Hydrogen Production from Ammonia Using Plasma Membrane Reactor

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ABSTRACT

In this study, an efficient method for using pulsed plasma to produce hydrogen from ammonia was developed. An original pulsed plasma reactor with a hydrogen separation membrane was developed for efficient hydrogen production, and its hydrogen production performance was investigated. Hydrogen production in the plasma was affected by the applied voltage and flow rate of ammonia gas. The maximum hydrogen production flow rate of a typical plasma reactor was 8.7 L/h, whereas that of the plasma membrane reactor was 21.0 L/h. We found that ammonia recombination reactions in the plasma controlled hydrogen production in the plasma reactor. In the plasma membrane reactor, a significant increase in hydrogen production was obtained because ammonia recombination reactions were inhibited by the permeation of hydrogen radicals generated in the plasma through a palladium alloy membrane. The energy efficiency was 4.42 mol-H_2/kWh depending on the discharge power.

KEYWORDS

Ammonia, Hydrogen, Plasma reactor, Membrane reactor, Dielectric barrier discharge.

INTRODUCTION

Development of high efficiency power generation systems such as an Integrated Coal Gasification Combined Cycle (IGCC) [1] and an Integrated Coal Gasification Fuel Cell (IGFC) [2] have been accelerated in Japan. In these coal gasification processes, ammonia is generated as a by-product, therefore effective utilization of ammonia is highly in need.

Ammonia has numerous favourable characteristics that stem from its molecular structure - the primary one being its high hydrogen storage capacity of 17.6 wt%. Another advantage is that it is carbon-free in its end uses, although CO_2 emitted during the production of ammonia depends on the energy source used. Therefore, ammonia is the most promising hydrogen carrier among all hydrogen-containing compounds [3].

A general technique for producing hydrogen from ammonia is catalytic thermal decomposition. Ammonia decomposition catalysts such as Ru/Al_2O_3 have been

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developed to produce hydrogen at high conversion rates and at the lowest possible temperature [4]. However, a critical issue is the long start-up time for hydrogen production because the process requires heating. For on-demand power generation systems, quick start-up devices are desired.

Compared with the aforementioned technologies, non-catalytic hydrogen production using pulsed plasma may provide a solution to the critical start-up issue. In particular, a Dielectric Barrier Discharge (DBD) plasma is appropriate for ammonia decomposition because the electric load to the plasma reactors can be quickly controlled by adjusting the output voltage or duty cycle, which can respond well to variations in gas volume. Furthermore, ammonia is expected to be completely decomposed by sufficient electron energy in the plasma without the need for heating [5].

Hydrogen production using plasma techniques has been progressed in steam reforming of methane [6], and decomposition of hydrocarbon fuels such as alcohols [7] and gasoline [8]. However, so far the studies of ammonia decomposition by plasma for hydrogen production has been superficial. It has been reported that the ammonia conversion to hydrogen by arc plasma decomposition is 18% at the power consumption of 227 W [9], which is a low energy efficiency for hydrogen production.

The present study aimed to develop an efficient method for using pulsed plasma to produce hydrogen from ammonia. The effects of applied voltages, ammonia concentrations and ammonia flow rates on hydrogen production were examined using a typical pulsed plasma reactor. As an efficient method for producing hydrogen, an original pulsed plasma reactor with hydrogen separation membrane was developed, and its hydrogen production performance was investigated.

EXPERIMENTAL

Two different plasma reactors with and without a hydrogen separation membrane were prepared for the hydrogen production experiment. Figure 1 shows a plasma reactor without a hydrogen separation membrane (Plasma Reactor: PR); it was used to examine the fundamental characteristics of hydrogen production from ammonia by pulsed plasma. Figure 2 shows a plasma reactor with hydrogen separation membrane (Plasma Membrane Reactor: PMR); it was used to improve hydrogen production efficiency. In both reactors, the electrodes had a coaxial configuration with quartz glass tubes as the dielectric material.

