

Direct Reforming of Methane–Ammonia Mixed Fuel on Ni–YSZ Anode of Solid Oxide Fuel Cells

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Abstract

To control the temperature distribution in the Ni–YSZ (yttria-stabilized zirconia) anode of solid oxide fuel cells (SOFCs) by efficiently utilizing the heat generated by electrochemical reactions, the supply of methane–ammonia mixed fuel is proposed. The reaction characteristics of reforming/decomposition of the mixed fuel on a Ni–YSZ catalyst are experimentally investigated. A mixture gas of methane, steam, ammonia, and balance argon is supplied to a packed bed catalyst placed in a quartz tube in an electric furnace. The crushed Ni–YSZ anode of SOFCs is used as the catalyst. The exhaust gas composition is analyzed by gas chromatography and the streamwise temperature distribution of the catalyst bed is measured by an infrared camera. It is found that ammonia decomposition preferentially proceeds and steam methane reforming becomes active after sufficient ammonia has been consumed. A low-temperature region is formed by steam methane reforming owing to its strongly endothermic nature. Its position moves downstream while its magnitude decreases as the ammonia concentration in the fuel increases. This shows that the local temperature distribution can be controlled by tuning the ratio of methane to ammonia in the mixed fuel. It is also found that, at a certain mixture ratio, the mixed fuel realizes a hydrogen production rate higher than that for only methane or ammonia.

Keywords

Solid oxide fuel cells, Steam methane reforming, Ammonia decomposition, Ni–YSZ anode, Mixed fuel

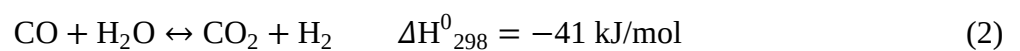
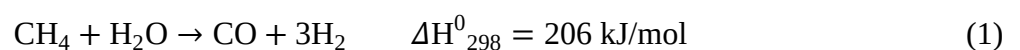
1. Introduction

As fuels for solid oxide fuel cells (SOFCs), various types of hydrogen carrier such as methane ¹⁻³, propane ⁴⁻⁶, methanol ^{3,7-9}, ethanol ^{3,7,10-13}, dimethyl ether ¹⁴⁻¹⁶, carbon monoxide ¹⁷⁻¹⁹, and ammonia ²⁰⁻²² have been considered as well as the conventional hydrogen fuel. This diversity of fuels is due to the high operating temperature of SOFCs, i.e., their working temperature, which ranges from 600 to 1000 °C, matches the temperature required for the on-site production of hydrogen through reforming reactions of hydrogen carriers. It is a common practice today to have a reformer in an SOFC system dedicated to the reforming of hydrogen carriers.

When a hydrocarbon fuel is employed among these hydrogen carriers, it is often reformed through the steam reforming reaction to produce a hydrogen-rich gas with the aid of a reforming catalyst such as Ni. Excess steam is usually contained in the supplied fuel to prevent the catalyst from coking²³⁻²⁵. In the case of ammonia, on the other hand, thermal decomposition is the main reaction because ammonia is easily decomposed on a Ni catalyst into a mixture gas of hydrogen and nitrogen. It is worth noting that the decomposition of ammonia does not require the addition of steam to the fuel flow. The reforming/decomposition reactions of these hydrogen carriers are endothermic, thus, the heat generated by the electrochemical reaction in SOFCs can be effectively utilized for the reforming/decomposition reactions in the reformer, which improves the efficiency of the SOFC system. The heat generated in an SOFC stack is transferred to the reformer by thermal radiation and convective heat transfer from the stack surface, which can also be regarded as an external cooling process of the stack.

As a more advanced operation mode, much attention has been paid to the direct reforming of SOFCs. Hydrogen carriers are directly supplied to the SOFCs in this operation instead of using a reformer. Typical SOFC anodes, such as Ni–YSZ (yttria-stabilized zirconia), contain Ni and the supplied fuel is reformed on the anode using Ni as a reforming catalyst. The reformer can thus be eliminated from the system, making it simple and cost-effective. Because the endothermic reforming reactions proceed inside the stack, it can be regarded as an internal cooling process of the stack. If the endothermic reaction in the stack can properly be controlled, it will also contribute to realizing a uniform stack temperature. This is an attractive advantage and the direct reforming operation of SOFCs has been intensively investigated.

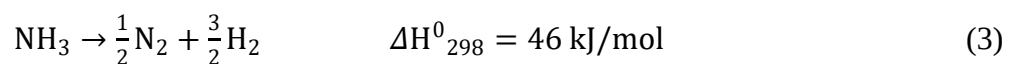
Methane is the most commonly adopted fuel in the literature of the direct reforming of SOFCs as it is the main component of city gas and biogas^{26–28}. When humidified methane is supplied to a Ni-based catalyst, a steam methane reforming reaction, Eq. (1), and a water–gas shift reaction, Eq. (2), proceed as dominant reactions.



The strongly endothermic nature of the steam methane reforming reaction proves its high potential to realize the advantages of the direct reforming operation explained above^{2,29–33}. One known problem is its rapid reaction near the inlet edge of fuel passages in cells. A large proportion of the supplied methane is reformed near the inlet, resulting in a decrease in local cell temperature. This leads to not only a decline of the cell performance but a steep temperature gradient, rather than a uniform temperature, which may generate

unacceptable thermal stress and increase the risk of mechanical failure of cells ^{34–36}. Several approaches have been attempted to cope with this problem. Peters et al. ³⁷ and Ni et al. ³⁸ proposed that methane be partially reformed by a reformer before it is supplied to SOFCs to prevent the intensive reforming reaction near the inlet of the cells. Andersson et al. ³⁹ experimentally investigated the effects of the pre-reforming rate, reported the effectiveness of using a pre-reformer, and successfully mitigated the temperature drop near the inlet. However, the use of a reformer cannot be the best solution because it is desirable to eliminate the reformer from the system by introducing the direct reforming operation as mentioned above. Boder et al. ⁴⁰ proposed the method of covering the surface of a Ni catalyst near the inlet region with Cu, which is a less active reforming catalyst. They also successfully prevented the sharp temperature drop near the inlet region. One drawback of this method is that there is little operation flexibility. The distribution of the Cu cover should be determined in the design stage and cannot be tuned during the operation, while in actual operation, the reforming reaction needs to be controlled depending on the operational load.

