Hydrogen production from ammonia as energy carrier by pulsed plasma

Yukio Hayakawa[1], Shinji Kambara[1] and Tomonori Miura[2]

[1] Environmental and Renewable Energy Systems Division, Gifu University, Japan.
[2] Sawafuji Electric Co., LTD., Japan

Corresponding e-mail: kambara@gifu-u.ac.jp

Abstract

Ammonia is the most promising hydrogen carrier among all hydrogen-containing compounds. The aim of the present research was to develop an efficient method for using pulsed plasma to produce hydrogen from ammonia. An original pulsed plasma reactor with a hydrogen separation membrane was developed for an efficient hydrogen production, and its hydrogen production performance was investigated Effects of the applied voltage, ammonia glow rates, and ammonia concentrations on hydrogen yields were examined. Hydrogen generation using a pulsed plasma reactor (no membrane) was insufficient performance, whereas hydrogen generation of a pulsed plasma reactor with a palladium alloy membrane was a significant increase comparing to the no membrane plasma reactor. The hydrogen generation flow rate was 21.0 L/h.

Keywords: Ammonia, Hydrogen production, Pulsed plasma

1. Introduction

Greenhouse effect gases are emitted from using various combustion resources such as fossil fuels. Progress of the global warming is concerned over the world. In order to reduce greenhouse effect gas, a key solution is construction of hydrogen energy society, but use of hydrogen energy has a large energy loss for its transportation and storages [1]. This energy loss can be solved by converting hydrogen into hydrogen carrier [2]-[3]. Particularly, ammonia is expected as a hydrogen carrier. Ammonia has a number of favorable characteristics, the primary one being its high capacity for hydrogen storage, 17.6 wt%, based on its molecular structure. Its secondary merit is that it is carbon-free at its end uses, although CO_2 emitted during the production of ammonia depends on the energy source. Therefore, ammonia is the most hopeful hydrogen carrier among all hydrogen carrier.

The general techniques for the production of hydrogen from ammonia, is thermal decomposition using a catalyst. However, it has a critical issue that a long time is required for the hydrogen production and the need for heating. By decomposing ammonia using a pulsed plasma, these problems are resolve. It is possible to significantly reduce the time required for the hydrogen production by using a pulsed plasma.

The purpose of this research was to develop a method for efficiently producing hydrogen from ammonia using the pulsed plasma. First, the applied voltage, ammonia concentration, and the influence of ammonia flow rate of the hydrogen production was examined using a typical plasma reactor. The efficiency of hydrogen production was carried out by further combining the typical plasma reactors and hydrogen permeable membranes.

2. Methodology

NH_3 is decomposed to H_2 and N_2 by electric discharge energy from atmospheric plasma as described in Eq. 1. However, hydrogen generation affects various factors, such as the applied voltage, gas concentrations, and gas flow rates.

$$NH_3 + e \rightarrow 0.5\,N_2 + 1.5\,H_2 + e \quad \text{(Eq. 1)}$$

Fig. 1 shows experimental setup for H_2 production in a typical plasma reactor (PLR). The electrodes are coaxial in configuration, with quartz glass tubes as the dielectric materials. The outer glass tube is 45 mm in diameter and 2 mm in thickness, whereas the inner glass tube is 38 mm in diameter and 2 mm in thickness. The pulsed plasma is generated in a 1.5 mm gap length between the outer glass and inner glass. The grounded electrode made of stainless steel, 360 mm in length and 0.2 mm in thickness, covers the outer side of the outer glass tube. The high-voltage electrode made of stainless steel, 34 mm in diameter and 450 mm in length, is positioned inside the inner quartz tube.

Fig. 2 shows experimental setup of a plasma reactor with a hydrogen separation membrane (PMR). The PMR is consisted of the glass tube and the hydrogen separation membrane module made by Nippon Seisen Co., Ltd.. In the module, the palladium alloy membrane of 20 μm in thickness was elaborately welded inside a thin punched metal. The PMR length is 400 mm, whereas the grounded electrode length is 300 mm. The gap length is 1.5 mm, same as the PLR. To analyze the concentration of generated hydrogen at the reactor exit, a micro gas chromatography system (GC) with a capillary column of molecular sieve 5A was prepared. The concentration of unreacted ammonia was continuously measured using a quadrupole mass spectrometer (Q–Mass). In the PMR experiments, flow rates of produced hydrogen were directly measured by a mass flow meter.

