

Development of 1 kW-class Ammonia-fueled Solid Oxide Fuel Cell Stack

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Abstract

Power generation performance and long-term durability of ammonia-fueled solid oxide fuel cell (SOFC) systems are investigated with SOFC stacks consisting of 30 planar anode-supported cells. SOFC systems with three different operation modes are employed: direct ammonia, external decomposition and autothermal decomposition. A novel BaO/Ni/Sm₂O₃/MgO catalyst is newly developed for the external ammonia cracker, whereas a Co-Ce-Zr composite oxide catalyst is used for the autothermal ammonia cracker. Initial performance measurement and 1,000 h long-term durability test of the stacks are conducted. The stack fueled with direct ammonia achieves 1 kW power output with 52% DC electrical efficiency; a slight decrease in its performance compared with the stack with the mixture fuel of hydrogen and nitrogen is attributed to the decrease in the stack temperature caused by the endothermic ammonia decomposition reaction. The external ammonia cracker helps to maintain the stack temperature, improving the initial performance of the stack. The stack performance with the autothermal ammonia cracker is also comparable to those with the other operation modes. It is also demonstrated that the stacks fueled with ammonia have excellent stability during the long-term tests and 57% energy conversion efficiency at ca. 700 W electrical output is achieved with the external ammonia cracker.

Keywords: Ammonia, Catalyst, Durability, Solid Oxide Fuel Cell, Stack

1. Introduction

Hydrogen is expected to be the next generation energy source as a carbon-free fuel for stationary, mobile and transportation applications; however, storage and delivery of hydrogen remain a serious challenge that hinders wider-scale introduction of hydrogen-driven energy systems. On the other hand, chemical compounds containing hydrogen, such as hydrocarbons, alcohols and ammonia, can be used as hydrogen carriers to transport and store hydrogen. In most cases there are already well-established infrastructures in our society to safely and effectively handle these hydrogen compounds. Among the hydrogen carriers, ammonia has been attracting great attention [1-3] because of the following reasons.

(i) Ammonia is one of the most widely available commodity chemicals and its worldwide production is currently over 170 million tons per year as of 2018; (ii) a high volumetric hydrogen fraction (121 kg m^{-3}) and weight fraction (17.8 wt.%); (iii) ease in liquefaction below -33.4°C at atmospheric pressure or 8.5 atm at room temperature; (iv) a narrow flammable range of 16–25% in air; and last but not the least, (v) no carbon emission.

Fuel cells are the typical energy devices that can convert the chemical energy of hydrogen fuels to electricity through electrochemical oxidation and have been widely investigated because of their higher energy conversion efficiency than the conventional energy systems. Among the various types of fuel cells, solid oxide fuel cells (SOFCs) are expected to have better compatibility with ammonia fuel because of the following reasons. (i) Their zirconia-based solid electrolyte is stable in the ammonia atmosphere; (ii) ammonia can be catalytically decomposed into hydrogen and nitrogen on the conventional Ni-based anodes; and (iii) the excess heat released from the electrochemical oxidation of hydrogen in an SOFC stack can be efficiently used for the endothermic ammonia decomposition reaction, which can improve the overall energy and exergy efficiency of the systems. When ammonia is supplied directly to the SOFCs, the utilization of ammonia is described by the following two steps [4, 5] with the enthalpy change of 42 kJ mol^{-1} at 25°C for the reaction (1).



Encouraging results have been reported from experiments of ammonia-fueled SOFCs [6-14]. At the cell/stack level, Cinti et al. [15] investigated an ammonia-fueled SOFC short stack consisting of four planar cells and found that the stack performance with ammonia fuel was almost comparable to that with hydrogen fuel. At the system level, Perna et al. [16] proposed an interesting combination of an ammonia-fueled SOFC, off-gas hydrogen separation and hydrogen compression and storage, enabling electric and thermal outputs and hydrogen production.

The catalytic activity of Ni-based anode materials has been also experimentally investigated in the literature. Yang and coworkers [5, 17] investigated the catalytic activity of Ni-based anode materials for the ammonia decomposition reaction and suggested that hydrogen in the gas mixture has an inhibition effect on the reaction. Then, Okura et al. [18] investigated Ni-based catalysts modified by rare-earth elements and revealed that the rare-earth elements can promote the ammonia decomposition reaction by alleviating the hydrogen inhibition effect on the catalyst Ni surface. Kishimoto et al. [19] quantitatively evaluated the dependency of the ammonia decomposition rate on the gas partial pressures and established a reaction rate equation that can be used in the numerical modelling of the ammonia-fueled SOFCs. However, most of the analysis remained at the laboratory scale, and hence investigations on the large-scale reactors suitable for commercial SOFC systems are limited.

Stability of the ammonia-fueled SOFCs has been also investigated by several groups. Yang et al. [20] found that Ni in the Ni-YSZ anode is prone to be nitrated, resulting in morphological change in the anode microstructures. Hashinokuchi et al. [21] investigated the stability of a Ni-SDC anode fueled with ammonia and found that Cr addition is effective for not only enhancing the catalytic activity but also improving stability. Hagen et al. [22] tested an SOFC single cell with ammonia fuel for 1,500 h

and confirmed comparable stability of the performance with that with hydrogen fuel, although degradation by 2-4% kh⁻¹ remains an issue to be overcome.

Alternatively, a combined system consisting of an external ammonia cracker and an SOFC stack can be also considered primarily aiming for avoiding undesirable effects of ammonia on the cell-stack components and for improving long-term stability of the systems. Ideally, the endothermic heat required for the ammonia decomposition reaction can be provided from the SOFC stacks, which still realizes efficient heat management of the systems [23]. Various metals have been investigated as the catalysts for the ammonia decomposition reaction. Ruthenium was reported as among the most effective and stable catalyst for the ammonia decomposition [24]; however, its limited availability and hence the higher cost requires further development of alternative catalysts with high activity and abundance. In our previous report [25], a Ni/Y₂O₃-based catalyst was developed and the addition of SrO was found to enhance catalytic activity because of its strong basic property. Also, the stability of the catalyst was confirmed for 1,000 h under ammonia atmosphere at 700°C. However, the catalytic activity of the developed catalyst was still not satisfactory at low temperature range (below 550°C). Although other state-of-the-art catalysts were also reported in the literature [26, 27], large-scale production has not been realized and their long-term stability of the catalysts has to be confirmed.

