INTERNAL REFORMING OF HYDROCARBON FUELS IN SOFCs WITH Ni-ScSZ ANODE

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ABSTRACT

The effects of carbon number in hydrocarbon fuels, steam-to-carbon ratios (S/Cs), fuel utilization ($U_f$), and CeO$_2$ dispersion into the anode on the internal reforming operation of solid oxide fuel cells (SOFCs) with Ni-ScSZ anode were examined at 1073K using the cell containing scandia-stabilized zirconia (ScSZ) electrolyte and Ni-ScSZ anode. The low reforming rate (20%) of methane led to a low maximum $U_f$ (only 20%). Propane, n-octane, and n-dodecane fuels were reformed easily, and a large amount of H$_2$ was produced, resulting in maximum $U_f$ of about 75, 80 and 85%, respectively. At S/C between 2 and 1 with n-dodecane fuel, stable operations at 100 mA (corresponding to about 45% $U_f$) were achieved for more than 120 hours with anode potential of about -0.77 V without degradation of Ni-ScSZ anode or Ni current collector. With increasing S/C, CO shift reaction was promoted but reforming reactions of hydrocarbons were not. With increasing $U_f$, oxidation reaction of H$_2$ and shift reaction of CO are promoted, and reforming reactions of hydrocarbons are slightly promoted. Dispersion of CeO$_2$ into the anode promoted H$_2$-producing reactions such as reforming of hydrocarbons.

INTRODUCTION

In principle, solid oxide fuel cells (SOFCs) can use hydrocarbons as well as hydrogen because the oxidant (oxide ion) is transported through the electrolyte from cathode to anode. However, direct oxidation or internal reforming of hydrocarbon fuels is very difficult with conventional nickel (Ni) based anodes (1-3). An external (or pre) reforming process is usually needed for higher hydrocarbons with conventional Ni–yttria stabilized zirconia (YSZ) cermet anode to avoid the carbon deposition on the anode and its related anode degradation. Recently, successful experiments of direct feeding of methane (CH$_4$) have been reported (4,5). Ukai et al. reported that Ni-scandia stabilized zirconia (ScSZ) cermet anode showed a lower overpotential and a higher stability than Ni-YSZ anode and could operate without disintegration for more than 200 hours with slightly humidified methane (5). We have already started the investigations on the direct feeding of n-dodecane as model fuel of kerosene with the cell consisting of ScSZ electrolyte and Ni-ScSZ cermet anode, and we have reported that Ni-based anode can be used for higher hydrocarbon fuels by selecting the operation conditions carefully (6-8).
In this study, we focused on the effect of several factors on the SOFC operation with internal reforming of higher hydrocarbon fuels. Effects of carbon number in the hydrocarbon fuels, steam to carbon ratios (S/Cs), fuel utilization ($U_f$) and CeO$_2$ dispersion into the anode were examined with the cell containing the ScSZ electrolyte and Ni-ScSZ anode.

**EXPERIMENTAL**

Electrolyte disks (0.5 mm thick) were prepared from 10 mol% Sc$_2$O$_3$ - 1 mol% CeO$_2$ - 89 mol% ZrC$_2$ (ScSZ, Daiichi kigenso kagaku kogyo Co., Ltd.). The powder was shaped into disks, pressed by CIP at 390 MPa, and sintered at 1673 K for 5 hours in air. The anode side of the sintered disks was polished.

Ni-ScSZ cermet anode with 50 vol% of Ni was prepared from NiO (Wako Chemicals Co., Ltd.) and ScSZ powders. Mixed and grounded powders were annealed at 1573 K for 5 hours in air and crushed in a ball mill. The slurry with 2-propanol was painted on the polished side of the electrolyte and fired at 1673K for 5 hours in air. On some prepared anodes, CeO$_2$ were dispersed as follows: 0.1 mL of an aqueous Ce(NO$_3$)$_3$ (0.005962 mol/L) was impregnated and then annealed at 1273K for 5 hours in air. Platinum (Pt) paste was used as a cathode electrode. The electrode area was 0.785 cm$^2$ for all samples. A platinum wire was attached on the side edge of the electrolyte as the reference electrode. Ni mesh and Pt mesh were used as current collector on the anode and cathode, respectively. Gold was used for lead wires. Pyrex glass was used as the sealing material for the anode side. A schematic drawing of the single cell is shown elsewhere (7,8).

