Research and Development of Ambient-Temperature Hydrogenation Technology for Low-Energy Startup of Ammonia Power Generation

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Abstract

Ammonia FC power generation using SOFC (solid oxide fuel cell) is considered to be capable of producing high purity hydrogen and highly efficient power generation because the waste heat from fuel cell power generation can be used to heat ammonia when cracking it to hydrogen. However, it is known that waste heat from fuel cell cannot be utilized during start-up because of the low temperature of the fuel cell, and heating of the reformer by using electric heater is necessary resulting in a large energy loss. Therefore, we conducted research and development of hydrogenation technology at room temperature by the reaction of fluidized ammonia gas and MH (alkali metal hydride) for low-energy startup without using an electric heater.

1. Introduction

Currently, as various efforts to combat global warming are being promoted worldwide, countries around the world are working to expand the use of hydrogen as an energy source that does not emit greenhouse gases.

Since hydrogen is in a gaseous state at room temperature, it poses challenges in transportation and storage. As a means of doing so, ammonia has gained attention since it has a high hydrogen density, is easy to liquefy, and excels as a hydrogen carrier.

In ammonia research, in addition to being considered a combustion fuel for engines and gas turbines, extensive studies have been conducted on extracting hydrogen from ammonia for use as a fuel in fuel cells to generate electricity. However, when decomposing (cracking) ammonia into hydrogen and nitrogen, a significant amount of thermal energy is required, including heating the catalyst.

During the startup of a fuel cell power generation system using ammonia, there is no heat source available for ammonia cracking. Therefore, it is necessary to preheat the catalyst using an electric heater or other means. However, this approach has the challenges of requiring a long heating time and consuming a large amount of energy. Alternatively, ammonia combustion could be used as a heat source instead of an electric heater, but this introduces a new issue of NOx emissions (see Figure 1).

As a warm-up method that does not use ammonia, electric heaters, or similar devices, hydrogen combustion using a hydrogen cylinder is available (see Figure 2).

This method allows for easy warm-up by using a hydrogen cylinder. However, a separate hydrogen supply system is required, leading to challenges such as increased system size

Figure 1 Challenges facing power generation systems

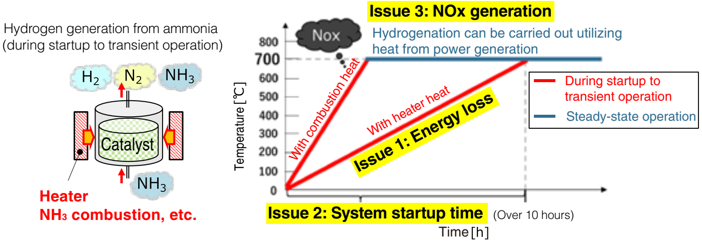


Figure 2 Warm-up method using hydrogen cylinder

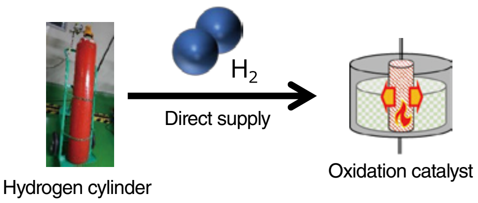
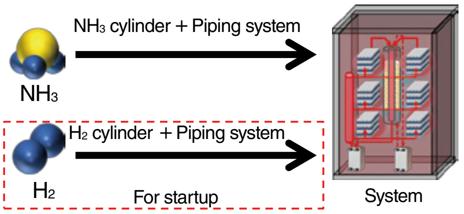


Figure 3 System exapnsion due to addition of hydrogen sypply system



due to the complexity of the power generation system and increased operational complexity due to the need to prepare multiple types of fuel (see Figure 3).