Table 1 lists experimental conditions for both the PLR and the PMR. In the experiment of the PLR, a 0.5 % ammonia gas (Ar based) or a 100 % ammonia gas was supplied to plasma reactor. In the PMR experiment, a 100 % ammonia gas was supplied to PMR.

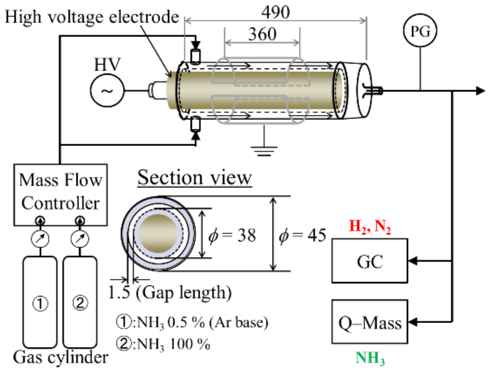

Fig. 1 Schematic diagrams of experimental apparatus for typical plasma reactor (PLR).

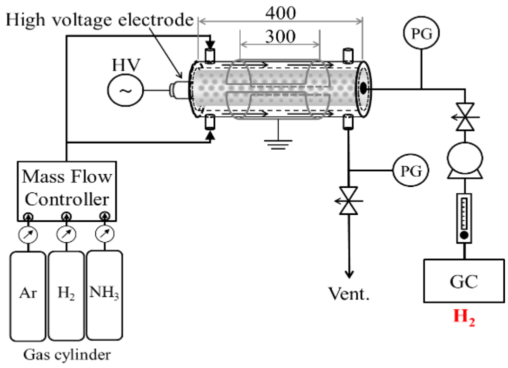

Fig. 2 Schematic diagrams of experimental apparatus for plasma reactor with hydrogen separation membrane (PMR).

Table 1 Experimental conditions

NH_3 conc. = 0.5 %		
Flow rate, F_0	[L/min]	0.2—2.0
Repetition rate, R_R	[kHz]	10
Applied voltage, V_{PP}	[kV]	3.5—15.0
NH_3 conc. = 100 %		
Flow rate, F_0	[L/min]	0.3—4.0
Repetition rate, R_R	[kHz]	10
Applied voltage, V_{PP}	[kV]	18.0—22.0

3. Results and discussions

3.1 Typical characteristics of the PLR

Fig. 3 shows the trend of hydrogen yield on applied voltage by each gas flow rate (0.2—2.0 L/min) at NH_3 concentration 0.5 %. The hydrogen yield was calculated according to following formula.

$$H_2 \text{ yield, } Y_{H2}\ [\%] = [H_2]_{out}/[H_2]_T \times 10 \qquad (1)$$

where, $[H_2]_{out}$ is the H_2 concentration in the plasma reactor exit, and $[H_2]_T$ is theoretical generated hydrogen concentration. H_2 yield was increased with the increase of the applied voltage and it showed maximum value 96 % at the flow rate of 0.2 L/min and the applied voltage 15 kV.

In addition, the reactor temperature is increased at about 200 °C by Joule heat of the atmospheric pressure plasma. However, since the thermal ammonia decomposition does not occur at 200 °C, results of Fig. 3 can be considered to be the ammonia decomposition due to electron energy of pulsed plasma.

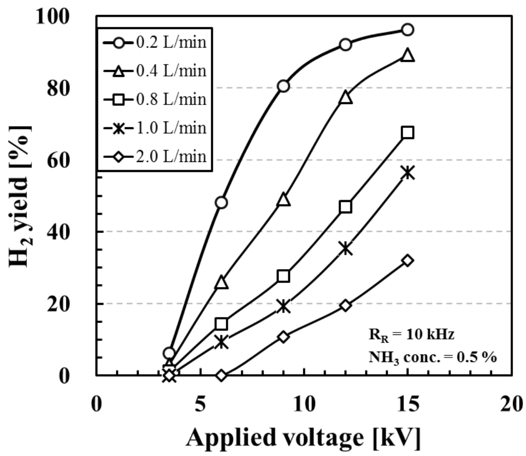

Fig. 3 H_2 yield by plasma decomposition of NH_3 (NH_3 conc. = 0.5 %).