Other than methane, the direct supply of ammonia to SOFCs is also drawing attention ²¹. The ammonia decomposition reaction can be expressed by the following Eq. (3).



This is also an endothermic reaction, but its reaction heat is less than that of steam methane reforming. The local temperature drop near the inlet is moderate but, in return, the advantage of excess heat utilization is also moderate. It is worth mentioning that the ammonia decomposition reaction does not require a supply of steam, which is one of the advantages of using ammonia as a fuel for SOFCs compared with the

reforming of hydrocarbons.

The reaction characteristics of the various hydrogen carriers such as the reaction rate and reaction heat are different from one another, but so far there seems to be no simple method of simultaneously achieving the high excess heat utilization and the suppression of the low-temperature region near the inlet in the direct reforming operation of SOFCs.

In this study, we propose a new approach to this problem: mixing fuels. Since the surface of a Ni catalyst is of primary importance for all reforming/decomposition reactions, if a mixed fuel is supplied, the reactions may compete with each other and proceed selectively. If this is the case, it provides us with an opportunity to delay the start of one (or more) reaction(s) by simply tuning the composition of the supplied mixture gas. It may also be possible to control the location and magnitude of the endothermic reactions while the amount of excess heat utilization is determined by the overall reactions taking place in the cells. Among the various types of fuel, we adopt a combination of methane and ammonia in this study. This is firstly because there is a large difference in the reaction activity of the two fuels ^{41–45}. Secondly, there is also a large difference in the endothermic reaction heat of the two reactions. So far, to the best of the authors' knowledge, not even basic data on the reactions of any mixed fuel of hydrogen carriers on the Ni–YSZ anodes of SOFCs with the aiming of controlling the reactions can be found in the literature, let alone the mixed fuel of methane and ammonia. Therefore, in this study, we experimentally clarify the characteristics of the reforming and decomposition reactions when methane–ammonia mixed fuel is supplied to Ni–YSZ catalysts, which represents the Ni–YSZ anode of SOFCs. The effects of the mixture composition and

catalyst temperature on the reaction rate are investigated. The temperature distribution of the catalyst is also measured at different mixture compositions to examine the possibility of controlling the local temperature of the cells. The efficiency of heat utilization is also evaluated.

2. Experimental

In this study, the experiments conducted are divided into two categories. The first is the experiment on the reaction characteristics of the methane-ammonia mixed fuel on the Ni–YSZ catalyst with the aim of understanding the local reaction characteristics under each condition. The second is the measurement of the catalyst temperature distribution. The effect of the mixture composition in the mixed fuel on the temperature distribution of the catalyst is investigated to examine the possibility of controlling the local temperature of cells.

2.1 Catalyst preparation

Ni–YSZ cermet (Ni : YSZ = 50 : 50 vol.%, 8 mol%Y₂O₃-ZrO₂) was used as a catalyst. NiO powder (Nickel (II) Oxide, Wako Pure Chemical Industries, Ltd.), YSZ powder (TOSOH-ZIRCONIA TZ-8Y, Tosoh Co.) were mixed with the addition of 3.3 wt% carbon black (Asahi #15, Asahi Carbon Co., Ltd.) as a pore-forming agent and ball-milled for 1 hour with zirconia balls and ethanol to disperse the particles. After milling, the ethanol was completely evaporated using a hot stirrer at approximately 130 °C. The resultant powder was uniaxially pressed in a die with a load of 64 MPa for 2 minutes to obtain a disk-shaped catalyst sample. The diameter and thickness of the disk were 30 mm and 3 mm, respectively. The disk was then sintered at 1400 °C for 5 hours and crushed into granules. By sieving with a mesh, the granules with a size ranging from 250 to 500 μm were screened and used as a catalyst. Note that NiO in the catalyst was reduced into Ni before the experiments. A mixture of nitrogen and hydrogen was supplied with a total flow rate of

100ml/min at a furnace temperature of 700 °C. The proportion of hydrogen in the mixture gas was set at 5% for the first 20 minutes and then increased to 10%. After that, the hydrogen concentration was increased by 10% every 5 minutes until it reached 100%. Finally, the catalyst was kept in pure hydrogen for 1 hour at 700 °C.

2.2 Experimental setup

To observe reactions under a certain condition accurately, it is necessary to keep the reaction amount as small as possible because the fuel concentration and catalyst temperature change through the reactions. Therefore, in the experiment to investigate the reforming characteristics of the mixed fuel, 0.3 g of the crushed catalyst, which corresponded to a streamwise length of 2.8 mm was packed in a quartz tube as shown in Fig. 1 (a). This enabled us to keep the reaction conditions in the catalyst as uniform as possible.

In the measurement of catalyst temperature distribution, on the other hand, 0.75 g and 1.5 g of the catalyst were packed to form lengths of 21 mm and 42 mm in the flow direction, respectively, as shown in Fig. 1 (b). The catalyst beds with sufficient lengths were employed to clearly observe the distribution of the local temperature.