To address the challenge of securing a heat source for warm-up during system startup, we examined the possibility of utilizing the AMMONOLYSIS reaction, which enables hydrogen production from ammonia at room temperature, as a heat source. The AMMONOLYSIS reaction is a technique that generates hydrogen at room temperature through the reaction between ammonia gas and MH. Additionally, since the AMMONOLYSIS reaction is a reversible process, it allows for the regeneration of the MH consumed during system startup (see Figure 4).

If the hydrogen does not contain ammonia, NOx will not be generated during combustion, and rapid warm-up can be achieved without consuming power. This enables a clean and low-energy startup in a short time (see Figure 5).

Figure 4 AMMONOLYSIS reaction

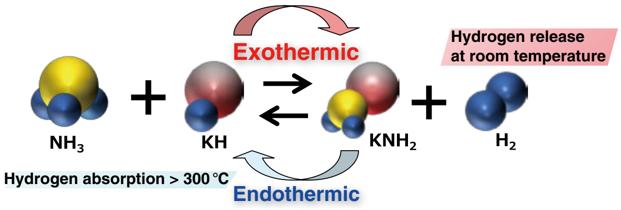
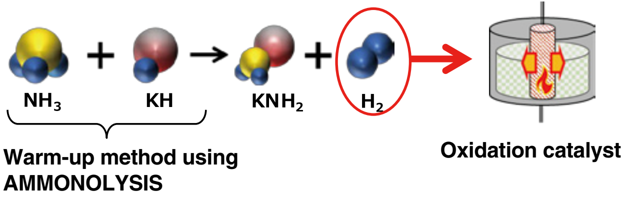


Figure 5 Warm-up method using AMMONOLYSIS



One of the challenges to utilizing the AMMONOLYSIS reaction is the "generation of the amount of hydrogen required for warm-up." Traditionally, research has been conducted on the static AMMONOLYSIS reaction using ambient ammonia gas (Yamamoto et al., 2009). However, for use in warm-up, it is necessary to react flowing ammonia gas with MH to generate the amount of hydrogen required for warm-up.

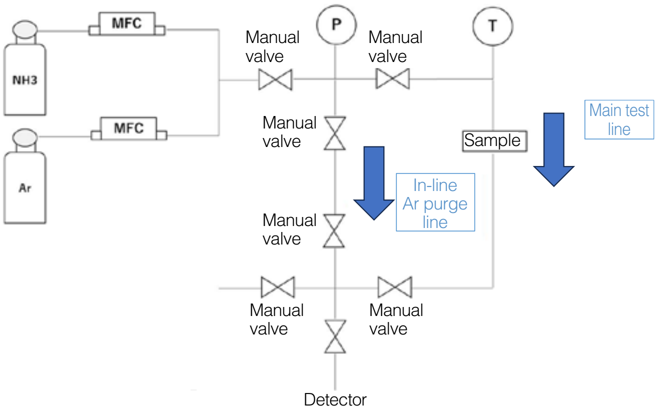
2. Evaluation Method

The evaluation of the AMMONOLYSIS reaction using flowing ammonia gas and MH was conducted with the apparatus shown in the diagram below (Figure 6).

First, the characteristics of the apparatus used for evaluating flowing gas are listed below:

- In previous studies evaluating the AMMONOLYSIS reaction using ambient ammonia gas, ammonia gas was supplied to a sealed container containing the sample and then sealed. However, since it was not possible to continuously supply flowing ammonia gas, an apparatus like the one shown in Figure 6 was constructed.
- A purge line was installed to remove residual gas in the piping.

Figure 6 System diagram of flowing gas evaluation apparatus



- A detector was used to analyze the reaction gas after passing through the sample, allowing for the monitoring of hydrogen generation.

The experimental flow is outlined below.

