Hydrogen production by ammonia decomposition using pulsed plasma

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Non-catalytic hydrogen production from ammonia gas using a pulsed atmospheric plasma have been developed to solve the problems of hydrogen transportation and storages. In this paper, characteristics of ammonia decomposition and hydrogen production from ammonia by the pulsed plasma were investigated. It was clear that ammonia almost all decomposed to hydrogen and nitrogen. Hydrogen conversion attained 100 % at an applied voltage of 15 kV and 0.5 % ammonia flow rate of 0.2 L/min. Decomposition of a high concentration ammonia concentration gas (100%) was examined to obtaine high energy efficiency. Hydrogen conversion was lower than 0.5 % ammonia, but hydrogen production energy efficiency was 800 times higher than that of 0.5 % ammonia.

Keywords: Ammonia, Hydrogen production, Pulsed plasma, Dielectric barrier discharge

I. INTRODUCTION

Green house effect gases are emitted from various combustion resources such as fossil fuel combustors. As a result, currently progress of the global warming is concerned in the world. In order to reduce greenhouse effect gases, the key technique is establishment of the hydrogen energy society. But hydrogen has energy loss for its transportation and storages[1]. To resolve these problems, it is effective process that hydrogen carrier accumulates and transports before it converts to hydrogen[2]–[3]. In particular, ammonia is expected as a hydrogen energy 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. 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.

The objective of this research is to develop hydrogen production devices integrating both ammonia and atmospheric plasma reactor to spread hydrogen energy economy.

In this paper, characteristics of ammonia decomposition and hydrogen production from ammonia at the various conditions were reported.

II. METHODOLOGY

Ammonia is decomposed hydrogen and nitrogen by electric discharge energy from atmospheric plasma (Eq. 1). But we expect that hydrogen conversion is changed by various factors. This research evaluates possibility for practical use as new hydrogen production devices.

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

Figure 1 shows experimental setup for hydrogen production in a plasma reactor. First, ammonia gas regulated mass flow controller is introduced into the plasma reactor, so ammonia gas is decomposed in atmospheric plasma generated by dielectric barrier discharge. In these experiments, the gases decomposed and generated by atmospheric plasma are analyzed by gas chromatography (GC) and quadrupole mass spectrometer (Q–Mass), so we calculate hydrogen conversion and hydrogen production energy efficiency.

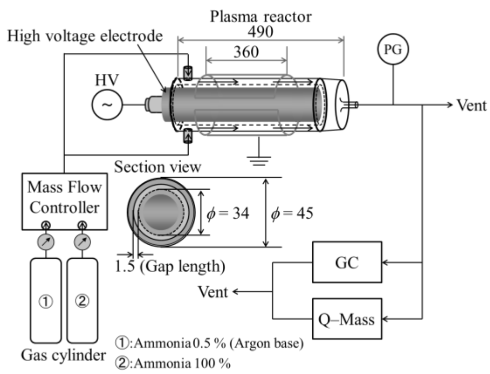

Fig. 1 Experimental setup for hydrogen production.

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III. RESULTS

A. Characteristics of ammonia decomposition

Figure 2 shows effects of applied voltage and flow rates on hydrogen conversion. Hydrogen conversion (C_{H2}) calculated this following equation (Eq. 2).

$$C_{H2} = [H_2]/([NH_3]_0 \times 1.5) \times 100 \qquad \text{(Eq. 2)}$$

$[H_2]$ means hydrogen concentration at the exit of the plasma reactor. $[NH_3]_0$ means initial ammonia concentration.

In figure 2, hydrogen conversion increased with an increase of applied voltage, and decreased with an increase of ammonia gas flow rate. At the condition (gas flow rate = 0.2 L/min, applied voltage = 15 kV), 100 % hydrogen conversion was attained.

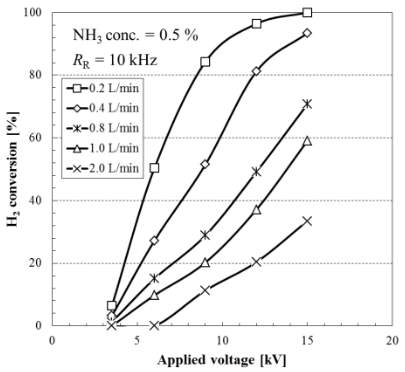

Fig. 2 Effects of applied voltage and flow rates on hydrogen conversion.