Fig. 1 (c) shows a schematic picture of the gas supply system. A mixture gas of methane, steam, ammonia, and balance argon were supplied to the Ni–YSZ catalyst. The flow rates of methane, ammonia, and balance argon were controlled by mass flow controllers. Steam was supplied by passing methane and argon through a bubbler. The concentration of steam was controlled to the desired values by changing the

water bath temperature of the bubbler. The catalyst temperature was controlled by an electric furnace, whose temperature was monitored by a thermocouple attached to the quartz tube. The remaining ammonia and steam after the reforming reaction were eliminated respectively by a sulfuric acid trap and a cold trap. The flow rate of the exhaust gas was measured by a film flow meter. The exhaust gas concentration was measured by a gas chromatograph (GC-8A, Shimadzu Co.) to evaluate the reaction rates of methane and ammonia.

The electric furnace was slightly opened to measure the temperature distribution of the catalyst with an infrared (IR) camera (TVS-8500, NEC Avio). The IR camera was equipped with a 2-D InSb sensor with detection wavelength ranges of 3.4–4.1 μm and 4.5–5.1 μm . This enabled us to measure the surface temperature of the Ni–YSZ catalyst through the quartz tube. We performed a preliminary experiment to calibrate the IR camera. A K-type thermocouple was attached to the surface of a Ni–YSZ catalyst (not crushed) and the catalyst was placed in a quartz tube. Nitrogen was supplied to the catalyst so that no chemical reaction occurs. The surface temperature of the catalyst was measured by using both the attached thermocouple and the IR camera in a range of the furnace temperature from 600 to 750 °C. The emissivity of the Ni–YSZ surface assumed in IR imaging was used as a tuning parameter so that the output of the IR measurement can reproduce the temperature measured by the thermocouple. The emissivity was set at 0.98. The root-mean-square error of the IR measurements estimated on the basis of the thermocouple measurements is 0.5 K in the temperature range of this study.

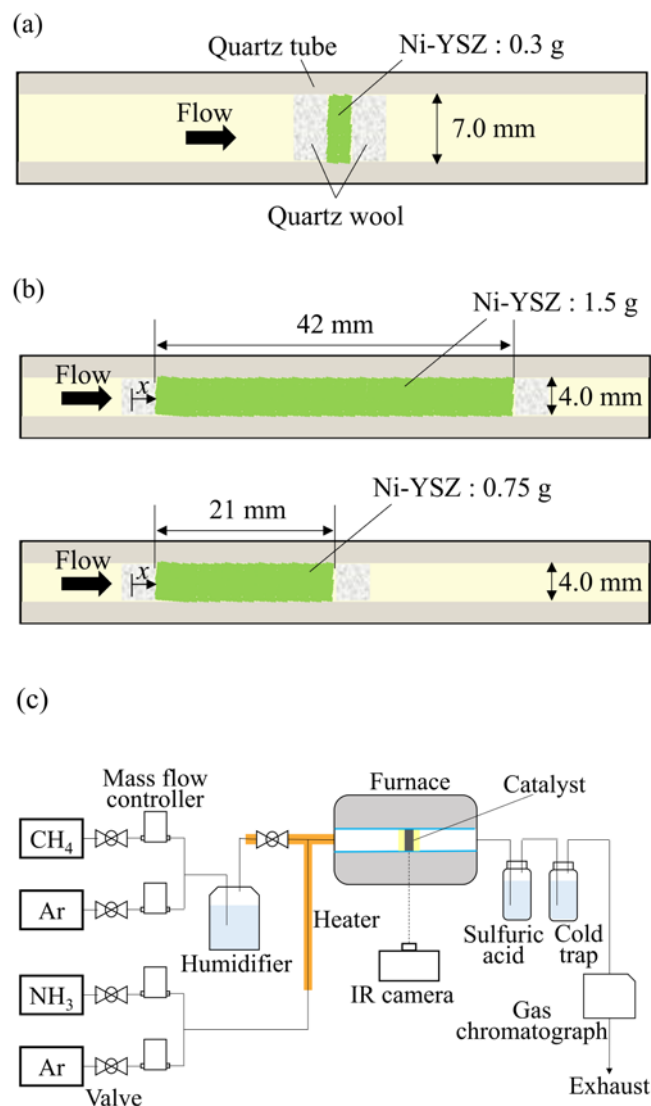


Fig. 1 Experimental setup. (a) Catalyst for the experiment on reforming characteristics, (b) catalyst for the measurement of the temperature distribution, and (c) gas supply system.

2.3 Experimental conditions

As the reaction characteristics of the mixed fuel, the effects of the gas composition and catalyst temperature on the reaction rates of steam methane reforming and ammonia decomposition were investigated. To investigate the effect of the gas composition, the mole fraction of methane was changed

from 0.056 to 0.17. For each mole fraction of methane, the mole fraction of ammonia was varied from 0 to 0.17. The total flow rate, the mole fractions of steam, and the temperature of the electric furnace were fixed at 360 ml/min, 0.28, and 700 °C, respectively. To investigate the effect of temperature, the temperature of the electric furnace in which the catalyst was placed was varied from 600 to 750 °C. The total flow rate and the mole fractions of methane and steam were fixed at 360 ml/min, 0.11, and 0.28, respectively. The mole fraction of ammonia was varied from 0 to 0.17.

In the measurement of temperature distributions, the flow rate of ammonia was 80 ml/min when a single fuel of ammonia without methane was supplied. The compositions of humidified methane and ammonia in the mixed fuel were determined by considering that the total hydrogen production rate from both methane and ammonia would become constant if the two fuels were completely converted to hydrogen. The total flow rate of the inlet gas and the temperature of the electric furnace were fixed at 360 ml/min and 700 °C, respectively.