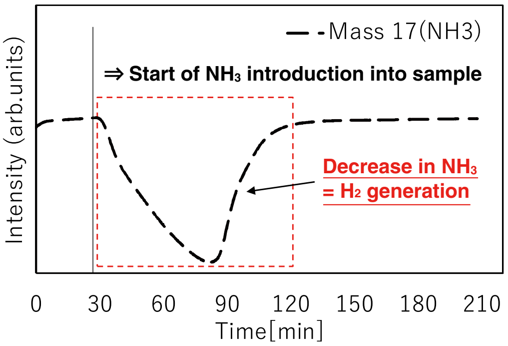
<Experimental Flow>

(1) Fill the test container with the measured sample inside a glove box filled with high-purity argon (Ar).
(2) Install the test container into the testing apparatus.
(3) To remove residual gas from the piping, switch the valve to the Ar purge line and perform purging.
(4) Switch the valve to the main test line and supply ammonia gas to the sample, controlling it with a mass flow controller (MFC).
(5) Analyze the outgoing gas that has passed through the sample using a detector and monitor the amount of hydrogen (H_2) generated.
(6) After the test, remove the residual ammonia gas in the piping through Ar purging, close the valves before and after the container, and detach the test container from the apparatus.
(7) Place the test container back into the glove box filled with Ar gas.
(8) Remove the sample from the test container and measure its weight.
By subtracting the pre-test sample weight from the post-test sample weight, the weight increase due to the reaction, A (mg), is obtained. Assuming a 100% reaction, the theoretical weight increase due to amidation is defined as B (mg). The reaction rate of the sample (i.e., the progress of the AMMONOLYSIS reaction) is expressed as the percentage ratio of A to B.
(9) Analyze the post-test sample using X-ray diffraction (XRD), which provides information on the components and crystal structure in the solid, to confirm the formation of the amidated compound.

3. Results

The evaluation results of the AMMONOLYSIS reaction of potassium hydride (KH) in flowing ammonia gas, conducted using the constructed apparatus, are shown in Figure 7.

Figure 7 Measurement results of amount of ammonia downstream of sample



The graph above (Figure 7) shows the results of measuring the ammonia concentration downstream of the sample using the detector inside the apparatus shown in Figure 6.

Compared to the point when ammonia introduction into the sample began (approximately 30 minutes elapsed), the ammonia concentration is observed to decrease between 30 and 120 minutes. From these results, it is evident that the AMMONOLYSIS reaction proceeds even in flowing ammonia gas, consuming ammonia and generating hydrogen.

To confirm the progress of the AMMONOLYSIS reaction, XRD analysis was performed on the samples before and after evaluation. The results are shown in Figures 8 and 9.

The AMMONOLYSIS reaction of KH is represented by the following reaction equation.

$$KH \quad + \quad NH_3 \quad \rightleftarrows \quad KNH_2 + H_2$$

Therefore, if the AMMONOLYSIS reaction is progressing, ammonia is consumed, KH is converted into potassium amide (KNH_2), and hydrogen is generated.

The confirmation was actually conducted using XRD. Comparing the XRD measurement results in Figures 8 and 9, it can be observed that the KH peak, which was identifiable before the reaction, has disappeared. Additionally, after the reaction, it was confirmed that KNH_2 was generated through the AMMONOLYSIS reaction, as indicated by the reaction equation.

Based on the above measurement results, it was confirmed that the AMMONOLYSIS reaction proceeds even in flowing ammonia gas.

Figure 8 XRD measurement results before evaluation

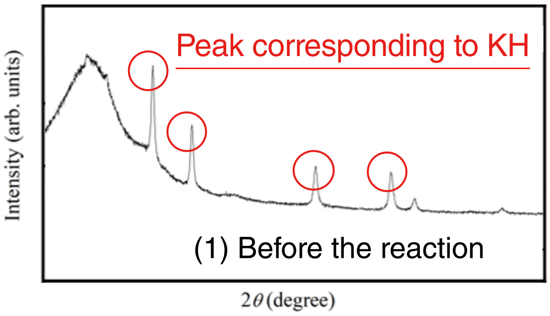
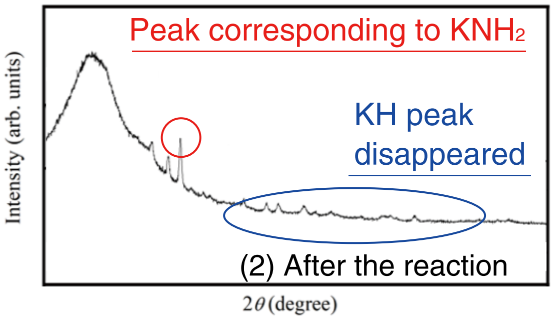