Subsequently, it was tried to consider terms of the hydrogen production efficiency with respect to hydrogen production characteristics by pulsed plasma. Fig. 4 shows the difference of hydrogen production efficiency for energy density at 0.5 % ammonia concentration. The hydrogen production efficiency and energy density were calculated according to the following formulas.

$$H_2 \text{ production efficiency [mol-}H_2\text{/kWh]} = Q_{H2}/P \qquad (2)$$

$$\text{Energy density, } E_P[\text{J/cm}^3] = (1000 \times P)/V \times \theta \qquad (3)$$

Where, Q_{H2} is hydrogen production [mol-H_2/s], P is input power [W], V is volume of plasma reactor [cm^3] and θ is gas residence time in the reactor [s]. From Fig. 4, it was revealed that hydrogen production efficiency indicates the secondary function trend in all conditions. From these results, it is presumed that hydrogen generation is inhibited by the reverse reaction to produce ammonia in high energy density side (higher applied voltage side).

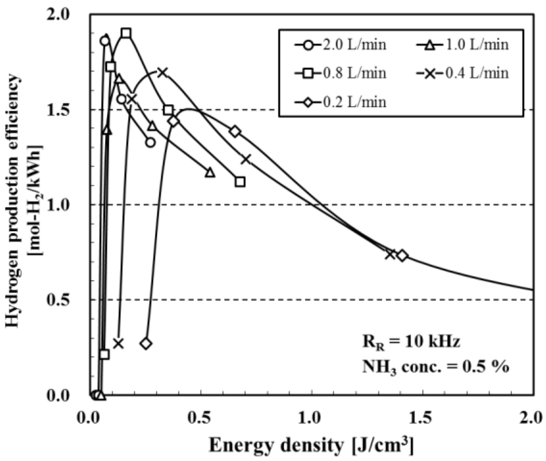

Fig. 4 Effects of energy density and flow rates on H_2 production efficiency.

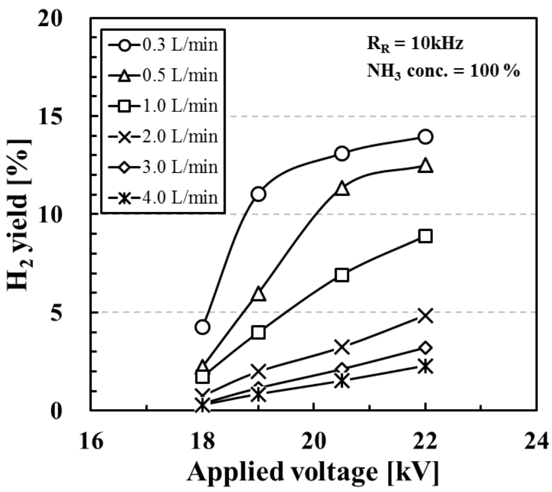

Fig. 5 H_2 yield by plasma decomposition of NH_3 (NH_3 conc. = 100 %).

Fig. 5 shows the trend of hydrogen yield on applied voltage by each gas flow rate (0.3—4.0 L/min) at NH_3 concentration 100 %. While H_2 yield was attained 96 % at low ammonia concentration, hydrogen yield was able to attain only 13.9 % at high ammonia concentration. So, it was clear that hydrogen yield was decreasing with the increasing of ammonia concentration. Plasma firing voltage becomes larger with the increasing of ammonia concentration in supplied gas. Therefore, the applied voltage becomes higher than the low ammonia concentration condition. A long with applied voltage become higher the reverse reaction to produce ammonia progresses and hydrogen yield is decreased.