2.4 Data reduction

To evaluate the experimental results, the reaction rates of methane and ammonia were calculated as

$$\text{CH}_4 \text{ Reforming rate} = \left(\frac{\Delta VF_{\text{CH}_4}}{VF_{\text{CH}_4, \text{in}}} \right) \times 100 = \left(1 - \frac{VF_{\text{CH}_4, \text{out}}}{VF_{\text{CH}_4, \text{in}}} \right) \times 100 \quad [\%], \quad (4)$$

$$\text{NH}_3 \text{ Decomposition rate} = \left(\frac{\Delta VF_{\text{NH}_3}}{VF_{\text{NH}_3, \text{in}}} \right) \times 100 = \left(1 - \frac{2VF_{\text{N}_2, \text{out}}}{VF_{\text{NH}_3, \text{in}}} \right) \times 100 \quad [\%], \quad (5)$$

where $VF_{\text{CH}_4, \text{in}}$ and $VF_{\text{NH}_3, \text{in}}$ are the volumetric flow rates of methane and ammonia at the inlet controlled by the mass flow controllers, whereas $VF_{\text{CH}_4, \text{out}}$ and $VF_{\text{N}_2, \text{out}}$ are those of methane and nitrogen at the outlet

measured by gas chromatography, respectively.

2.5 Stability, durability, and reproducibility

To confirm that the catalyst was not degraded during the experiment, the reaction rate under the reference condition, i.e., an ammonia flow rate of 40 ml/min with balance argon of 320 ml/min at the inlet, was examined at the beginning and end of each series of experiments. In all cases, the difference in ammonia decomposition rate between the beginning and end of the experiment was less than 3.5%, which confirms the stability of the catalyst and the reproducibility of the results.

3. Results and discussion

3.1 Local reaction characteristics of mixed fuel

The local reaction characteristics of methane–ammonia mixed fuel on a Ni–YSZ catalyst were examined.

The catalyst bed shown in Fig. 1 (a) was used.

3.1.1 Effect of gas composition

The effects of the gas composition were investigated keeping the furnace temperature at 700 °C. Figs. 2 (a) and (b) show the methane reforming and ammonia decomposition rates of the mixed fuel, respectively. Note that the data on the vertical axis in Fig. 2 (a) are those obtained when the mole fraction of ammonia in the mixed fuel is zero, i.e., a single fuel of humidified methane is supplied. In Fig. 2 (b), the results obtained when a single fuel of ammonia is supplied are included as a reference. It is shown in Fig. 2 (a) that the methane reforming rate decreases as the inlet mole fraction of ammonia increases. When the inlet mole fraction of ammonia is more than 0.10, the methane reforming is almost completely suppressed regardless of the inlet mole fraction of methane in the mixed fuel. It is shown in Fig. 2 (b) that, under this condition, the ammonia decomposition rate of the mixed fuel is close to that of the reference case, indicating that the ammonia decomposition reaction preferentially proceeds and methane has no effect on the ammonia decomposition reaction. When the inlet mole fraction of ammonia is relatively low, on the other hand, differences in ammonia decomposition rate are observed between the mixed fuels and the reference. This shows that the ammonia decomposition reaction is affected by the steam methane reforming reaction.

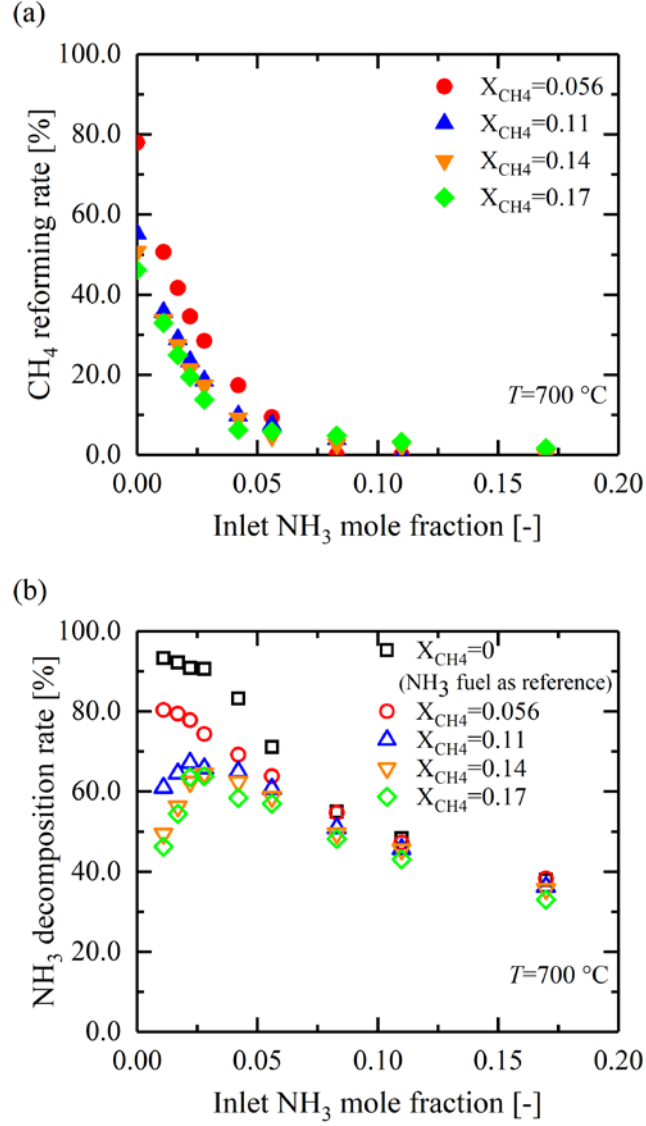
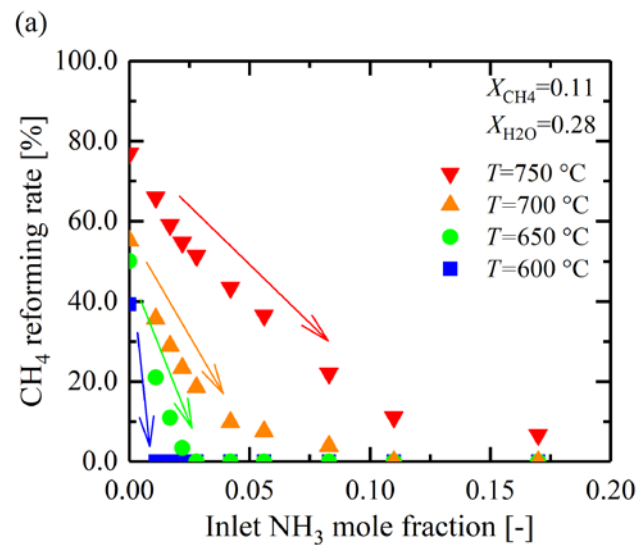


