Hydrogen production at room temperature by ammonia decomposition using pulsed plasma

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ABSTRACT

Ammonia is one of hydrogen storage material, which may solve problems of hydrogen transportation and storages in hydrogen economy. Catalytic thermal decomposition is a promising technique to produce hydrogen from ammonia. As an original hydrogen production, pulsed plasma decomposition has been examined. It found that molecular ammonia was rapidly decomposed by electron energy in plasma, which was converted to molecular hydrogen. Hydrogen production rate was affected by ammonia flow rates, ammonia concentrations, applied voltages, and repetition rates. The maximum energy efficiency to produce hydrogen from ammonia was 0.11%. To improve the energy efficiency, an original high voltage electrode with hydrogen separation membrane was developed and applied. The energy efficiency increased to 65.3% by the improvement.

Key words: Ammonia, Hydrogen, Plasma, Membrane, Dielectric barrier discharge

INTRODUCTION

Ammonia has a number of favourable characteristics, the primary one being its high capacity for hydrogen storage, 17.6 wt%, based on its molecular structure. The secondary merit is that ammonia itself is carbon-free at the end users, although CO_2 emission on production of ammonia is dependent on the source of energy. Therefore, ammonia is the most promising of all chemicals containing hydrogen as a hydrogen carrier [1].

A general technique for hydrogen production from ammonia is catalytic thermal decomposition. Ammonia decomposition catalysts such as Ru/Al_2O_3 have been developed to produce hydrogen at high conversion rates and at a temperature as low as possible [2]. However, there is a critical issue that start-up time for hydrogen production is long since it requires heating. For on-demand power generation systems, quick start-up devices are desired.

Compared with the above technologies, non-catalytic hydrogen production using pulsed plasma may give a solution to the critical issue. In particular, a dielectric barrier discharge (DBD) plasma is appropriate for ammonia decomposition, because the electric load to plasma reactors can be quickly controlled by adjusting either the output voltage or the duty cycle, which can respond well to variations in gas volume. Furthermore, it is expected that ammonia is completely decomposed by enough electron energy in plasma without heating [3].

The aim of the present research was to find an efficient way to use pulsed plasma for hydrogen production from ammonia. First, effects of flow rates of ammonia and applied voltages on hydrogen production were investigated. Second, an efficient way for hydrogen production was considered based on mechanisms of ammonia decomposition in plasma.

EXPERIMENTAL

A schematic diagram of the experimental apparatus for hydrogen production is shown in Figure 1. 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, while 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. The grounded electrode, 360 mm in length and 0.2 mm in thickness, covers the outer side of the outer glass tube. The high voltage electrode, 34 mm in diameter and 450 mm in length, is set into the inner quartz tube.

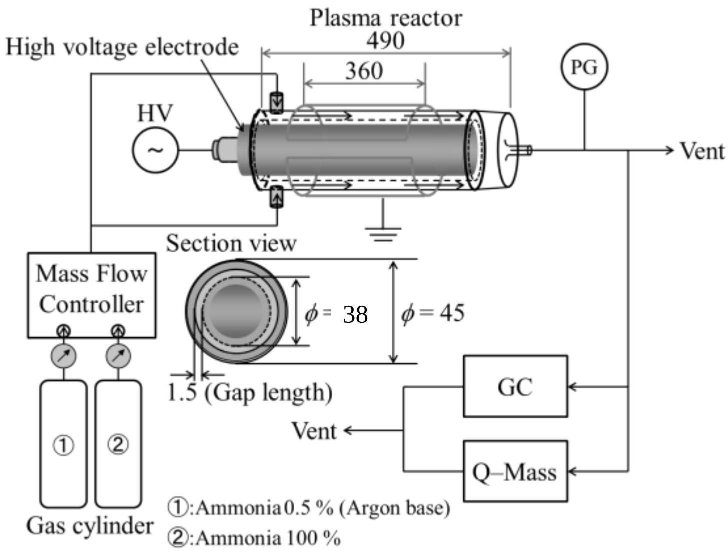


Figure 1. Experimental setup for hydrogen production using pulsed plasma.