It must be controlled reverse reaction to form ammonia in order to achieve high hydrogen yield. In order to suppress the reverse reaction, it is necessary to produce hydrogen which is separated from the reaction field. So, we have produced a breakthrough plasma reactor was introduced hydrogen permeable membrane in high-voltage electrode. (Fig. 2)

3.2 Characteristic of hydrogen production in PMR experiment

Fig. 6 shows conceptual diagram of mechanism of hydrogen permeable in PMR. Generally, hydrogen permeable membrane required temperature around 400 °C in order to decompose ammonia to H radical, adsorb on surface of permeable membrane and take in H radical. However, using the PMR, it is possible to decompose ammonia by electrical energy of the plasma to the H radicals. Then, by going through the following four mechanisms, we consider that it is possible to separate hydrogen without restrictions in temperature.

(1) Ammonia is decomposed by the pulsed plasma
(2) H radicals are adsorbed to the membrane surface
(3) H radical is penetrated through the membrane
(4) H radicals recombine to hydrogen

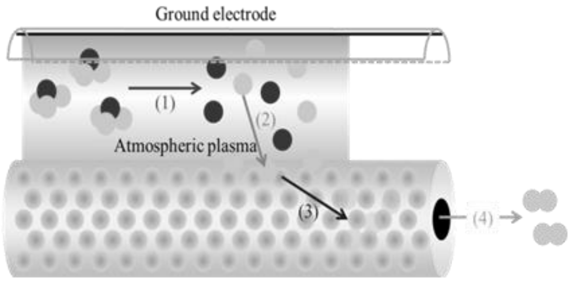

Fig. 6 Mechanism of H_2 permeable in the PMR.

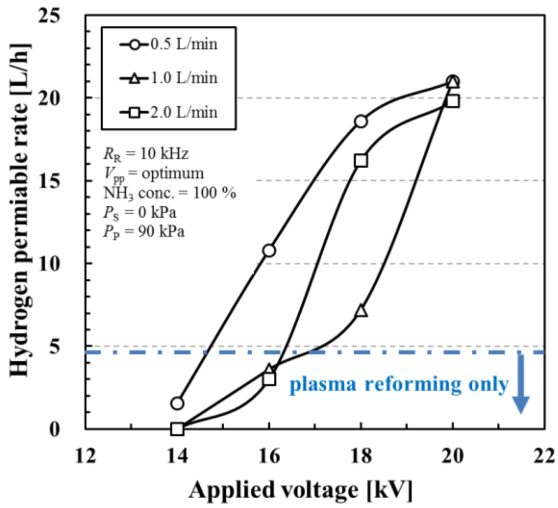

Fig. 7 Hydrogen production characteristics of the PMR.

Fig. 7 shows variation in hydrogen production flow rates with the applied voltage at various ammonia flow rates. At any ammonia flow rate, maximum hydrogen flow rate was around 21.0 L/h. The hydrogen production performance of the PLR was indicated by a dot line in Fig.7, which is clear that the PMR is available for hydrogen generation from ammonia.

4. Conclusions

Hydrogen production experiments were conducted to develop an efficient method for using pulsed plasma to produce hydrogen from ammonia. First, fundamental characteristics of hydrogen yield was investigated by the typical plasma reactor (PLR). 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 PLR was examined using the 100% ammonia gas, however, the performance was insufficient to use for a hydrogen generator.

the plasma membrane reactor (PMR) was developed as an efficient method for using pulsed plasma to produce hydrogen from ammonia. The hydrogen production performance of the PMR was investigated using the 100% ammonia gas. A maximum hydrogen production flow rate of the PMR was 21.0 L/h, which represented a significant increase compared to that of the PLR.

References

[1] Okada O:” Current status of hydrogen production technology from fossil energy resources”, Journal of the Japan Institute of Energy, 85, 499-509 (2006)

[2] Okada Y, Yasui M:” Mass storage transit technologies of the hydrogen energy-Organic chemical hydraid method "SPERA hydrogen" storage transportation system-”, Journal of the Chemical Engineering of Japan, 77(1), 46(2013)

[3] Ito Y:” Ammonia prospective as a hydrogen storage, a transportation medium”, Journal of the Chemical Engineering Japan, 77(1), 51(2013)