Fig. 2 Effect of mixture composition (a) on CH_4 reforming and (b) on NH_3 decomposition rates.

3.1.2 Effect of temperature

To investigate the effects of the local temperature, the furnace temperature was varied in a range from 600 to 750 °C. Figs. 3 (a) and (b) show the methane reforming and the ammonia decomposition rates, respectively. It is shown in Fig. 3 (a) that the methane reforming rate increases with the temperature. On the other hand, the gradient of the methane reforming rate as a function of the inlet ammonia mole fraction

becomes gentle with increasing temperature, as shown by arrows in Fig. 3 (a). This indicates that, with increasing temperature, the increase in the reaction activity of steam methane reforming is larger than that of ammonia decomposition and the reaction activity of ammonia decomposition becomes relatively lower. This mitigates the effect of ammonia in the mixed fuel on suppressing the steam methane reforming. It is shown in Fig. 3 (b) that the ammonia decomposition rate decreases even when the temperature increases when the mole fraction of ammonia in the mixed fuel is less than 0.03. This also implies that the effect of ammonia in the mixed fuel on suppressing the steam methane reforming decreases with increasing temperature.



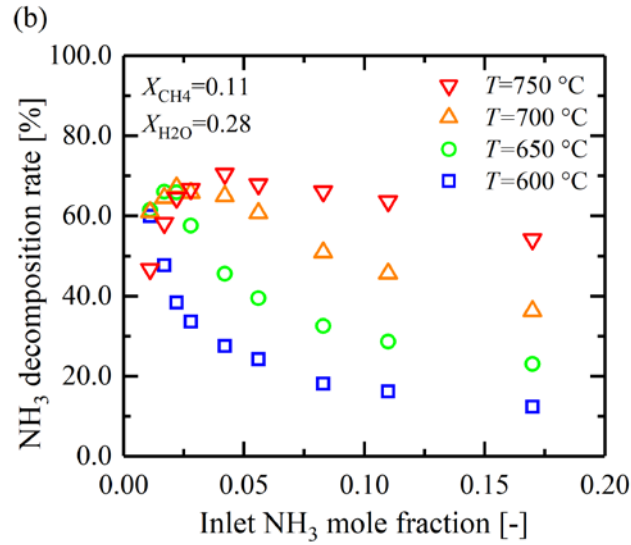


Fig. 3 Effect of temperature (a) on CH_4 reforming and (b) on NH_3 decomposition rates.

3.2 Reaction of mixed fuel along length of catalyst

As discussed in the previous section, the ammonia decomposition reaction preferentially proceeds over the steam methane reforming reaction. Moreover, the steam methane reforming reaction has a strongly endothermic nature, which is suitable for efficient heat utilization, whereas the ammonia decomposition reaction has a weakly endothermic nature, which can realize a gentle temperature distribution. From these characteristics, in the case of using the mixed fuel, it can be predicted that ammonia decomposition preferentially proceeds mainly in the upstream region of the cell, thus avoiding the steep temperature drop around the inlet, and methane steam reforming, which probably follows the decomposition of ammonia, enables the high efficiency of heat utilization to be retained. Therefore, the temperature distribution along the length of the Ni-YSZ catalyst was investigated by using an IR camera. The hydrogen production rate and the amount of endothermic heat of both reactions were also examined.

In this analysis, the amount of the catalyst was increased to 0.75 g and 1.5 g, which were equivalent to the streamwise lengths of 21 mm and 42 mm, respectively. To clearly recognize changes in local temperature on the catalyst caused by the reactions, a subtraction process was applied to the thermal images obtained by the IR camera as follows. First, a thermal image when argon was supplied was obtained as a reference, as shown in Fig. 4 (a), then another image was obtained when the fuel was supplied, as shown in Fig. 4 (b). Fig. 4 (c) was then obtained as the difference between the two. There appears to be a temperature distribution in the spanwise direction; however, this is due to the measurement of the cylindrical tube from the side. Therefore, the temperature at the center of the flow channel was used as the representative temperature at each position x in the evaluation.

The flow rate of ammonia was 80 ml/min when a single fuel of ammonia without methane was supplied. The compositions of humidified methane and ammonia in the mixed fuel were determined by considering that the total hydrogen production rate from both methane and ammonia would become constant if the two fuels were completely converted to hydrogen. The total flow rate of the inlet gas was fixed at 360 ml/min and the temperature of the electric furnace was fixed at 700 °C.