As another SOFC system using ammonia, a combined system consisting of an autothermal ammonia cracker and an SOFC stack is also possible. The ammonia oxidation reaction is described as follows with an enthalpy change of -317 kJ mol⁻¹ at 25°C.



Considering the exothermic heat of the reaction (3) and the endothermic heat of the reaction (1), the ammonia cracking is thermo-neutral at the following reaction.



In an autothermal ammonia cracker, the ammonia oxidation reaction takes place and the generated heat can be used to quickly heat up the autothermal cracker itself and also the SOFC stack during the start-up of the SOFC systems. Noble metals such as Pt, Pd, Ru and Rh have been recognized as highly active catalysts for ammonia oxidation [28, 29]. In our previous report [25], a Co-Ce-Zr composite oxide catalyst for the autothermal ammonia cracking was demonstrated. The catalyst was operated at an air-to-fuel ratio (AFR) of 0.75 for 1,000 h and showed a stable ammonia conversion of ca. 80% without external heat supply.

Although there has been a great number of reports investigating SOFCs with ammonia fuel in laboratory scale, typically using button cells, those on the commercial-size cells and stacks with an electrical output range of kW remain limited. Therefore, it is still unclear if the insights obtained from the experiments using the button cells are applicable to the commercial-size SOFC stacks. In our research group, the ammonia-fueled SOFC stacks consisting of 10 anode-supported planar cells with an active area of 95 cm² were operated in the following three modes: direct ammonia supply, external decomposition supply and autothermal decomposition supply [25]. The catalysts for the external ammonia decomposition and the autothermal ammonia decomposition were developed and their stability was confirmed for 1,000 h. Also, an SOFC stack fueled with the direct ammonia supply was successfully operated with an electrical output of ca. 200 W for 1,000 h at 770°C. However, the electrical output of the short stack was still insufficient and further scale-up is required to provide more practical insights for realization of the ammonia-fueled SOFC systems. Also, the energy conversion efficiency was no more than 40% because of the lower fuel utilization around 60%. Furthermore, small degradation was observed in the stack voltage, which needs to be overcome to improve reliability of the systems.

Therefore, in this study, the performance of the SOFC stacks with 1 kW-class electrical output is investigated using commercial-size SOFC stacks consisting of 30 cells. Fuel utilization is increased to over 80% to achieve higher energy conversion efficiency. The three operation modes: direct ammonia supply, external decomposition supply and autothermal decomposition supply are similarly employed to compare the initial performance. A novel catalyst for the external ammonia decomposition is also developed to achieve higher catalytic activity and hence scalability, and its durability is tested for 1,000 h. In addition, stability of the ammonia-fueled SOFC stacks is evaluated for 1,000 h and the effect of external ammonia decomposition is investigated.

2. Experimental

2.1 SOFC Stack and Evaluation System

Figure 1 shows the stack evaluation system and the 30-cell SOFC stack used in this study, and Figure 2 shows the schematic flow diagram of the ammonia-fueled SOFC systems investigated in this study: (i) the direct ammonia-fueled SOFC system, (ii) the combined system of an external ammonia cracker and an SOFC stack and (iii) the combined system of an autothermal ammonia cracker and an SOFC stack.

The SOFC stack used in this study was fabricated by Noritake Co., Ltd. (Japan) and consisted of 30 anode-supported planar cells with a diameter of 120 mm and an active area of 95 cm². Detailed composition of the consisting cells is summarized in Table 1. The sintering temperature of the anode and cathode was 1350°C and 1100°C, respectively. Each cell was held in the metallic separators (SUS430) and sealed with glass material consisting of Na₂O-SiO₂-Al₂O₃. The cathode side of the separators was barrier-coated to avoid chromium evaporation.

Supplied fuel and air flow rates were controlled by mass flow controllers (SLA5851, Brooks

Instrument, U.S.A.). A part of the fuel gas line was heated above 100°C to avoid condensation of water produced in the autothermal ammonia cracker and SOFC stack. The air gas line was also pre-heated to 200°C before supplying to the SOFC stack. The anode off-gas went through a water trap and exhausted to the vent line, while the cathode off-gas was released to the atmosphere from the stack. The fuel gas pressure was measured at the upstream and downstream of the stack, whereas the air pressure was measured at the upstream of the stack. Inconel® 600 was used for the fuel supply tubes to avoid undesirable reaction with the ammonia fuel. The SOFC stack was installed in an electronic furnace, whose temperature was monitored using a K-type thermocouple situated in the inner wall of the furnace. The furnace temperature was kept at 750°C in this study.

The terminal voltage of each cell in the stack was measured using platinum wires ($\phi = 0.5$ mm), while the load current went through a bundle of platinum wires ($\phi = 1.0$ mm x 5). The stack temperature was measured using K-type thermocouples inserted to the top and bottom separators in the stack.

2.2 External Ammonia Decomposition Catalyst

In our previous report, the supported catalyst of SrO-Ni/Y₂O₃ for ammonia decomposition was developed and investigated [25]. It was found that the strong basic property of SrO as an additive enhanced ammonia decomposition [18, 30] and almost 100% ammonia was decomposed into hydrogen and nitrogen at 650°C at a space velocity (SV) of 2,400 h⁻¹. Long-term stability of the catalyst was also confirmed at the operation temperature of 700°C for 1,000 h at the SV of 2,400 h⁻¹, and no degradation was observed.