A pulsed high voltage output (Sawafuji Co. Ltd.) is employed as the power source for generating the DBD plasma. The flow rates of argon-diluted ammonia gas (0.5%) were adjusted between 0.2 L/min and 2.0 L/min by mass flow meters. The applied voltages defined by peak to peak voltage were varied from 3.5 kV to 15 kV. The repetition rate was fixed 10 kHz. Ammonia is decomposed to H_2 and N_2 by electron energy in plasma as equation (1), therefore, gas composition was measured by a gas chromatography for H_2 and N_2 at the plasma reactor exit to obtain ammonia decomposition rates. The ammonia decomposition rate was calculated by equation (2).

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

$$NH_3 \text{ decomposition, \%} = [H_2 \text{ concentration at the exit, ppm}] / (1500[\text{initial } NH_3 \text{ concentration, ppm}]) \qquad (2)$$

RESULTS AND DISCUSSION

Fundamental characteristics of NH_3 decomposition

Figure 2 shows NH_3 decomposition as a function of the applied voltage (V_{pp}) at a repetition rate of 10 kHz for gas flow rates from 0.2 to 0.8 L/min. NH_3 decomposition generally increases with increasing V_{pp} at all gas flow rates. In plasma processing, electron-impact dissociation of molecular ammonia produces NH_i (NH_2, NH, and N) and H radicals. The concentrations of these radicals are a function of the electron mean energy, which depends on V_{pp}. An increase in the concentrations of NH_i and H radicals facilitates hydrogen production in the gas phase reactions. Approximately 100% decomposition of ammonia was attained at a flow rate of 0.2 L/min at applied voltage of 15 kV. However, the energy efficiency of hydrogen production, η, defined by equation (3), was only 17.7%. It estimated that ammonia was formed again by recombination reaction between H_2 and NH radical.

$$\eta = (\text{enthalpy of produced } H_2\text{, J/s}) / [(\text{enthalpy of fed } NH_3\text{, J/s}) + (\text{power consumption, J/s})]\cdot 100 \quad (3)$$

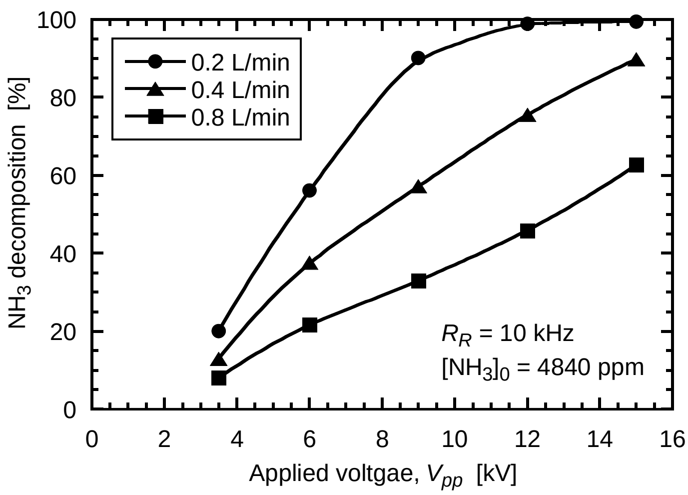


Figure 2. Effect of V_{pp} and flow rates on NH_3 decomposition

Improvement of the plasma reactor

It is necessary to control NH_3 recombination reaction to attain a high energy efficiency of hydrogen production: that is, generated H radical in plasma has to take away from plasma region. To achieve the aim, the advanced plasma reactor as shown in Figure 3 was precisely designed. In the plasma reactor, original hydrogen separation membrane was applied to a high voltage electrode. It can be expected that H radical generated by NH_3 decomposition in plasma is rapidly diffused in the membrane, and NH_3 recombination is inhibited.

Hydrogen production experiment was carried out using 100% ammonia gas at the flow rate of 1.0 L/min by using the advanced plasma reactor as shown in Figure 3. NH_3 was completely converted to pure hydrogen at the applied voltage of 9 kV (total power consumption of the high voltage power source was 200 W). The energy efficiency was 65.3% as listed in Table 1, which significantly increased comparing with the conventional plasma reactor shown in Figure 1.