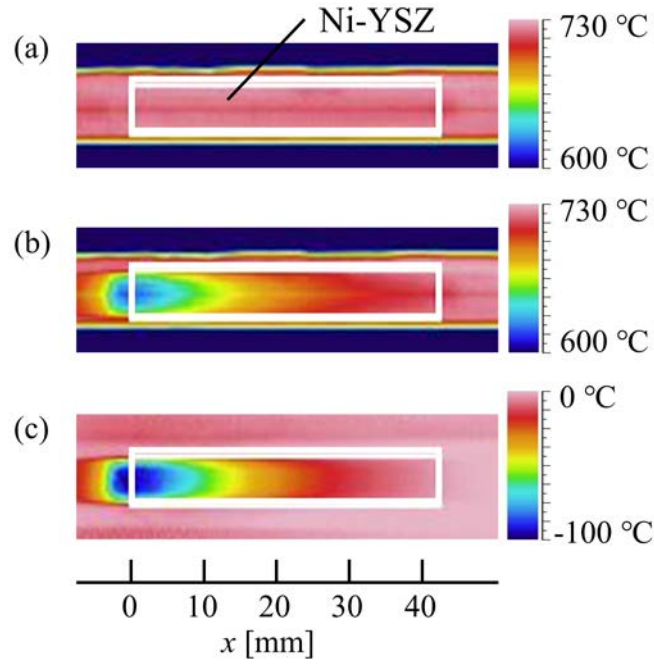


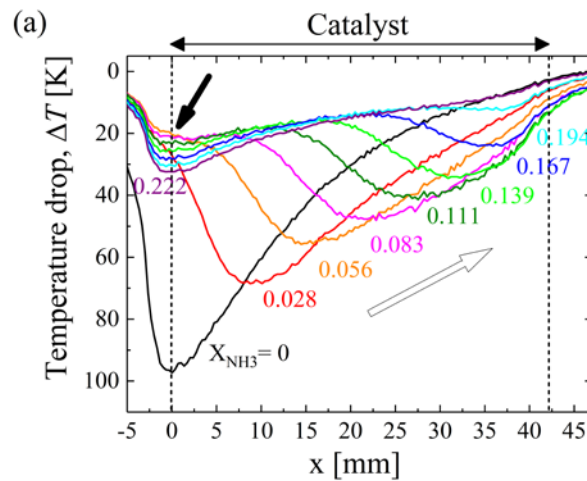
Fig. 4 Thermal images of the catalyst (a) without and (b) with reactions. (c) Difference between (a) and (b).

3.2.1 Temperature distribution

Figs. 5 (a) and (b) show the one-dimensional distributions of the temperature drop in the flow direction at the center of the flow channels with the catalyst lengths of 42 mm and 21 mm, respectively. For the catalyst with a length of 42 mm, as shown in Fig. 5 (a), when the mole fraction of ammonia is 0, i.e., humidified methane is supplied without ammonia, there is a sharp drop in local temperature at the upstream edge of the catalyst. This is because of the strongly endothermic nature of the reforming reaction. As the mole fraction of ammonia increases, the magnitude of the temperature drop decreases and the peak position moves downstream, as shown by a white arrow. When the mole fraction of ammonia further increases, another peak appears at the upstream edge, as shown by a black arrow. This is associated with the

endothermic ammonia decomposition. Fig. 5 (a) clearly shows that the temperature distribution can be controlled by tuning the inlet composition of the mixed fuel.

For the catalyst with a length of 21 mm, as shown in Fig. 5 (b), the temperature distribution where the catalyst is placed is almost the same as that in the upstream half of the catalyst with a length of 42 mm. On the other hand, in the downstream half, where no catalyst is placed, no peak of the temperature drop caused by steam methane reforming is observed. This is because there is no catalyst in the downstream half and the steam methane reforming reaction, which is delayed because of the ammonia decomposition reaction, cannot take place. Regarding the ammonia decomposition reaction, since it proceeds preferentially in the upstream region, a peak position similar to that observed in Fig. 5 (a) is also observed in Fig. 5 (b), as shown by a black arrow.



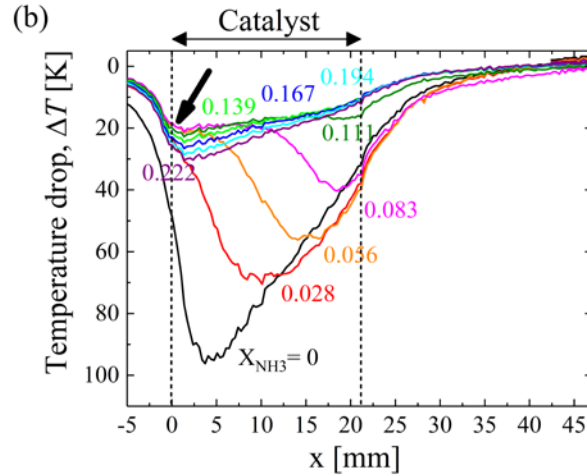


Fig. 5 Temperature distributions on the catalyst with lengths of (a) 42 mm and (b) 21 mm.

3.2.2 Hydrogen production rate

Figs. 6 (a) and (b) show the reaction rates of steam methane reforming and ammonia decomposition with the catalyst lengths of 42 mm and 21 mm, respectively. They also show the total hydrogen production rate from both reactions for each catalyst length. Note again that the compositions of humidified methane and ammonia in the mixed fuel are determined by considering that the total hydrogen production rate from both methane and ammonia would become constant if the two fuels were completely converted to hydrogen.

For the catalyst with a length of 42 mm, as shown in Fig. 6 (a), the hydrogen production rate slightly increases up to an ammonia mole fraction of 0.11. When the mole fraction of ammonia is more than 0.16, on the other hand, the hydrogen production rate starts to decrease. This is associated with the drop in the methane reforming rate caused by the reaction preference of ammonia decomposition at a high ammonia concentration.