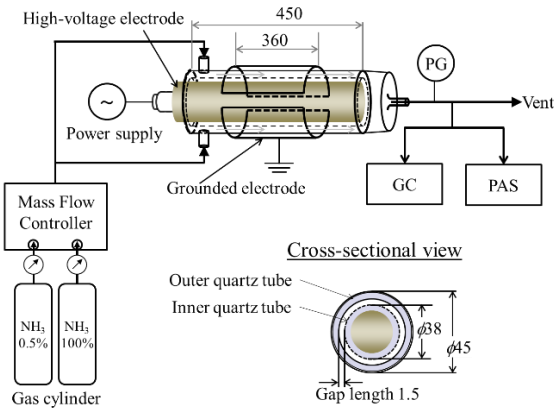

Figure 1. Experimental setup for hydrogen production by plasma reactor

The PR experimental setup is shown in Figure 1. The outer glass tube was 45 mm in diameter and 2 mm in thickness, whereas the inner glass tube was 38 mm in diameter and

2 mm in thickness. The pulsed plasma was generated in a 1.5 mm gap between the outer and inner glass tubes. The grounded electrode was made of stainless steel (SUS 304). It was 360 mm in length and 0.2 mm in thickness and covered the outside surface of the outer glass tube. The high-voltage electrode was made of stainless steel (SUS 304). It was 34 mm in diameter and 450 mm in length and was positioned inside the inner quartz tube.

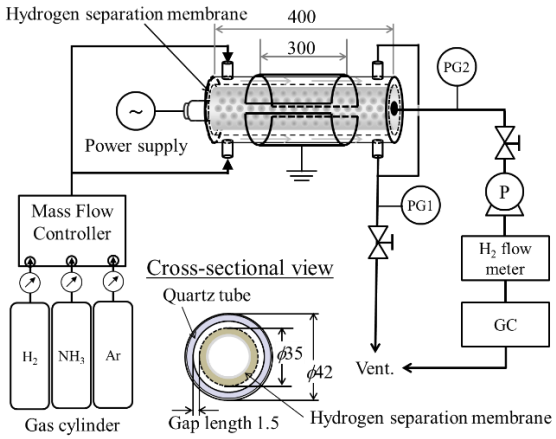

Figure 2. Experimental setup for hydrogen production by PMR

Figure 2 shows the PMR experimental setup. The PMR consisted of a glass tube and a hydrogen separation membrane module made by Nippon Seisen Co., Ltd. [10]. In this module, a palladium alloy membrane of 20 μm thickness was carefully welded inside a thin punched metal (SUS 304). The hydrogen separation membrane module served as the high-voltage electrode of the PMR. The PMR length was 400 mm, whereas the grounded electrode length was 300 mm. The gap length was 1.5 mm, same as that in the PR. The gap volumes of the PR and PMR were 67.0 and 51.6 cm^3, respectively.

To analyse the concentration of hydrogen generated at the reactor exit, micro Gas Chromatography (GC) system (Agilent 3000A) with a capillary column of molecular sieve 5A was prepared. The concentration of unreacted ammonia was continuously measured using photo acoustic spectroscopy (PAS: Gasera F10). In the PMR experiments, the flow rates of the produced hydrogen were directly measured by mass flow meter (Figure 2).

A pulsed high-voltage power source (Sawafuji Co., Ltd.) was used to generate the pulsed DBD plasma. Figure 3 depicts the waveform of the applied voltage observed in the NH_3/Ar gas mixture. The applied voltage V_{pp} is defined as the peak-to-peak value measured using an oscilloscope (Tektronix, TDS3034B) with a high voltage probe (Tektronix, P6015A) and current probe (Tektronix, P6021). The duration of one cycle of the waveform, T_1, was approximately 100 μs during the experiments. The discharge power in the plasma was estimated from the discharge energy per one cycle of the applied voltage multiplied by the repetition rate. The energy was calculated by analysing a Lissajous figure comprising the accumulated charge on a series capacitor and the source voltage [11].

Table 1 lists the experimental conditions in the PR and PMR experiments. In the PR experiments, 0.5% ammonia gas diluted with argon or 100% ammonia gas was supplied to the reactor, whereas 100% ammonia gas was used for hydrogen production in the PMR experiments. The flow rates of ammonia gas were adjusted between 0.2 and 4.0 L/min using mass flow controllers. The repetition rate of the power source was fixed at 10 kHz. The applied voltages were varied from 3.5 to 22 kV.

