 1273 K. ($P(\text{H}_2\text{O})=3.0$ kPa)

Under open circuit condition, $P(\text{H}_2\text{O})=3.0$ kPa

Ni, H$_2$

Ni, CH$_4$(con.)

Ni, CO

Fe, H$_2$

Fe, CO

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Figure 3 Temperature dependence of open circuit voltage(a) and outlet gas evolution rate(b) at Ni/YSZ and Fe/YSZ cermet anodes ($P(\text{CH}_4)=3.6$ kPa and $P(\text{H}_2\text{O})=3.0$ kPa).

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Figure 4 Anodic polarization and outlet gas evolution rate of Ni/YSZ under various fuel condition.

(a): Outlet gas evolution rate under dry CH₄ fuel
(b): Outlet gas evolution rates under CH₄-H₂O fuel
(c): Anodic polarization curves under various kinds of fuels

\( \text{H}_2-\text{H}_2\text{O}: \text{Ar}/\text{H}_2/\text{H}_2\text{O}=88/12/3, \)
\( \text{CH}_4-\text{H}_2\text{O}: \text{Ar}/\text{CH}_4/\text{H}_2\text{O}=96.4/3.6/3.0, \)
\( \text{dry CH}_4: \text{Ar}/\text{CH}_4=96.6/3.4. \)
Figure 5

$P(\text{CH}_4)$ dependence of anodic polarization curves of Ni/YSZ.

Figure 6

Anodic polarization of Fe/YSZ cermet under various fuel conditions.