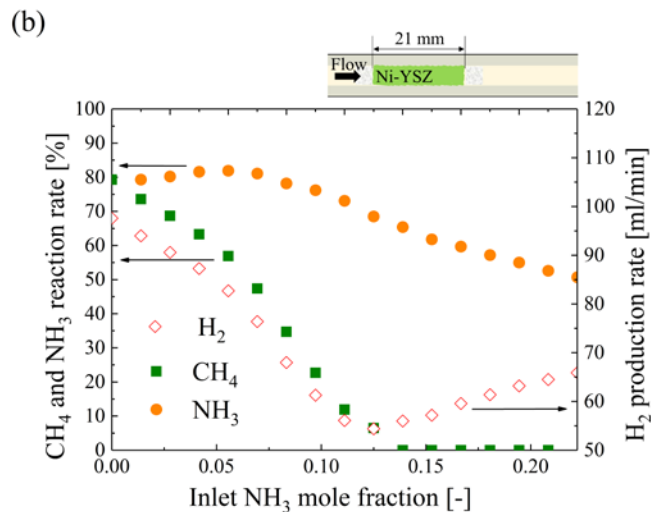
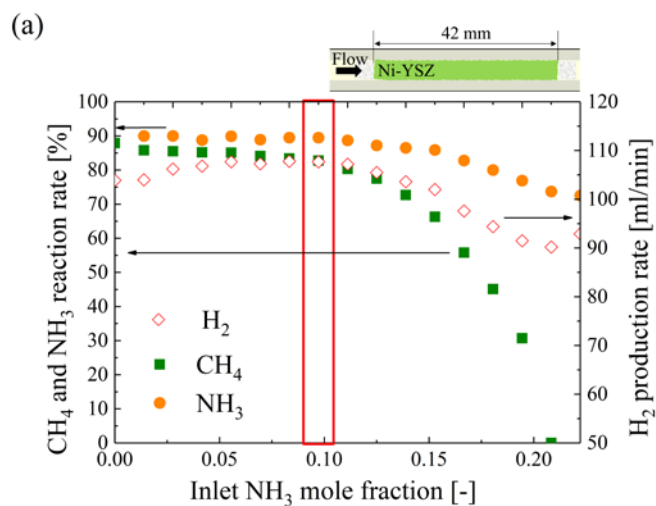
For the catalyst with a length of 21 mm, as shown in Fig. 6 (b), the methane reaction and hydrogen

production rates decrease with increasing ammonia even though the ammonia decomposition rate itself slightly increases up to a mole fraction of ammonia of 0.056. This indicates that sufficient steam methane reforming cannot take place within the catalyst with a length of 21 mm owing to the reaction preference of ammonia decomposition. It is worth mentioning that no steam methane reforming reaction is observed when the mole fraction of ammonia is larger than 0.14.

Fig. 6 (c) shows the differences in the reaction rates of methane and ammonia between the two lengths of the catalyst. Since the temperature distribution in the catalyst with a length of 21 mm is almost the same as that in the upstream half of the catalyst with a length of 42 mm, shown in Figs. 5 (a) and (b), it can be considered that the composition of the gas exhausted from the catalyst with a length of 21 mm represents that of the gas passing through the upstream half of the catalyst with a length of 42 mm. Therefore, the differences in the reaction rates of methane and ammonia between the two lengths of the catalyst shown in Fig. 6 (c) represent the estimated rates of the reactions that proceed in the downstream half of the catalyst with a length of 42 mm. It is shown that up to an ammonia mole fraction of 0.14, the estimated reaction rate of methane increases. This indicates that the region where the methane reforming reaction proceeds shifts to the downstream part of the catalyst because a longer region of the catalyst from the inlet was occupied mainly by the preferential reaction, namely, the ammonia decomposition reaction. When the mole fraction of ammonia is more than 0.14, on the other hand, the estimated reaction rate of methane reforming rapidly decreases. This is because the amount of ammonia remaining after passing through the upstream half of the catalyst increased; thus, the downstream half of the catalyst was also used mainly for the

ammonia decomposition reaction, resulting in the reduced activity of the steam methane reforming reaction.

From these results, it can be predicted that the remaining ammonia when the ammonia mole fraction is high can be consumed if the catalyst is further longer. Furthermore, this shows that the region of the catalyst in which steam methane reforming proceeds can be controlled by changing the composition of the mixed fuel.



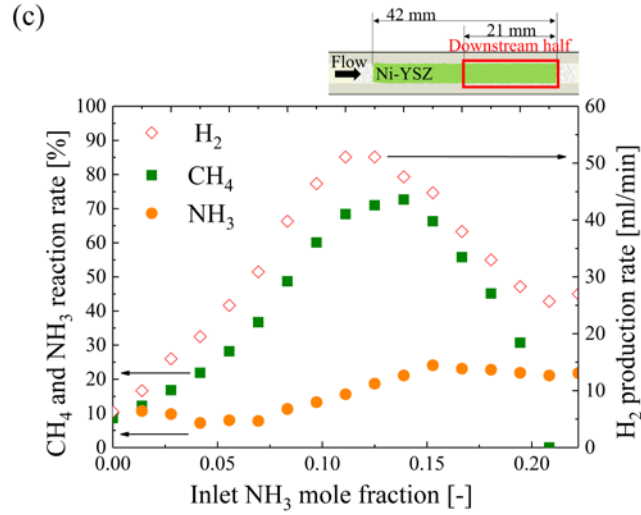


Fig. 6 Reaction rates and hydrogen production rate with the catalyst length of (a) 42 mm, (b) 21 mm, and (c) the difference of the two which represents the estimated rate of the reactions proceeding in the downstream half part of the catalyst with 42 mm length.

3.2.3 Heat utilization

Fig. 7 shows the amounts of endothermic heat associated with the steam methane reforming and ammonia decomposition reactions when the catalyst length is 42 mm. It also includes the average, minimum, and maximum temperatures within the catalyst for each condition. It is shown that the total amount of endothermic heat decreases with an increase of ammonia mole fraction, resulting in an increase in average temperature. This is because the amount of endothermic heat of the ammonia decomposition reaction is smaller than that of the steam methane reforming reaction.