In this study, a novel catalyst, BaO/Ni/Sm₂O₃/MgO, is newly developed and verified to further improve the catalytic activity for ammonia decomposition and thereby to achieve scalability. Ni(NO₃)₂•6H₂O was used as a nickel source, Sm(NO₃)₃•6H₂O and Mg(NO₃)₂•6H₂O were used as support sources, and

$\text{Ba}(\text{NO}_3)_2$ was used as an additive source. All of these metal nitrates were supplied from FUJIFILM Wako Pure Chemical Corporation (Japan). First, Na_2CO_3 (FUJIFILM Wako Pure Chemical Corporation) was dissolved in distilled water. Then, $\text{Ba}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in distilled water and the resultant aqueous solution of these nitrates was added to the aqueous sodium carbonate solution under vigorous stirring at room temperature, which resulted in precipitation. The resultant precipitation was filtered and repeatedly washed with distilled water to remove sodium components. Then, the obtained wet solid was dried at 120°C for 15 h. The dried precursor was calcined at 600°C for 5 h in the air, and then the resultant powder was pelletized to a diameter of 3–6 mm and a thickness of 3–6 mm. The composition of the catalyst was evaluated using an inductively coupled plasma optical emission spectrometry (iCAP 7400 ICP-OES, Thermo Fisher Scientific, U.S.A.), and was confirmed to be $\text{BaO} : \text{Ni} : \text{Sm}_2\text{O}_3 : \text{MgO} = 6 : 45 : 12 : 37$ in weight.

To evaluate the ammonia conversion and long-term durability, the prepared catalyst was packed in a metal tube and ammonia was supplied at $\text{SV} = 2,400\text{--}5,000 \text{ h}^{-1}$. The catalyst temperature was controlled by an electric furnace. The ammonia conversion was measured by using a gas chromatograph (GC-3200, GL Sciences, Japan) with Haysep T and Molecular Sieve 5A columns.

For the stack experiment, about 105 mL of the developed catalyst was filled in the fuel channel located at the upstream of the SOFC stack and heated by the electric furnace as shown in Figure 2(b). The supplied ammonia flow rate of ammonia during the stack experiment was 5.22 L min^{-1} , which corresponded to an SV of ca. $3,000 \text{ h}^{-1}$. The supplied air flow rate at the cathode side was fixed at 30 L min^{-1} .

2.3 Autothermal Ammonia Cracker

A Co-Ce-Zr catalyst for the autothermal ammonia cracker was developed and verified in our previous report [25]. Metal nitrates of the constituent elements were dissolved in distilled water and mixed with an alkaline solution. The obtained precipitation was collected by suction filtration and then dried. The resultant solid was calcined at 500°C in the air and wet-milled with a binder using a ball mill. After the obtained catalyst slurry was wash-coated on a ceramic honeycomb support, the honeycomb was calcined at 500°C in the air. The catalyst on the honeycomb support was placed in a packed-bed flow reactor and installed at the upstream of the SOFC stack as schematically shown in Figure 2(c).

Table 2 summarizes the fuel conditions for the initial performance measurement of the SOFC stack using the autothermal ammonia cracker. Mixture gas of ammonia and air was supplied to the autothermal ammonia cracker with three different air-to-fuel ratio (AFR). A part of the supplied ammonia was oxidized to produce the heat required for the ammonia decomposition reaction. The thermo-neutral condition, i.e., reaction (4), corresponds to the AFR of 0.45. The amount of remaining ammonia after oxidation was maintained at 8.1–8.2 L min⁻¹ and the stack with the direct ammonia supply at the same ammonia flow rate was also measured as a reference. The supplied air flow rate at the cathode side was fixed at 90 L min⁻¹. At the beginning of the experiment, the reactor was preheated to ca. 200°C by an electric heater to initiate the ammonia oxidation on the honeycomb catalyst. After the oxidation starts, the reaction (4) proceeds without external heat supply.

2.4 Electrochemical Measurement

To evaluate the initial performance of the stacks, the current-voltage (I-V) and the current-power (I-P) characteristics were measured by controlling the current load on the stack using an electronic load (PLZ1004W, Kikusui Electronics Corp., Japan). Also, dependency of the stack performance on the fuel utilization was measured by altering the fuel gas supply rate at a constant current load.

After the measurement of the initial performance, long-term stability test was performed at a constant current load of 30 A ($= 0.316 \text{ A cm}^{-2}$) for 1,000 h. The fuel and air utilizations were fixed at 80% and 50%, respectively. Two stacks were tested for the stability test in this study; one was operated with the direct ammonia fuel (Figure 2(a)), and the other was with the externally decomposed ammonia fuel (Figure 2(b)). Note that the stability of the stack with the auto-thermal ammonia cracker (Figure 2(c)) was not tested in this study because the autothermal ammonia cracker is supposed to be used only during the start-up of the system. The voltage of each cell in the stack was monitored every second by using a multi-channel data logger (GL840, Graphtec Corp., Japan).

The DC electrical efficiency of a stack η was evaluated as follows based on the ammonia oxidation reaction (3).

$$\eta = \frac{VI}{\Delta H_{\text{NH}_3} F_{\text{NH}_3, \text{in}}} = \frac{nF\bar{V}U_f}{\Delta H_{\text{NH}_3}} \quad (5)$$

where V is the stack terminal voltage; $\bar{V}$ is the average cell terminal voltage; ΔH_{NH_3} is the enthalpy change of the reaction (3); $F_{\text{NH}_3, \text{in}}$ is the supplied molar flow rate of ammonia; n is the number of electrons involved in the reaction (3) ($n = 3$); F is the Faraday constant; and U_f is the fuel utilization. The experimental uncertainty on the evaluated DC electrical efficiency was also estimated based on the law of propagation of uncertainty. The errors that could occur in the cell voltages by the data logger, the stack current by the electronic load, and the ammonia flow rate by the mass flow controller were 0.1% F.S. (full scale), 0.1% F.S. + 0.2% S.V. (set value) and 1% S.V., respectively. As a result, the maximum uncertainty in the DC electrical efficiency in this study was estimated as no more than 0.75%.