Dry air was fed to the cathode side during the whole cell test at 50 mL/min. The NiO-ScSZ mixture was reduced in H$_2$-Ar mixture gas at 1173K for 2 hours, then cell tests were started at 1073 K. Methane (CH$_4$), propane (C$_3$H$_8$), $n$-octane (C$_8$H$_{18}$) and $n$-dodecane (C$_{12}$H$_{26}$) were used as fuel. For methane and propane fuel, about 380 $\mu$L/min and 150 $\mu$L/min, respectively, of fuel gas was mixed with humidified argon (Ar) gas and then fed into the anode chamber. $n$-octane and $n$-dodecane fuel was fed as described previously for $n$-dodecane (7,8): Ar gas was bubbled through liquid fuel and mixed with humidified Ar gas before being fed to the anode. From the gas chromatograph, the actual amounts of fed hydrocarbons were confirmed to be 14.8x10$^{-6}$ mol/min for methane, 5.4x10$^{-6}$ mol/min for propane, 2.4x10$^{-6}$ mol/min for $n$-octane and 1.7x10$^{-6}$ mol/min for $n$-dodecane. Fuel concentrations were about the same for all hydrocarbon fuels. The S/C ratio was controlled by water vapor pressure in the humidified Ar gas. As a result, all fuel gases were diluted within 50 mL/min of Ar gas.

The electrochemical measurements (the galvanostatic, impedance, and DC polarization measurements) were carried out with an electrochemical interface and an impedance/gain-phase analyzer (Solartron 1287A and 1260, Hampshire, UK) or with automatic polarization system (Hokuto Denko HZ-3000, Tokyo). Quantitative analysis of the outlet gas was carried out with gas chromatography (Agilent Technologies, Micro GC 3000, USA) and a dewpoint meter (Vaisala, DM-500, Helsinki, or General Eastern Instruments, Optica, MA). In this study, the fuel utilization was calculated from total amounts of C, H, and O in the outlet gas and the current passed through the electrolyte.
**RESULTS AND DISCUSSION**

**Effect of Carbon Number in Hydrocarbons**

Figure 1 (a) and (b) show the results of anodic polarization measurements and impedance measurements with methane, propane, n-octane and n-dodecane, respectively, at 1073 K. Except for the methane, open circuit voltages (OCV) were nearly the same, -0.98 V, and polarization curves also showed the same features. Maximum current densities ($I_{\text{max}}$) were about 160 mA/cm$^2$, 200 mA/cm$^2$ and 235 mA/cm$^2$ for propane, n-octane and n-dodecane, respectively and these values were equivalent to the $U_f$ of about 75, 80, and 85%, respectively. For methane, however, OCV was the lowest, about -0.92 V and $I_{\text{max}}$ was also the lowest as 45 mA/cm$^2$, which correspond to the $U_f$ as 20%. Carbon number dependence of outlet gas compositions under the OCV conditions at 1073 K is shown in Figure 2. Except for the methane, detected amounts of H$_2$ and CO were much

![Figure 1](image_url)

**Figure 1.** (a) Anodic polarization curves and (b) impedance spectra for the Ni-ScSZ anode with methane (CH$_4$), propane (C$_3$H$_8$), n-octane (C$_8$H$_{18}$) and n-dodecane (C$_{12}$H$_{26}$) fuels at 1073 K.