Figure 9 XRD measurement results after evaluation



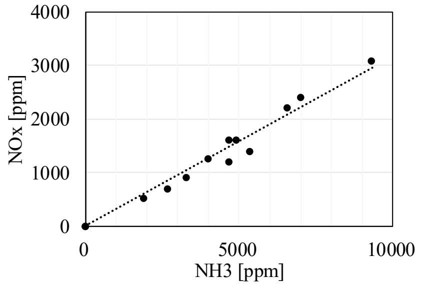
4. Challenges and Solutions

From the results of this study, it has been determined that the hydrogen obtained through the AMMONOLYSIS reaction in flowing ammonia gas can be used for warming up the power generation system by combustion.

However, the hydrogen produced through the AMMONOLYSIS reaction in flowing ammonia gas contains a certain amount of residual ammonia. When this residual ammonia-containing hydrogen is combusted, the issue of NOx generation remains.

Figure 10 shows the relationship between the amount of ammonia remaining and the amount of NOx generated.

Figure 10 Relationship between amount of ammonia remaining and amount of NOx generated



To address this issue, a warm-up system (Figure 11) was constructed that prevents NOx generation by removing ammonia through adsorption after the AMMONOLYSIS reaction.

Figure 11 Warm-up system under consideration for NOx reduction

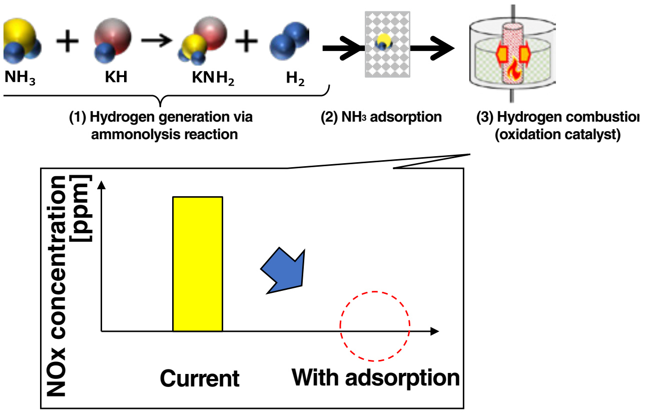
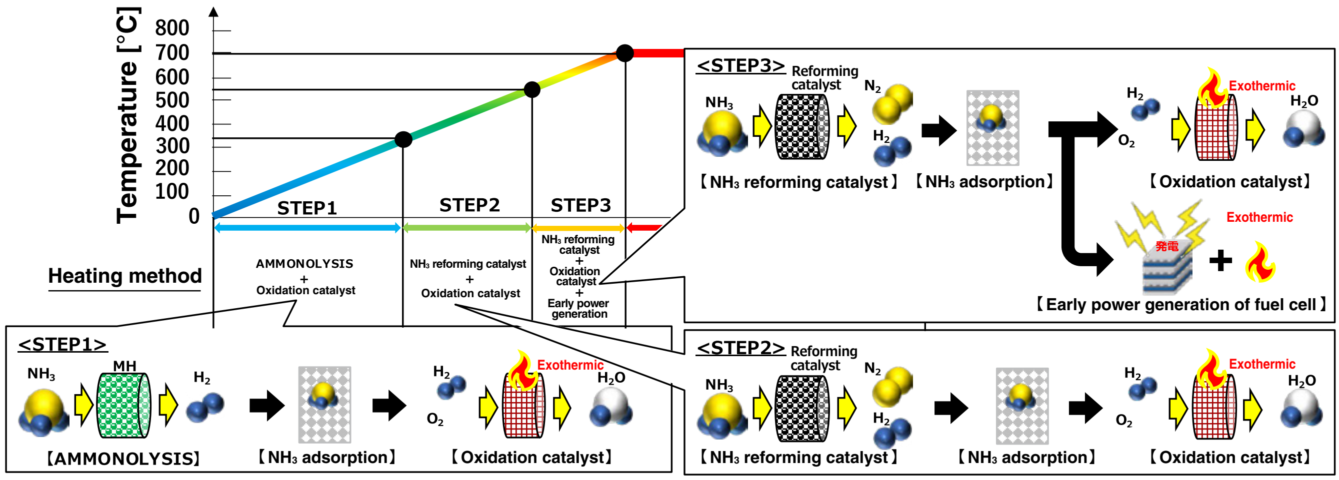