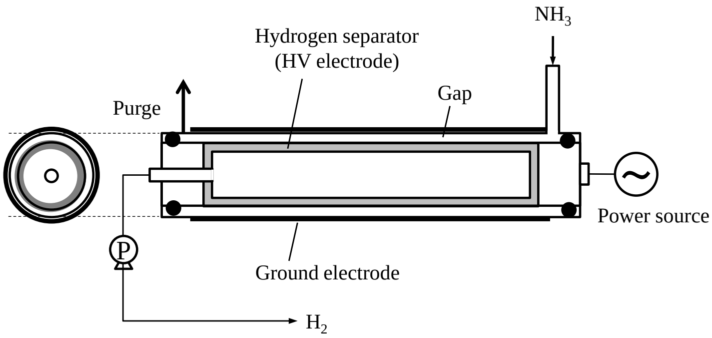
The advantage of the advanced plasma reactor was considered as follows:

(1) Molecular ammonia is rapidly decomposed to N and H radicals by electron impact.

(2) Generated H radical is adsorbed on the surface of the hydrogen separation membrane, therefore, NH_3 recombination in gas phase is inhibited.

(3) H radical diffuses in the membrane, and then molecular hydrogen is formed by recombination at outside of the membrane.

As a surprising phenomenon, it found that the hydrogen separation membrane was worked at a lower temperature by the advanced plasma reactor. The estimated temperature of the membrane surface was approximately 373 K. It should be noted that hydrogen separation membrane was required above 573 K for H radical generation and adsorption on the membrane surface in general conditions such as thermal reforming of methane. Such mechanisms were concluded in Figure 4. This advantage contributes quick start-up of hydrogen production device and fuel cell power generation system.



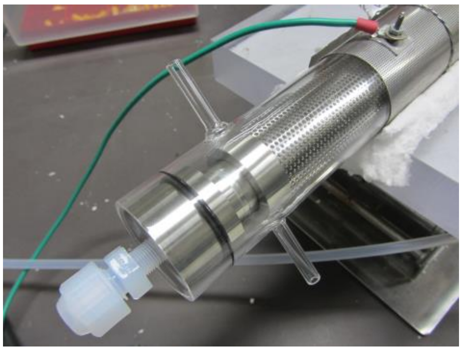


Figure 3. Improved plasma reactor with hydrogen separation membrane

Table 1. Comparison between conventional plasma reactor and advanced plasma reactor

Hydrogen membrane	NH_3 concentration	V_{pp} for complete decomposition	Flow rate for complete decomposition (L/min)	η (%)
Nothing	4840 ppm	15.0 kV, 300W	0.2	0.11
As electrode	100 %	9.0 kV, 200W	1.0	65.3

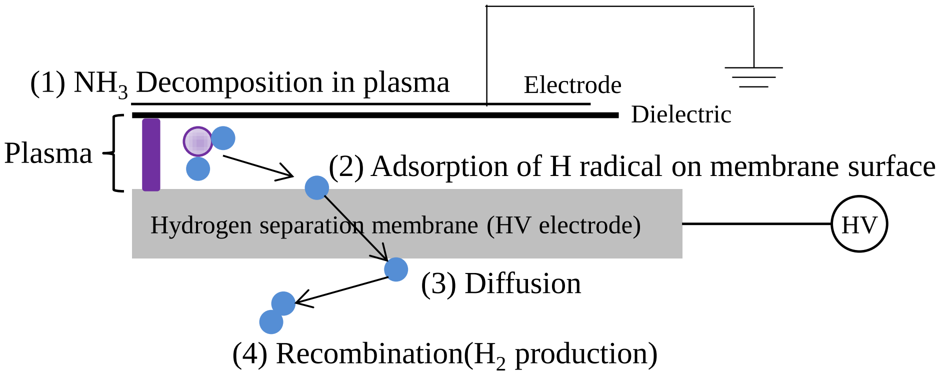


Figure 4. Mechanisms of hydrogen separation in plasma reactor with hydrogen membrane

CONCLUSION

Hydrogen production experiments were carried out using a pulsed plasma. Effects of the applied voltage and flow rates of ammonia gas on the hydrogen conversion rate were investigated. However, its energy efficiency was only 0.11%, because NH_3 recombination was occurred in gas phase in plasma. To improve the energy efficiency, hydrogen separation membrane was applied as a high voltage electrode. It considered that H radical generated in plasma rapidly diffused the membrane, and large amount of hydrogen was recovered. The energy efficiency of 65.3% was attained using the advanced plasma reactor with hydrogen separation membrane.

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