When the ammonia concentration in the mixed fuel is 0.10, as shown by a red column in Fig. 6 (a) and Fig. 7, the hydrogen production rate is maximized; its amount is larger than that for the single fuel of

humidified methane and that for the single fuel of ammonia. In addition, although the amount of endothermic heat is 27% smaller than that of the single fuel of humidified methane because of the less endothermic nature of the ammonia decomposition reaction, it is 98% larger than that of the single fuel of ammonia, indicating the efficient utilization of the heat generated by the electrochemical reaction. Furthermore, the difference between the maximum and minimum temperatures within the catalyst is 56% smaller than that in the case of humidified methane without ammonia and almost equivalent to that of the single fuel of ammonia without methane. From these results, it can be concluded that the mixed fuel has advantages in terms of hydrogen production rate, temperature distribution, and heat utilization over the single fuels of humidified methane and ammonia.

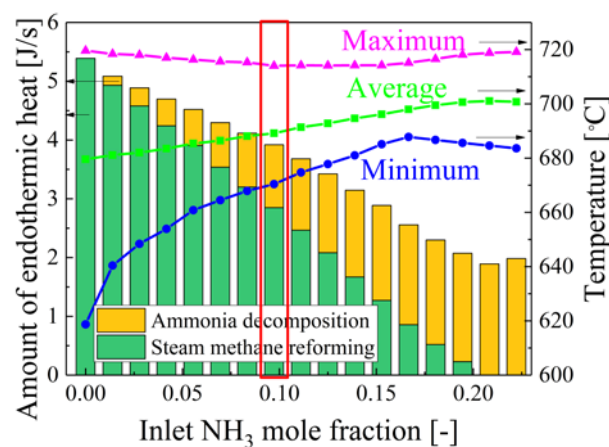


Fig. 7 Amounts of endothermic heat and catalyst temperature.

3.2.4 Water reuse in SOFCs

Considering the fact that ammonia decomposition preferentially proceeds over steam methane reforming, there is one more advantage that can be expected from mixing methane and ammonia. When

methane–ammonia mixed fuel is supplied to SOFCs, hydrogen is first produced from the decomposition of ammonia. This hydrogen is used as fuel for the electrochemical reaction to generate electricity and, as a result, water is produced. This water can be used for steam methane reforming so that hydrogen is again produced and used for the electrochemical reaction. This shows a possibility that the hydrogen atoms originally contained in ammonia act twice as a fuel for the electrochemical reaction. To clarify the reuse of water in the methane–ammonia mixed fuel in SOFCs, further research is needed.

4. Conclusions

To control the temperature distribution and make it gentle along the flow direction in the anode of SOFCs while efficiently utilizing the heat generated by the electrochemical reaction, the concept of mixing fuels was examined. The combination of methane and ammonia, which have large differences in their reaction activity and endothermic nature, was adopted, and the fundamental characteristics of the reforming/decomposition reaction of methane–ammonia mixed fuel on a Ni–YSZ catalyst were experimentally investigated. It was found that the ammonia decomposition reaction preferentially proceeded over the steam methane reforming reaction when methane and ammonia coexisted. When the mole fraction of methane in the mixed fuel was large, the ammonia decomposition reaction was partially suppressed. On the other hand, the steam methane reforming reaction was immediately suppressed even when a small amount of ammonia existed. As a result, as the mole fraction of ammonia in the mixed fuel was increased, ammonia was preferentially consumed and the reaction region of steam methane reforming on the catalyst was moved downstream, resulting in the shift of the position where the temperature of the catalyst sharply drops. The temperature distribution can be controlled by tuning the compositions of methane and ammonia in the mixed fuel.

When the mixture ratio of methane to ammonia was suitably adjusted, a higher hydrogen production rate was achieved compared with the cases of a single fuel of humidified methane and a single fuel of ammonia. The temperature difference within the catalyst was 56% smaller than that in the case of humidified methane and the amount of endothermic heat was 98% larger than that in the case of ammonia.

Moreover, it shows a possibility that the hydrogen atoms originally contained in ammonia are used twice as a fuel for electrochemical reaction in an SOFC. Therefore, methane–ammonia mixed fuel has advantages in terms of hydrogen production rate, temperature distribution, and heat utilization over the single fuels of humidified methane and ammonia, and the concept of mixing fuels with large differences in their reaction activity and endothermic nature is an attractive option for realizing the more flexible operation of SOFCs.

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Figure captions

- Fig. 1 Experimental setup. (a) Catalyst for the experiment on reforming characteristics, (b) catalyst for the measurement of the temperature distribution, and (c) gas supply system.
- Fig. 2 Effect of mixture composition (a) on CH_4 reforming and (b) on NH_3 decomposition rates.
- Fig. 3 Effect of temperature (a) on CH_4 reforming and (b) on NH_3 decomposition rates.
- Fig. 4 Thermal images of the catalyst (a) without and (b) with reactions. (c) Difference between (a) and (b).
- Fig. 5 Temperature distributions on the catalyst with lengths of (a) 42 mm and (b) 21 mm.
- Fig. 6 Reaction rates and hydrogen production rate with the catalyst length of (a) 42 mm, (b) 21 mm, and (c) the difference of the two which represents the estimated rate of the reactions proceeding in the downstream half part of the catalyst with 42 mm length.
- Fig. 7 Amounts of endothermic heat and catalyst temperature.

- Methane–Ammonia mixed fuel on Ni–YSZ anode of SOFCs is experimentally studied.
- Ammonia decomposition preferentially proceeds over steam methane reforming.
- Temperature distribution of anode catalyst is controlled by tuning mixture ratio.
- The mixed fuel has an equivalent heat utilization to a single fuel of methane.
- The mixed fuel realizes larger hydrogen production compared to methane and ammonia.