![Figure 2](image_url)

**Figure 2.** Carbon number dependence of outlet gas compositions under the OCV conditions at 1073 K. Amount of H$_2$O for methane (CH$_4$) fuel was a calculated value.
higher than methane and those of hydrocarbon components were very low. On the other hand, detected amount of H\textsubscript{2} for the methane was less than one-third of those for the other fuels and only 20\% of fed methane was reformed; this is the reason why the OCV and \( I_{\text{max}} \) for the methane was the lowest. Maximum \( U_f \) almost corresponded to the detected gas compositions except the hydrocarbon components; unreformed hydrocarbon components could not be used as fuel for SOFC operation. The results of impedance measurements for all fuels (Figure 1 (b)) were essentially the same although carbon numbers in the hydrocarbon fuels were different. This suggests that the anode reaction (electrochemical oxidation reaction) was the same for all hydrocarbon fuels; H\textsubscript{2} formed by reforming reactions and CO shift reaction should be used as fuel for electrochemical oxidation on the anode.

**Effect of Steam to Carbon Ratios**

Time dependence of the anode potentials at S/C = 0.5, 1.0 and 2.0 with \( n \)-dodecane fuel under the galvanostatic condition (\( I = 100 \) mA) at 1073K are shown in Figure 3. \( U_f \) was about 45\%. Stable operations were achieved at about \(-0.77 \) V for all S/Cs. After the cell tests, the Ni mesh current collector partly disintegrated only at S/C = 0.5; at other S/Cs, the anode and the current collector were not damaged. Carbon was slightly deposited on the gas inlet tube and gas outlet tube.

![Figure 3](image)

**Figure 3.** Time dependence of anode potentials at S/C = 0.5, 1, and 2 with \( n \)-dodecane fuel under galvanostatic condition (\( I = 100 \) or 150 mA) at 1073 K. Fuel utilization under 100 and 150 mA were about 45 and 66\%, respectively.

Figures 4 (a) and (b) show the S/C dependence of outlet gas compositions with \( n \)-dodecane fuel under the OCV condition and the galvanostatic condition (\( I = 100 \) mA) at 1073 K, respectively. Except for S/C = 0.5, at which Ni mesh disintegrated, detected amounts of H\textsubscript{2}O, H\textsubscript{2}, and CO\textsubscript{2} increase with increasing S/C under both the OCV and the galvanostatic conditions. Under the OCV condition, CO and CO\textsubscript{2}, which were formed only by reforming reaction, were not detected, and the detected amount of H\textsubscript{2} was also very small for the cell with Au anode and Au current collector. In contrast, CO, CO\textsubscript{2}, and a large amount of H\textsubscript{2} were detected. The amount of C\textsubscript{2}H\textsubscript{4} detected was much smaller than that with Au anode for the cells with Ni anode and Ni current collector; however, detected amounts of CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{6} were almost the same.
Figure 4. S/C dependence of outlet gas compositions with n-dodecane fuel under OCV condition and galvanostatic condition (I = 100 mA) for the Ni-ScSZ anode at 1073 K. Results for Au anode without Ni under OCV condition at S/C = 2 and CeO2 dispersed Ni-ScSZ anode under the galvanostatic condition at S/C = 2 also shown. Fuel utilization was about 45% under galvanostatic condition for all S/Cs.

This suggests that thermal decomposition reactions of n-dodecane occur without catalysis, but the steam reforming reactions of hydrocarbons proceed only with Ni anode and current collector. The catalytic activity of Ni is necessary for steam reforming reaction of hydrocarbons. Under the galvanostatic condition, detected amounts of hydrocarbon components were essentially the same for all S/Cs. Increasing S/C promotes the CO shift reaction but not the reforming reaction of hydrocarbon components. One of the reasons hydrocarbon components remained in the outlet gas is that some parts of gases flow out of the cell without contacting with Ni owing to the cell configuration.