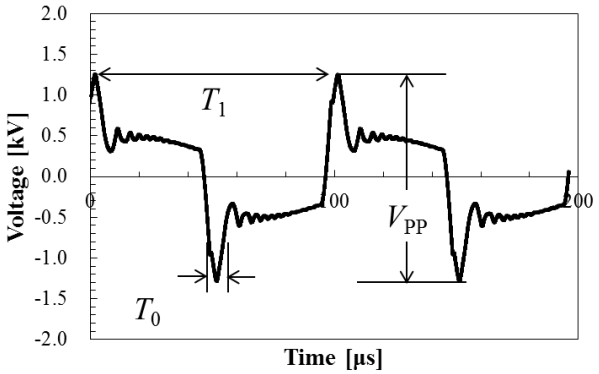

Figure 3. Waveform of applied voltage for NH_3/Ar gas mixture

Table 1. Experimental conditions

NH_3 concentration	[%]	0.5	100
Flow rate F_0	[L/min]	0.2-2.0	0.3-4.0
Repetition rate R_R	[kHz]	10	10
Applied voltage V_{pp}	[kV]	3.5-15.0	18.0-22.0

RESULTS AND DISCUSSION

Fundamental characteristics of hydrogen yield by the PR

First, the effects of the applied voltage and flow rates on hydrogen yield were examined using the PR. In the DBD pulsed plasma, electrons collide with background Ar gas molecules, wherein subsequent secondary and tertiary electron collisions convert a fraction of NH_3 into positive ions, radicals and electrons. NH_2, NH, N and H radicals are also generated by electron impact reactions. After their generation, molecular hydrogen and nitrogen are formed by recombination reactions. The overall reaction of ammonia decomposition by the pulsed DBD plasma is given by eq. (1):

$$NH_3 + e \rightarrow 0.5\ N_2 + 1.5\ H_2 + e \quad (1)$$

Figure 4 shows hydrogen yield as a function of V_{pp} for the 0.5% ammonia gas flow rates, which ranged from 0.2 to 2.0 L/min. The hydrogen yield was calculated according to the following equation:

$$H_2\ \text{yield}, \% = [H_2]m/[H_2]s \times 100 \quad (2)$$

where $[H_2]_m$ is the measured H_2 concentration by GC at the PR exit, and $[H_2]_s$ is the stoichiometric concentration of H_2 according to eq. (1). For example, $[H_2]_s$ is 0.746% for the 0.5% ammonia gas.

Hydrogen yield increased with increasing V_{pp} at all gas flow rates. The concentration of H radicals in the pulsed DBD plasma is a function of the electron mean energy, which depends on the discharge energy for plasma or the power consumption of the power source at the plug. Table 2 details the variation in the discharge energy and power consumption with change in V_{pp}. The discharge energy and power consumption increased proportionally with increasing V_{pp}. Therefore, an increase in V_{pp} facilitates hydrogen production in the gas phase reactions. The hydrogen yield achieved was 96.3% at a flow rate of 0.2 L/min and V_{pp} of 15 kV. However, it should be noted that a gradual increase in hydrogen yield was observed at a high V_{pp}.

An increase in the flow rates of the 0.5% ammonia gas decreased the hydrogen yield, as shown in Figure 4. Figure 5 depicts the effect of the flow rates as a relationship between gas residence time at a standard condition and hydrogen yield. At V_{pp} = 15 kV, the hydrogen yield proportionally increased with increasing gas residence time, up to 5.0 s. Beyond this time, a gradual increase in hydrogen yield was observed.

Such a gradual increase in hydrogen yield was observed at a high V_{pp} and the long residence time shown in Figures 4 and 5 indicates that ammonia was formed again through a recombination reaction between H and NH_i radicals as follows:

$$NH_2 + H \rightarrow NH_3 \quad (3)$$

$$NH + 2H \rightarrow NH_3 \quad (4)$$

For efficient hydrogen production from ammonia, reverse reactions to ammonia should be inhibited.