3. Results and Discussion

3.1 Initial Performance

Figure 3 shows the initial performance of the SOFC stack fueled with the direct ammonia fuel. First, Figure 3(a) shows the I-V and I-P characteristics of the stack fueled with ammonia and those fueled

with hydrogen-nitrogen mixture fuel ($\text{H}_2:\text{N}_2 = 3:1$) as a reference. The ammonia flow rate F_{NH_3} was 8.19 L min^{-1} and the air flow rate at the cathode side F_{Air} was 50 L min^{-1} , which correspond to the fuel and air utilization of 85% and 50%, respectively, at the current load of 50 A ($= 0.526 \text{ A cm}^{-2}$). The open-circuit voltage (OCV) obtained with the direct ammonia fuel (1.222 V per cell) is almost the same as that with the mixture fuel (1.219 V per cell), which agrees with the results obtained from a five-cell SOFC stacks reported by Cinti et al. [15] The output power of 1048 W ($= 0.368 \text{ W cm}^{-2}$) at the current load of 50 A is achieved with the direct ammonia fuel, which is among the largest value reported in the literature for practical SOFC stacks fueled with ammonia. Also, the value is one order of magnitude larger than that obtained from an anion exchange membrane fuel cell (AEMFC) stack fueled with direct ammonia [31]. This clearly demonstrates the feasibility of the ammonia-fueled SOFCs even at the stack level. However, the performance of the stack fueled with ammonia is found to be slightly lower than that with the hydrogen-nitrogen mixture fuel. This difference can be attributed to the temperature drop in the stack caused by the endothermic ammonia decomposition reaction. The stack temperature measured at the bottom separator is found to decrease by ca. 15 K when ammonia fuel is supplied. Cinti et al. [15] also reported a similar temperature drop in the stack with ammonia fuel; however, the value was only about 3 K at the furnace temperature of 750 °C. As a result, their stack fueled with ammonia fuel showed almost the same performance as that with the mixture fuel. On the other hand, Yang et al. [20] reported lower performance of the electrolyte-supported button cells fueled with ammonia compared with that with the mixture fuel, although the temperature of the cells was likely to be the same because of the size of the cells. From these results of the cell/stack performance and their temperature, it can be concluded that there are two mechanisms of the performance decrease when the cell/stack was operated with ammonia fuel: in small-size cells, such as button cells, their performance is decreased owing to incomplete ammonia decomposition on the cell, whereas in large-size stacks, their performance is decreased owing to the temperature drop within the stack. For practical application of the ammonia-fueled SOFCs, precaution needs to be paid for the

thermal boundary conditions of the stack to minimize the influence of the temperature drop on the stack performance.

Next, Figure 3(b) shows the dependency of the stack voltage and electrical efficiency on the current load at a constant fuel utilization of 80% with the direct ammonia fuel. It is found that the stack voltage and the electrical efficiency decreases as the current density increases. At the current load of 50 A, although the output power is over 1 kW, the electrical efficiency is 52.3%, which is not sufficient compared with, for example, the residential SOFC system “ENE-FARM type S” commercialized in Japan [32]. It has an AC electrical efficiency of 53.5% as a system, which indicates that its DC electrical efficiency of the stack is higher than 53.5%. Therefore, it is suggested that the balance between the power output and the voltage drop needs to be considered to improve the DC electrical efficiency. For example, the DC electrical efficiency of the stack with 40 A current load is expected as ca. 55%, and its power output is still around 900 W.

Figure 4 shows the catalytic activity of the newly developed BaO/Ni/Sm₂O₃/MgO catalyst and that of the SrO-Ni/Y₂O₃ catalyst in our previous report [25] as a reference. First, Figure 4(a) shows the dependency of the ammonia conversion on the reactor temperature at SV = 2,400 h⁻¹. It is clearly shown that the ammonia conversion is improved with the developed catalyst at the lower temperatures. The reason can be attributed to the stronger basic property of BaO compared with the SrO and Y₂O₃. Although the external ammonia cracker was operated at 750°C in this study, and hence the improvement from the previous catalyst was not apparent in the stack testing, this result indicates possibility to use the external ammonia cracker at much lower temperatures. This will be beneficial for the thermal management of the entire SOFC systems. Although the ammonia conversion obtained in this study is slightly lower than that of the state-of-the-art catalysts, such as LiNH₂ [27] and carbon-nanotube-supported Fe [26], it is comparable to the ruthenium-based catalyst Ru/AlO₃ [33] at similar

temperature and SV conditions. It should be also emphasized that the scalability of the developed catalyst has been confirmed in this study.

Next, Figure 4(b) shows the time course of the ammonia conversion for 1,000 h at $SV = 5,000 \text{ h}^{-1}$. Note that the catalyst temperature was kept at 700°C during the durability test, but the measurement of the catalytic activity was carried out also at 515°C and 565°C . This is because the change in the catalytic activity was more clearly observed at lower temperatures. This result shows excellent stability of the developed catalyst for ammonia decomposition.

Figure 5 shows the initial performance of the SOFC stack fueled with the externally decomposed ammonia fuel. First, Figure 5(a) shows the I-V and I-P characteristics of the stack fueled with the externally decomposed ammonia and those with the hydrogen-nitrogen mixture fuel ($\text{H}_2:\text{N}_2 = 3:1$) as a reference. The ammonia flow rate F_{NH_3} was 5.22 L min^{-1} and the air flow rate at the cathode F_{Air} was 30 L min^{-1} , which corresponds to the fuel and air utilization of 80% and 50%, respectively, at the current load of 30 A. The space velocity for the ammonia decomposition catalyst was ca. $3,000 \text{ h}^{-1}$. It is found that the difference in performance between the two stacks is almost negligible. This is because the temperature drop caused by the endothermic ammonia decomposition reaction no longer occurs in the stack, which helps to maintain the stack temperature. It should be noted that the gas supply rates and the power output were decreased compared with the case in Figure 3 to pursue higher fuel utilization and higher electrical efficiency. As a result, although the maximum output power is decreased to 692 W at 30 A compared to 1048 W at 50 A in the previous case, the electrical efficiency is significantly improved from 52.3% to 56.2% at 30 A.

Next, Figure 5(b) shows the dependency of the stack voltage and the electrical efficiency on the fuel utilization at the current load of 30 A with the externally decomposed ammonia fuel. This test was

conducted to determine the condition that yields the highest DC electrical efficiency of the stack. It is found that the stack voltage decreases as the fuel utilization increases; however, the electrical efficiency has a peak value of 57.1% at the fuel utilization of 83%. Although long-term stability of the stack performance is not known at this point, the stack with the externally decomposed ammonia fuel can be operated at 83% fuel utilization; at this condition the output power is 678 W.