Effect of Fuel Utilization

Time dependence of the anode potential at S/C = 2 with n-dodecane fuel under the galvanostatic condition (I = 150 mA) at 1073 K is also shown in Figure 3. $U_f$ was corresponding to about 66%. Anode potential became about −0.71 V after 120 hours with some potential degradation. After the cell test under $I = 150$ mA, carbon deposition on the outlet gas tube was negligible.

Figure 5 shows the $U_f$ dependence of gas composition with n-dodecane fuel at 1073 K. Detected amounts of H2 and CO were linearly decreased and those of H2O and CO2 were linearly increased with increasing of $U_f$. Hydrocarbon components also slightly decreased with increasing of $U_f$. Proceeding of electrochemical oxidation of H2 and CO shift reaction leaded to increasing of $U_f$. Reforming reactions of hydrocarbons were slightly promoted by increasing of $U_f$ but were not promoted by increasing of S/C although partial pressure of H2O increased with both increasing of $U_f$ and S/C; change of current density and/or change of anode potential may affect on the reforming reactions. Roughly speaking, the hydrogen concentration decreases linearly with fuel utilization. This is the same tendency with the thermodynamic calculation result. However, the extrapolated value becomes zero at $U_f = 90\%$. This is mainly due to the fact that there remain some amounts of CH4, C2H4 or C2H6.
Figure 5. Fuel utilization dependence of outlet gas composition with n-dodecane fuel at S/C = 2 and 1073 K.

Effect of CeO₂ Dispersion into the Anode

Volume fraction of dispersed CeO₂ in the anode was less than 1 vol% of the anode. Dispersed CeO₂ was detected by XRD measurement but was not detected by SEM observation and EDX elemental analysis maps; CeO₂ was finely dispersed in the anode. The result of outlet gas analysis for the cell with CeO₂ dispersed anode at 1073 K is also shown in Figure 3. Detected amount of H₂O decreased and that of H₂ obviously increased by CeO₂ dispersion. Amounts of hydrocarbon components also decreased slightly. It is suggested that CeO₂ dispersion into the anode affects the hydrogen producing reaction, in other words, reforming reactions of hydrocarbons are promoted by the dispersed CeO₂. Furthermore, this dispersion effect of CeO₂ was higher than that of samaria doped ceria (SDC).

DISCUSSION

The present results have revealed the interesting feature that the performance of Ni cermet anodes exhibits quite different behaviors in methane and other higher hydrocarbons. Reforming reaction occurs between hydrocarbons and adsorbed H₂O molecule on the Ni metal. The most important catalytic activity of nickel is to dissociate H-H, C-H, or C-C bonds. In the present anode configuration, the C-H bond in methane is quite stable, whereas C-C bonds in higher hydrocarbons are easily disconnected. Resulting decomposition products of methylene (CH₂) and methyl (CH₃) are quite reactive with water vapor to form hydrogen and CO. Since rather high value of fuel utilization was obtained for higher hydrocarbon fuels, reaction products that are detected in outlet gases are also expected to be reactive in anode atmosphere or on the nickel metals. On the other hand, reaction of methane with H₂O molecule does not tend to be promoted under the anodic polarization, resulting in quite low fuel utilization.
In the present anode configuration, there always remained some amount of methane and other \( \text{C}_2 \) compounds. When comparison is carefully made in concentration of such lower hydrocarbons, the following can be derived; with increasing S/C under the same fuel utilization, their amount did not show any significant change. On the other hand, their amounts decreased with increasing of \( U_f \) at the same S/C value. This implies that the water vapor emitted as electrochemical reaction products at the three phase boundaries is effectively utilized in the reforming process. In other words, some parts of water vapor that are introduced initially with hydrocarbons do not work fully as reactants. This is consistent with the observation by Bae et al. [9] that the main technological issue associated with the autothermal reforming process is diffusion. This is also consistent with our model [10,11] proposed to explain the experimental fact that oxygen was transferred from oxide to nickel surface. In this mode, it is also expected that hydrogen as dissociation product of hydrocarbons or water vapor can be transferred inside the nickel metal to the three phase boundaries. This model can provide one of the possible explanations for why electrochemical reactions are faster for hydrogen than carbon monoxide. Note that there is no path for carbon monoxide to be transferred inside condensed phases.