Figure 12 Conceptual image of warm-up system under consideration



In addition, since the alkali metals used in the AMMONOLYSIS reaction pose a high risk, reducing the amount of alkali metal used is also a challenge.

Regarding this challenge, as shown below (Figure 12), it is desirable not to generate all the hydrogen used for warm-up through the AMMONOLYSIS reaction but to switch to the reformer as soon as possible. By changing the hydrogen generation method according to the system temperature, the required amount of alkali metals can be minimized. Below is a system proposal detailing the relationship between system temperature and hydrogen generation methods.

<STEP 1>

· Temperature	Room temperature to approximately 350°C
· Hydrogen generation method	AMMONOLYSIS reaction
· Details	At the startup of fuel cell power generation, hydrogen is generated at room temperature using the system shown in Figure 11, followed by combustion. The temperature is increased until the ammonia reformer within the system can operate (approximately 350°C).

<STEP 2>

· Temperature	350°C-550°C
· Hydrogen generation method	Ammonia reformer
· Details	The ammonia supply source has been changed from the AMMONOLYSIS reaction to an ammonia reformer. Ammonia that could not be reformed in the ammonia reformer is removed through adsorption. Warm-up is conducted using hydrogen combustion.

<STEP 3>

· Temperature	550°C-700°C
· Hydrogen generation method	Ammonia reformer
· Details	As in STEP 2, hydrogen is generated using an ammonia reformer. A portion of the hydrogen previously used for combustion is supplied to the fuel cell to initiate power generation at an early stage. Additionally, the heat generated from power generation is utilized to raise the temperature to 700°C.

5. Conclusion and Future Outlook

In systems that use ammonia as a fuel, ammonia is difficult to combust at room temperature, so system warm-up is often performed using an alternative fuel such as hydrogen. In contrast, by utilizing the AMMONOLYSIS reaction, we examined the possibility of converting ammonia into hydrogen at room temperature, enabling system warm-up using only ammonia. In this evaluation, it was confirmed that ammonia could be converted into hydrogen via the AMMONOLYSIS reaction even under dynamic gas supply conditions. Additionally, it was found that NOx emissions caused by ammonia can be mitigated by incorporating ammonia adsorption.

Moving forward, we will optimize the system utilizing the AMMONOLYSIS reaction, reduce the amount of alkali metal used, and establish safety measures. Furthermore, we will demonstrate the low-temperature startup system currently under consideration and aim to establish a warm-up method that does not require a heater. In addition to FC power generation, we will also explore the technological application of this system for ignition sources in combustors and other uses.

Reference:

(1) H. Yamamoto, H. Miyaoka, S. Hino, H. Nakanishi, T. Ichikawa, Y. Kojima, Recyclable hydrogen storage system composed of ammonia and alkali metal hydride, International Journal of Hydrogen Energy, 34, 9760-9764, 2009.

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