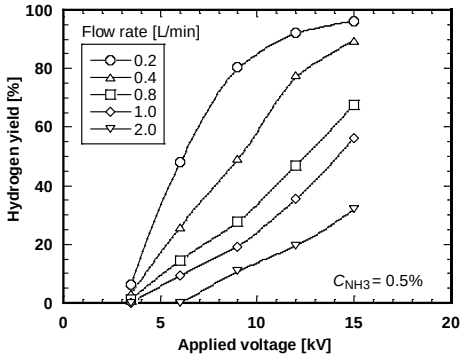

Figure 4. Effect of V_{pp} on hydrogen yield as a parameter of flow rates of 0.5% ammonia gas

Table 2. Input power and power consumption of PR for 0.5% ammonia gas supply

Applied voltage V_{pp}	[kV]	3.5	6.0	9.0	12.0	15.0
Discharge power	[W]	5.2	7.7	13.4	28.9	55.6
Power consumption P	[W]	11.4	17.0	29.5	63.6	122.4

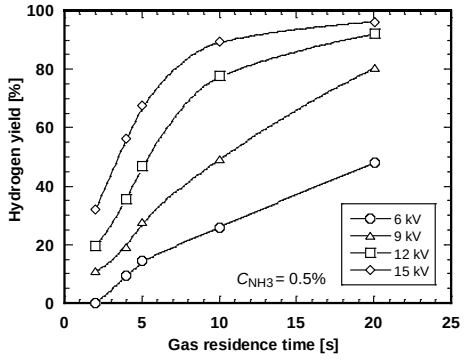

Figure 5. Effect of gas residence time on hydrogen yield as a parameter of V_{pp}

Performance of hydrogen production of the PR

Using 100% ammonia gas, the maximum hydrogen production performance was obtained by the PR. Furthermore, it can be expected that reverse reactions from hydrogen

to ammonia formation were controlled by the high ammonia concentration because the partial pressure of the generated hydrogen diminished.

Figure 6 shows hydrogen yield as a function of discharge energy for the 100% ammonia gas. The discharge power and power consumption corresponding to V_{pp} are listed in Table 3. Figure 7 depicts variation in the flow rates of hydrogen production with gas residence time. The maximum hydrogen yield was 14.0% at a flow rate of 0.3 L/min and V_{pp} of 22.0 kV (Figure 6), whereas the maximum flow rate of hydrogen yield calculated by eq. (5) was 8.7 L/h at a flow rate of 2.0 L/min and V_{pp} of 22.0 kV (Figure 7):

$$F_{H_2}, \text{L/h} = (\text{Hydrogen yield, \%}) \times [F_{H_2}]_s \times 60 \quad (5)$$

where F_{H_2} is the flow rate of the generated hydrogen and $[F_{H_2}]_s$ is the H_2 flow rate at stoichiometry according to eq. (1). For example, $[F_{H_2}]_s$ is 3.0 L/min for the 100% ammonia flow rate of 2.0 L/min.

As shown in Figure 6, we found that the performance of hydrogen production of the PR was insufficient for use as a hydrogen generator, because it would be difficult for the fuel cells to obtain a high hydrogen concentration. This is because the reverse reactions were somewhat encouraged by increasing the gas residence time at V_{pp} = 20.5 and 22 kV, as shown in Figure 7.

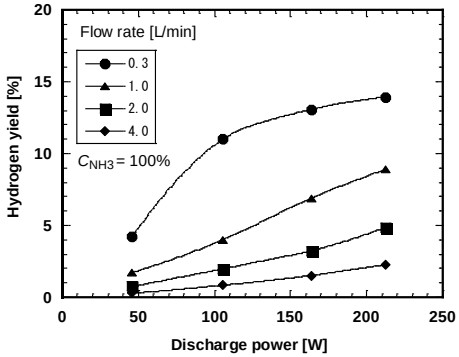

Figure 6. Hydrogen yield as a function of discharge power for 100% ammonia gas

Table 3. Input power and power consumption for 100% ammonia gas supply

Applied voltage V_{pp}	[kV]	18.0	19.0	20.5	22.0
Discharge power	[W]	46.1	105.3	163.7	212.3
Power consumption P	[W]	100	200	300	400