Figure 6 shows the I-V and I-P characteristics of the stacks fueled with the decomposed ammonia fuel provided by the autothermal cracker and that with the direct ammonia fuel. Although there is a small difference in the stack voltages near the OCV conditions, the curves are almost overlapping with each other, indicating that the steam and nitrogen generated from the ammonia oxidation in the autothermal cracker do not have an adverse influence on the stack performance. The reason of the lower voltage near the OCV conditions compared with the case of direct ammonia fuel is because of the contained steam in the fuel from the autothermal reactor. The OCV values obtained in the experiment are 31.3, 30.9 and 30.6 V for the AFR of 0.45, 0.60 and 0.75, respectively, which shows good agreement with the theoretical values of 31.3, 30.8 and 30.5 V, respectively, obtained using the Nernst equation by assuming that the oxygen is fully used for the ammonia oxidation and that the remaining ammonia is fully decomposed in the reactor.

3.2 1,000 h Durability Test

Stability of the stack performance was investigated for up to 1,000 h with a stack fueled with the direct ammonia and with that fueled with the externally decomposed ammonia. Figure 7 shows the average cell voltage of the stacks during the durability test. When ammonia was directly supplied to the stack (Stack 1, black line in Figure 7), a small decrease is observed in the average cell voltage at the beginning of the test. However, it is gradually recovered in the first 200 h and then the voltage becomes almost stable. The output power is ca. 690 W and the electrical efficiency is 55.9%. These results

clearly indicate the feasibility of the ammonia-fueled SOFC systems. Note that this is an improvement from our previous report [25], where ca. 5% degradation was observed when ammonia fuel was supplied to an SOFC short stack consisting of 10 planar cells. Also, this is superior to the value reported by Hagen et al. [22], where degradation by 2–4% kh^{-1} was reported in a single cell (53 x 53 mm^2) with pure ammonia fuel at 850°C.

After the durability test, Stack 1 was disassembled and the cells and separators were observed using the scanning electron microscope (SEM) and the electron probe micro analyzer (EPMA). It is found that there is no change in the anode and cathode microstructures compared with the original microstructures, but that the surface of the separators is affected by ammonia fuel. Figure 8 shows the cross-section of the separator including its surface on the anode side. It is clearly seen that the surface is significantly deformed and that Fe rich particles are observed on the surface. Also, nitrogen is detected in the separator bulk, indicating that the separator material (SUS430) is nitrided during the operation. Although the reaction rate is still unknown, it is found that the metal separator is prone to react with ammonia at high temperature to form a nitrided layer in the bulk and Fe rich particles on the surface. Nitriding of the anode materials was already reported by Yang et al. [20] from their button-cell experiments, whereas that of the separator materials is, as far as the authors recognize, first reported in this study.

Figure 9 shows the time course of the pressure loss measured in the anode channel of Stack 1, indicating that the pressure loss increases as time. This can be attributed to the aforementioned morphology change of the separator surface. The deformed separator surface makes the fuel channel slightly narrower and increases the pressure loss. Although this morphological change does not have a negative influence on the stack performance in the macroscopic point of view, it is liable to locally blocking or altering the fuel flow in the anode side, and eventually degrade the stack performance in

much longer time scale. Therefore, the issue of nitriding of the separator materials needs to be emphasized as a critical issue when SOFC stacks are operated with direct ammonia. Development of new separator materials and/or barrier coating technique is a possible approach to overcome this.

Next, another stack (Stack 2, red line in Figure 7) was operated with the external ammonia cracker. From the results in Figure 4, the supplied ammonia is considered to be fully decomposed in the cracker and the mixture gas of nitrogen and hydrogen is expected to be supplied to the stack. As expected from the results shown in Figure 3(a) and Figure 5(a), the initial performance is improved from the Stack 1 because of the higher stack temperature. The average cell voltage slightly decreases at the very beginning of the durability test, but it quickly recovers in the first 100 h, which is a similar trend as observed in Stack 1. After that, the stack voltage is almost stable and no degradation is observed for 1,000 h with ca. 705 W electrical output and 57.3% conversion efficiency. Note that the small spikes in the voltage observed every ca. 200h is caused by the scheduled ammonia cylinder exchanges.

Although the system without an external ammonia cracker is preferable in terms of simplicity and the cost of the whole system, the combined system of the ammonia decomposition catalyst developed in this study and an SOFC stack is also a possible choice to stably operate SOFC systems with ammonia fuel.

4. Conclusions

In this study, performance and durability of the 1 kW-class ammonia-fueled SOFC stacks have been demonstrated in three operation modes: the direct ammonia supply, the external ammonia decomposition supply, and the autothermal decomposition supply.

The performance of the stack with the direct ammonia fuel is found to be almost comparable to that of

the stacks fueled with hydrogen. Slight decrease in performance is attributed to the temperature decrease by the endothermic ammonia decomposition reaction. The maximum electrical output power of over 1 kW is among the largest value reported in the literature.

A novel BaO/Ni/Sm₂O₃/MgO catalyst is newly developed for the external ammonia decomposition, and its catalytic activity has been proved to be superior to that of the previously reported SrO-Ni/Y₂O₃ catalyst at lower temperatures. This is expected to be beneficial for the thermal management of the SOFC systems. 1,000 h durability of the catalyst is also confirmed with pure ammonia fuel at SV = 5,000 h⁻¹. The stack fueled with the decomposed ammonia is found to have almost the same performance as that with the hydrogen-nitrogen mixture fuel, and achieved the maximum DC electrical efficiency of 57.1% at 678 W power output.

The stack has been also operated with the autothermal ammonia cracker and its performance is found to be also comparable to that with direct ammonia fuel, indicating that the combustion products, such as nitrogen and steam, do not have a negative influence on the stack performance.