Reaction processes of fed hydrocarbon fuels are summarized as follows:

1. Thermal decomposition reactions of hydrocarbon fuels into the unstable lower hydrocarbons at the high temperature part of the inlet tube (more than 873 K) and on the Ni mesh current collector.
2. Steam reforming reactions of such decomposed hydrocarbons and shift reaction of CO on the Ni mesh current collector and Ni-ScSZ anode. In the present anode configuration, however, these reactions do not proceed completely. One of the possible limiting factors is diffusion of water vapor to the reforming reaction sites.
3. Electrochemical oxidation of \( \text{H}_2 \) formed during step 2.
4. Emitted water vapor is supplied for further reforming reaction or shift reaction in the vicinity of three phase boundaries, at least inside the cermet anodes.

**CONCLUSIONS**

In this study, effects of several factors on the SOFC operation with internal reforming of hydrocarbon fuels were examined at 1073 K. Hydrogen was used as fuel for electrochemical oxidation reaction on the anode, so it is important to promote the reforming reaction of hydrocarbons, especially stable methane, to obtain high fuel utilization. Increasing \( U_f \) and CeO\(_2\) dispersion into the anode were effective to promote reforming reactions of hydrocarbons. Moreover, with direct feeding of \( n \)-dodecane, stable operation was obtained at \( \text{S/C} = 1.0-2.0 \) with \( U_f = 45-65 \% \) for more than 120 h without anode or current collector disintegration.

**REFERENCES**

1. K. Eguchi, *Handbook of Fuel Cells - Fundamentals, Technology and Applications*,
W. Vielstich, H. A. Gasteiger, and A. Lamm, eds., John Wiley & Sons, 4, 1057 (2003).

2. T. Takeguchi, Y. Kani, T. Yano, R. Kikuchi, K. Eguchi, K. Tsujimoto, Y. Uchida, A. Ueno, K. Omoshiki, and M. Aizawa, J. Power Sources, 112, 588 (2002).

3. R. J. Gorte, H. Kim, and J. M. Vohs, J. Power Sources, 106, 10 (2002).

4. E. P. Murray, T. Tsai, and S. A. Barnett, Nature, 400, 649 (1999).

5. K. Ukai, Y. Mizutani, and Y. Kume, Solid Oxide Fuel Cells VII, H. Yokokawa and S. C. Singhal, eds., PV 2001-16, p. 375, The Electrochemical Society Proceedings Series, Pennington, NJ (2001).

6. H. Kishimoto, T. Horita, K. Yamaji, Y. P. Xiong, N. Sakai, and H. Yokokawa, Solid State Ionics, 175, 107-111 (2004).

7. H. Kishimoto, T. Horita, K. Yamaji, Y. P. Xiong, N. Sakai, and H. Yokokawa, “Feasibility of n-dodecane Fuel for SOFC with Ni-ScSZ Anode,” J. Electrochem. Soc., 152.

8. H. Kishimoto, T. Horita, K. Yamaji, Y. P. Xiong, N. Sakai, and H. Yokokawa, 6th European Solid Oxide Fuel Cell Forum, M. Mogensen, Editor, 3, 1560, European Fuel Cell Forum, Oberrohrdorf (2004).

9. J. M. Bae, S. Ahmed, R. Kumar, and E. Doss, “Microchannel development for autothermal reforming of hydrocarbon fuels,” J. Power Sources, in press.

10. T. Horita, K. Yamaji, T. Kato, N. Sakai, and H. Yokokawa, J. Power Sources, 131, 299 (2004).

11. H. Yokokawa, T. Horita, N. Sakai, K. Yamaji, M. E. Brito, Y-P. Xiong, and H. Kishimoto, Solid State Ionics, 174, 205 (2004).