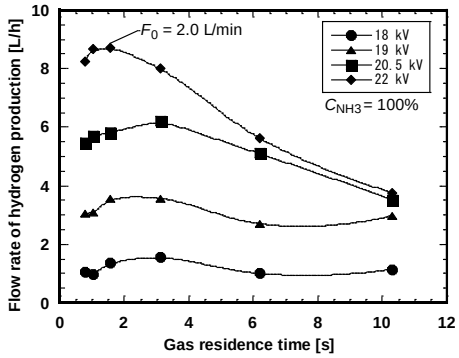

Figure 7. Variation in flow rates of H_2 production with gas residence time

Hydrogen separation performance of the PMR

The ammonia recombination reactions must be controlled to attain a high efficiency of hydrogen production. In other words, the H radicals generated in the plasma must be removed from the plasma region. To achieve this, we precisely designed the advanced plasma reactor shown in Figure 2. We expected the H radicals generated by ammonia decomposition in the plasma to diffuse rapidly through the membrane, thereby inhibiting ammonia recombination.

Prior to the hydrogen production experiments by the PMR, pure hydrogen was supplied to the PMR to examine the hydrogen separation characteristics of the membrane. Figure 8 shows the hydrogen separation characteristics of the PMR as variables of induced pressure (PG2 in Figure 2) and feed pressure (PG1 in Figure 2). The applied voltage and pure H_2 flow rate were fixed at 14 kV and 60 L/h, respectively. The grounded electrode was heated by joule heating from the power source. It's surface temperature was 408 K, which was measured by a radiation thermometer (Hioki 3460-50).

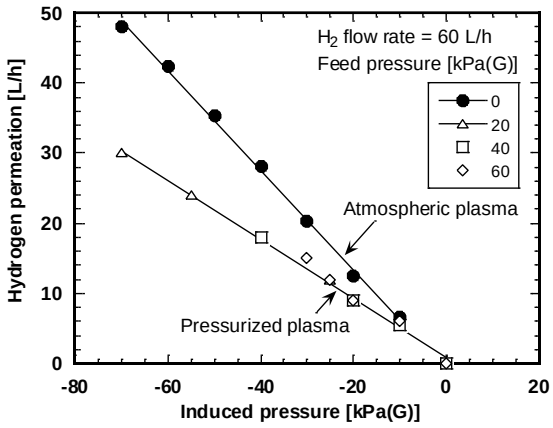

Figure 8. Hydrogen separation characteristics of PMR for pure hydrogen supply

The flow rate of hydrogen permeation increased proportionally with an increase in induced pressure. It is well known that the performance of hydrogen permeation through a palladium membrane is proportional to the differential pressure between PG1 and PG2 [12]. Meanwhile, an increase in feed pressure reduced the flow rate of hydrogen permeation. The concentration of H radicals in the plasma may decrease under pressurised plasma relative to atmospheric plasma.

The strongest point of the PMR is that hydrogen permeation is unnecessary at high temperatures owing to the generation of H radicals in low-temperature plasma. In general, palladium alloy membranes are effective at 673 K [13]. However, attention should be paid to the problem of hydrogen absorption below a critical temperature (571 K) [14].

Hydrogen permeation in the PMR is estimated from a solution diffusion mechanism [15], as follows:

- Molecular ammonia is rapidly decomposed to N and H radicals by electron impact in plasma;
- Generated H radicals are adsorbed onto the surface of the hydrogen separation membrane; consequently, ammonia recombination in the gas phase is inhibited;
- H radicals diffuse through the membrane;
- Molecular hydrogen is subsequently formed by recombination outside the membrane.

The estimated mechanism is illustrated in Figure 9.