1,000 h durability tests have been performed at the operation mode of the direct ammonia supply and the external decomposition supply, and stable performance has been demonstrated at both operation modes. The direct ammonia supply mode achieved 668 W power output with 55.9% efficiency, while the external decomposition mode achieved 705 W with 57.3% efficiency. Post-mortem analysis of the stack operated with the direct ammonia fuel revealed the nitriding of the separator materials, resulting in morphology change of the separator surface. Although such morphology change did not have a negative influence on the stack performance in the time scale in this study, it is liable to alter the fuel flow within the stack and thereby degrade the stack performance in much longer time scale. Therefore, the utilization of the external ammonia cracker is considered as a possible choice to operate SOFC

stacks to avoid such adverse influence of the ammonia fuel on the stack materials.

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Figures

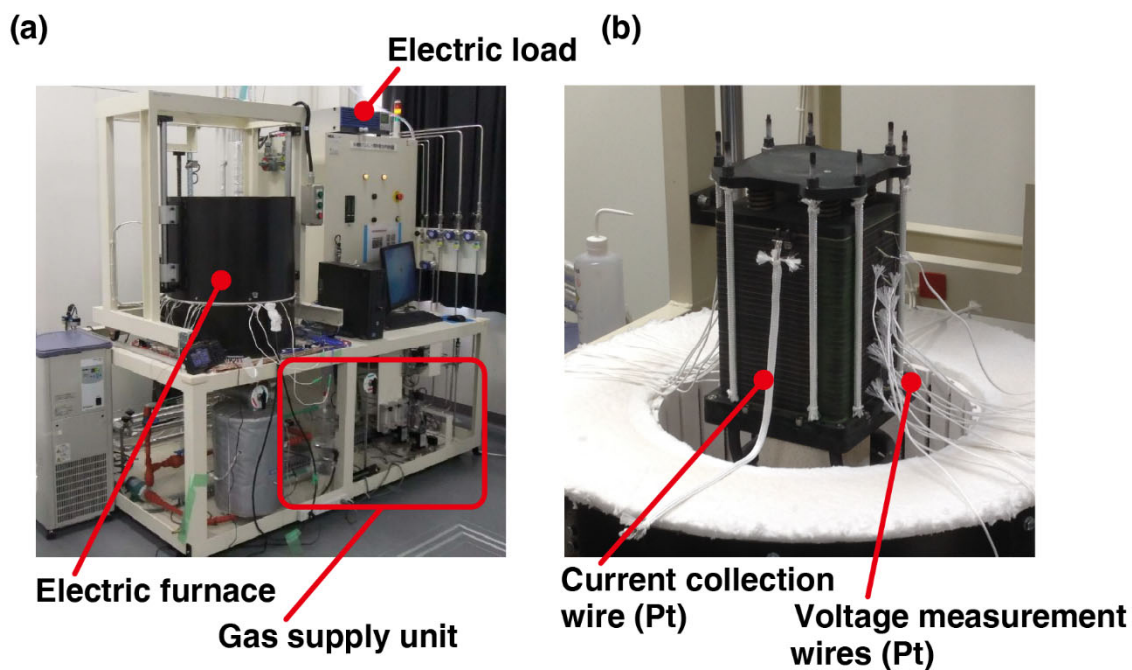


Figure 1: Photograph of (a) the stack evaluation system and (b) the 30-cell SOFC stack.

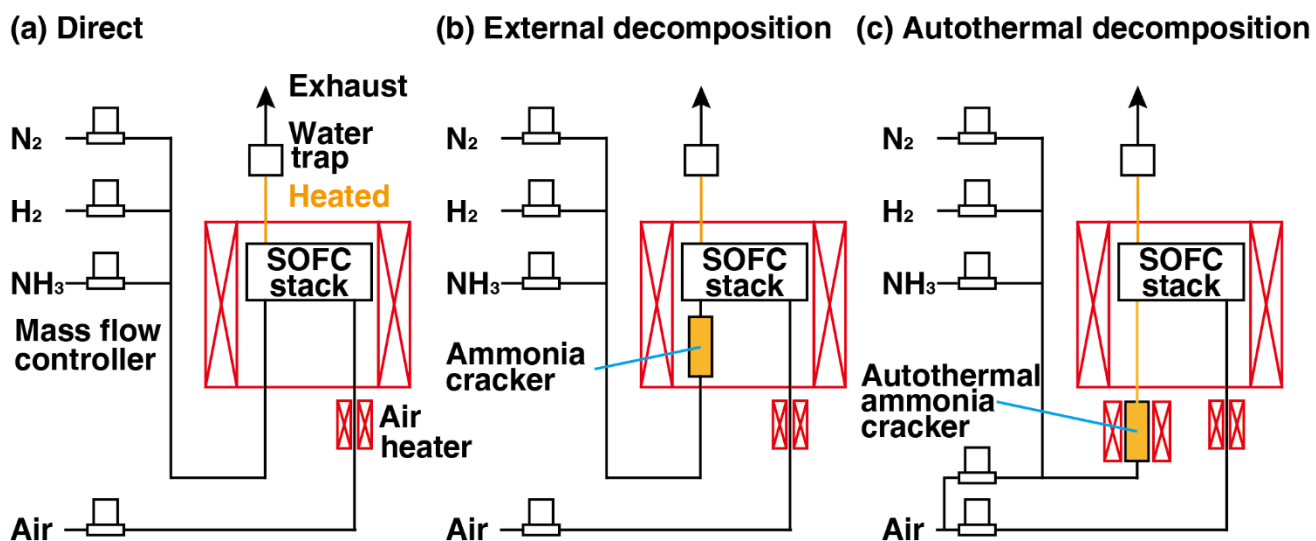


Figure 2: Schematic flow diagram of the ammonia-fueled SOFC systems.