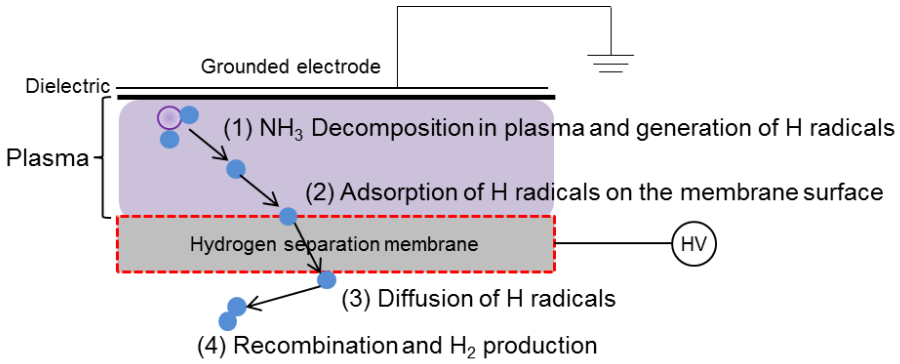

Figure 9. Estimated mechanism of hydrogen separation in PMR

Hydrogen production performance of the PMR

Hydrogen production experiments were conducted in the PMR using the 100% ammonia gas at various flow rates (Table 1). Feed pressure and induced pressure were 0 kPa (G) and 70 kPa (G), respectively; maximum hydrogen permeation performance of the membrane was 48 L/h, as shown in Figure 8. Therefore, maximum hydrogen production of 48 L/h is expected in the PMR experiments, if reverse reactions from hydrogen to ammonia in eqs. (3) and (4) can inhibit by effect of the membrane. The surface temperature of the grounded electrode was 573 K at V_{pp} of 22 kV.

Figure 10 shows variation in the flow rates of hydrogen production with an increase in the flow rate of ammonia gas for both the PMR and PR. The hydrogen production by the PR was constant above the NH_3 flow rate of 60 L/h. This result indicated that ammonia decomposition in eq. (1) is reached equilibrium in plasma. On the other hand, the hydrogen production of the PMR represented a significant increase compared with that of the PR. This result indicates that ammonia recombination in plasma is inhibited by using a hydrogen separation membrane, and equilibrium is moved to hydrogen production side in eq. (1).

The maximum hydrogen production flow rate in the PMR was 21.0 L/h at the NH_3 flow rate of 30 L/h, which is equivalent to complete decomposition of the NH_3 flow rate of 14 L/h. Therefore, it was found that the ammonia decomposition in the plasma was a rate-controlling step in eq. (1). The energy efficiency was 4.42 mol-H_2/kWh depending on the discharge power.

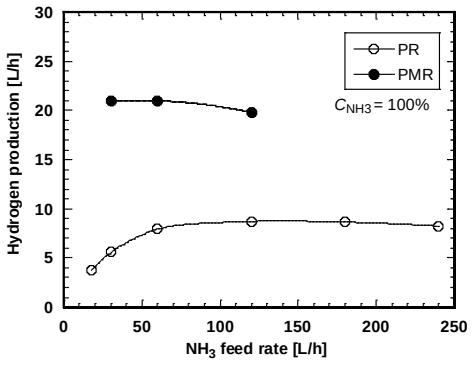

Figure 10. Hydrogen production performance of the PMR and PR

CONCLUSION

Ammonia is a hydrogen storage material that may solve many problems related to hydrogen transportation and storage in a hydrogen economy. Therefore, devices that

produce hydrogen from ammonia will become increasingly important. In this study, hydrogen production experiments were conducted to develop an efficient method for using pulsed plasma to produce hydrogen from ammonia.

First, the fundamental characteristics of hydrogen yield were investigated using a typical PR. The hydrogen yield increased with an increase in the applied voltage and with a decrease in the flow rate of ammonia gas.

Second, the hydrogen production performance of the PR was examined using 100% ammonia gas. However, the performance was inadequate for use as a hydrogen generator. This is because the hydrogen production flow rate was only 8.7 L/h because of ammonia recombination reactions in the plasma.

To inhibit reverse reactions from hydrogen to ammonia in the plasma, PMR was developed. The PMR contained a hydrogen separation membrane made from palladium alloy. The maximum hydrogen permeation for the PMR was 48 L/h, which was affected by the differential pressure between the feed and induced pressures.

Finally, the hydrogen production performance of the PMR was investigated using 100% ammonia gas. The maximum hydrogen production flow rate of the PMR was 21.0 L/h, which represents a significant increase compared with that of the PR. The energy efficiency was 4.42 mol-H_2/kWh depending on the discharge power. Since the rate-controlling step is the ammonia decomposition in the plasma, an improvement in hydrogen production is expected by investigating the optimum conditions for the plasma decomposition of ammonia.

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