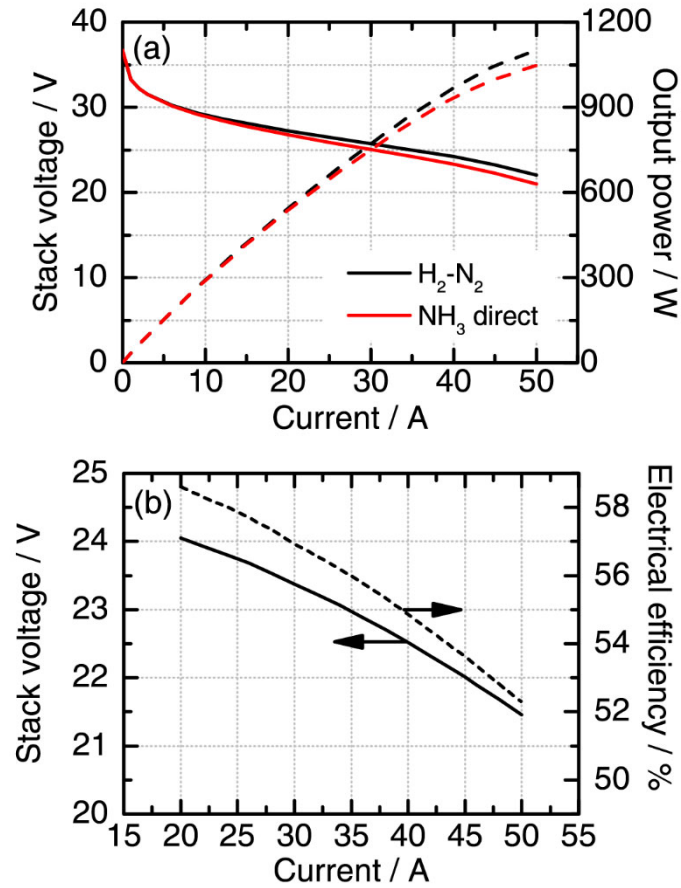


Figure 3: Performance of the SOFC stack fueled with direct ammonia fuel. (a) I-V and I-P characteristics of the stack with direct ammonia fuel ($F_{NH_3} = 8.19 \text{ L min}^{-1}$, $F_{Air} = 50 \text{ L min}^{-1}$) and hydrogen-nitrogen mixture fuel ($F_{H_2} = 12.3 \text{ L min}^{-1}$, $F_{N_2} = 6.14 \text{ L min}^{-1}$, $F_{Air} = 50 \text{ L min}^{-1}$). (b) Dependency of the stack voltage and electrical efficiency on the current load at a constant fuel utilization of 80%.

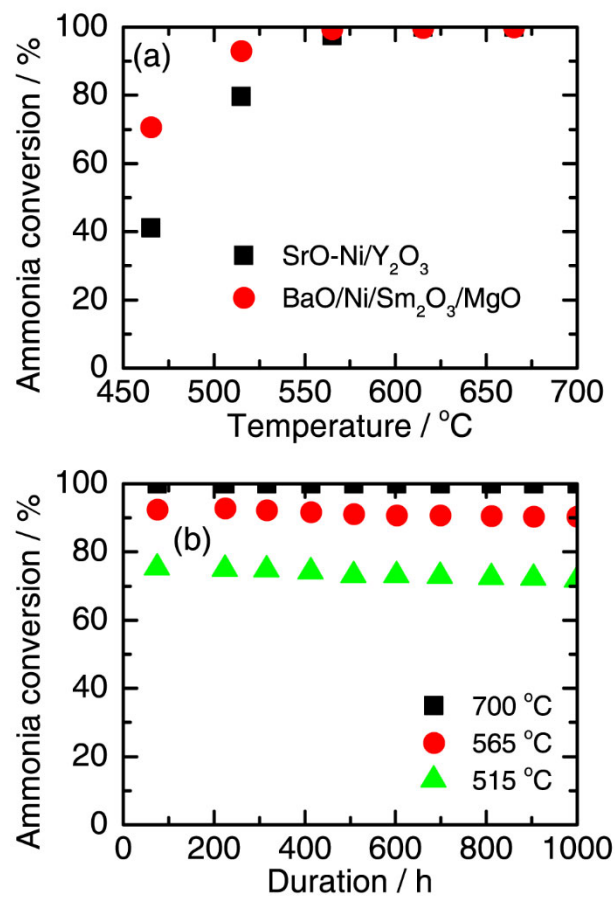


Figure 4: Characteristics of the BaO/Ni/Sm₂O₃/MgO catalyst for ammonia decomposition. (a) Dependency of the ammonia conversion on the reactor temperature at SV = 2,400 h⁻¹. (b) Durability of the catalyst over 1,000 h at SV = 5,000 h⁻¹.

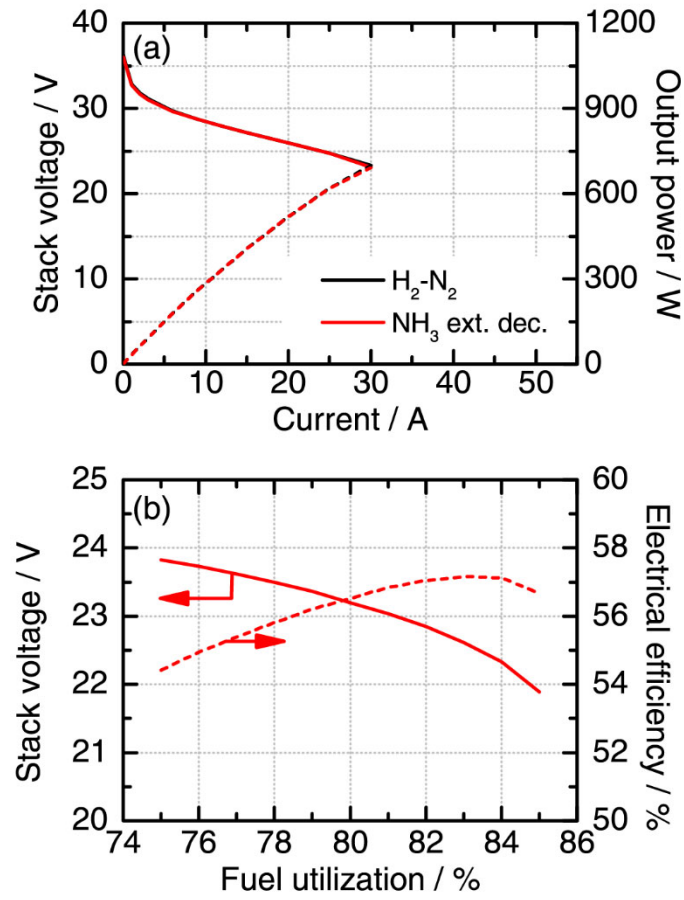


Figure 5: Performance of the SOFC stack fueled with externally decomposed ammonia. (a) I-V and I-P characteristics of the stack with externally decomposed ammonia ($F_{NH_3} = 5.22 \text{ L min}^{-1}$, $F_{Air} = 30 \text{ L min}^{-1}$) and with hydrogen-nitrogen mixture fuel. (b) Dependency of the stack voltage and the electrical efficiency on the fuel utilization at the current load of 30 A.

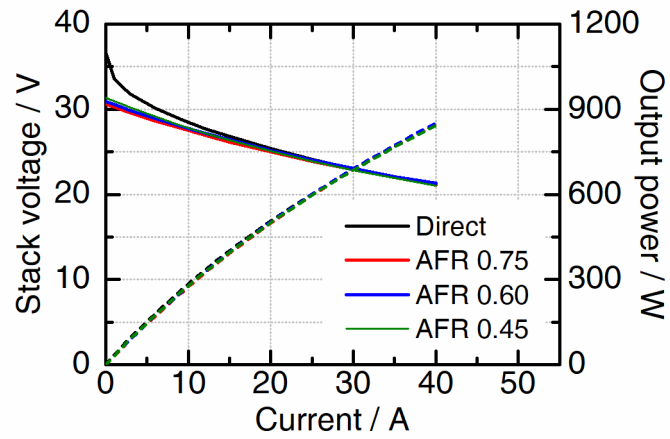


Figure 6: I-V and I-P characteristics of the stack with the autothermal ammonia cracker.

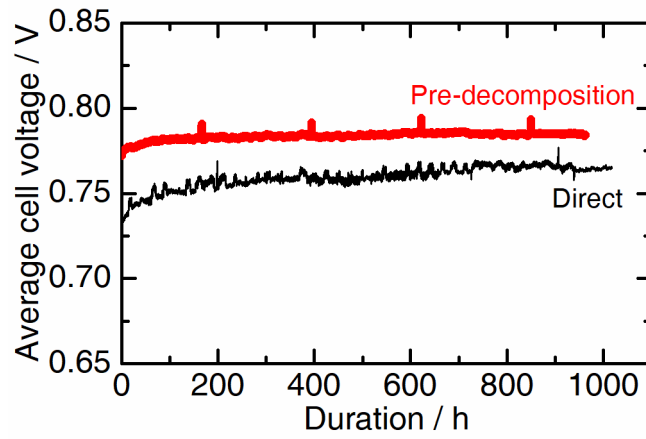


Figure 7: Average cell voltage during 1,000 h durability test.

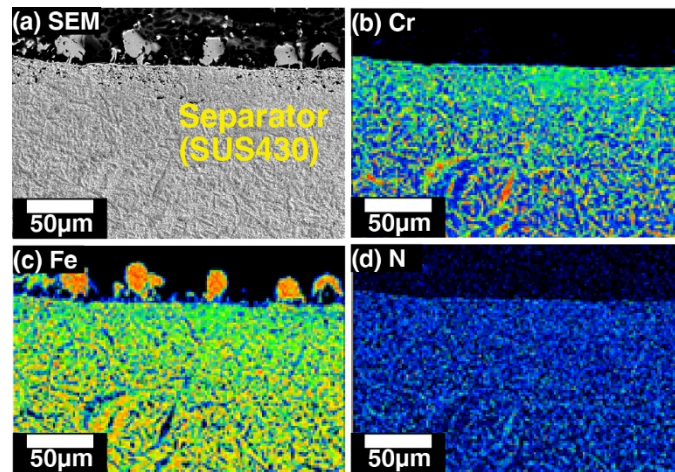


Figure 8: Cross-sectional images of the separator on the anode side after 1,000 h durability test with direct ammonia fuel. (a) scanning electron microscopy image, and the distribution of (b) Cr, (c) Fe and (d) Ni.

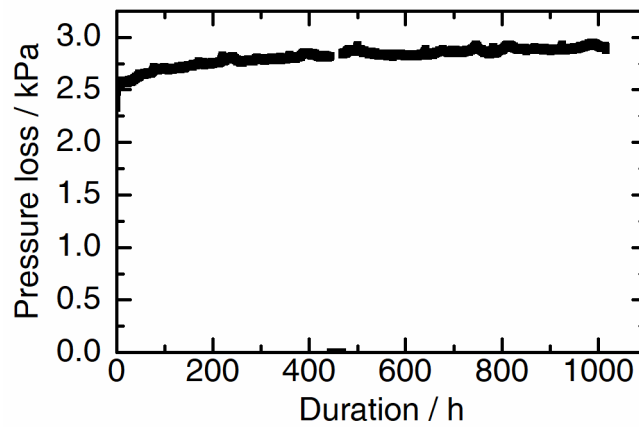


Figure 9: Pressure loss in the anode channel in the stack during the 1,000 h durability test with direct ammonia fuel.

Table Captions

Table 1: Configuration of the anode-supported cell stacks.

Table 2: Experimental conditions with the autothermal ammonia cracker.

Tables

Table 1: Configuration of the anode-supported cell stacks.

Layer	Composition	Thickness / μm	Diameter / mm
Anode support layer	Ni/YSZ (NiO:YSZ = 60:40 wt.%)	1,000–1,100	120
Anode functional layer	Ni/YSZ (NiO:YSZ = 60:40 wt.%)	7–13	120
Electrolyte layer	ZrO ₂ -based material	7–13	120
Cathode layer	LaNiO-based perovskite material	30–90	110

Table 2: Experimental conditions with the autothermal ammonia cracker.

	Supplied NH ₃ / L min ⁻¹	Air / L min ⁻¹	AFR / -	Oxidized NH ₃ / L min ⁻¹	Remaining NH ₃ / L min ⁻¹
Direct (ref)	8.2	0	0	0	8.2
AFR 0.45	9.3	4.2	0.45	1.2	8.1
AFR 0.60	9.8	5.9	0.60	1.7	8.1
AFR 0.75	10.3	7.7	0.75	2.2	8.1