Figure 3 shows chemical composition at various applied voltages (gas flow rate = 0.8 L/min). Observed chemical species were hydrogen, nitrogen, and unreacted ammonia. Hydrogen and nitrogen fraction increased with an increase of applied voltage. An earlier study[4] about ammonia decomposition reported that unknown species (N_2H_2 and N_2H_4 may be expected) were obsereved, therefore we tried to analyze unknown species.

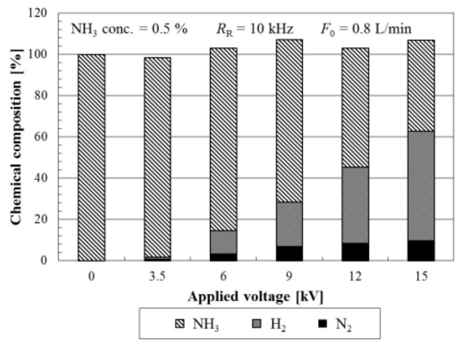

Fig. 3 Chemical composition at various applied voltages.

Figure 4 shows real time tracking of mass numbers (m/z = 32, 30, 29) in production gas (m/z = 32; N_2H_4, m/z = 30; N_2H_2, m/z = 29; NNH including nitrogen fragment). In figure 4, two peaks (m/z = 32, 30) were no change while atmospheric plasma was firing. On the other hand, only NNH peak increased with generation of atmospheric plasma.

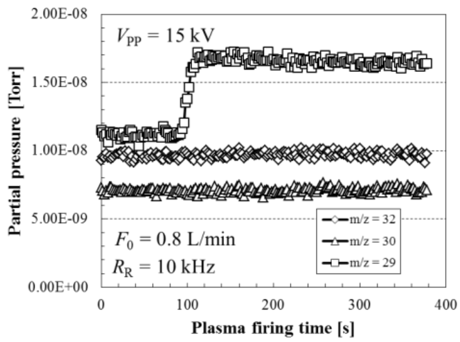

Fig. 4 Real time tracking of mass numbers (m/z = 32, 30, 29) in production gas (m/z = 32; N_2H_4, m/z = 30; N_2H_2, m/z = 29; NNH including nitrogen fragment).

Based on the above results, this device can produce hydrogen at low temperature without catalyst and carbon dioxide. According to figure 2, 100 % hydrogen conversion was attained, so this device is expected new process for hydrogen production. To put this device to practical use, it is important to improve hydrogen production and energy efficiency for hydrogen production.

B. Investigation of optimum conditions for hydrogen production

In this section, we investigated optimum conditions for hydrogen production device to increase hydrogen production.

Figure 5 shows effects of energy density and flow rates on hydrogen production. Hydrogen production (P_{H2}) and energy density (E_P) calculated this following equation (Eq. 3 and Eq. 4)

$$P_{H2} = ([H_2] \times F_0)/100 \qquad \text{(Eq. 3)}$$
$$E_P = (1000 \times P)/V \times \theta \qquad \text{(Eq. 4)}$$

F_0 means ammonia gas flow rate. And P means input electric power, V means volume of plasma reactor, θ means residence time. In figure 5, hydrogen production increased with an increase of gas flow rate and applied voltage. Compared with figure 2, it was clear that hydrogen production lead to the opposite result. Next, we investigated same characteristic using 100 % ammonia gas.

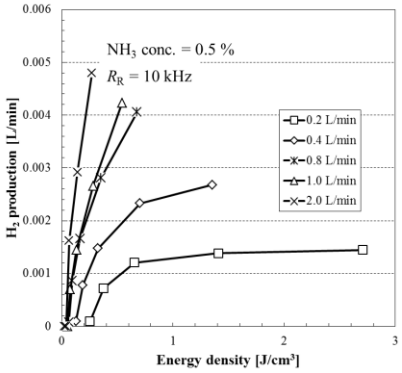

Fig. 5 Effects of energy density and flow rates on hydrogen production.

Figure 6 shows effects of electric power and flow rates on hydrogen conversion. In figure 6, hydrogen conversion increased with an increase of electric power, and decreased with an increase of ammonia gas flow rate. While 100 % hydrogen conversion was attained at low concentration ammonia, only 16 % hydrogen conversion was able to attained at high concentration ammonia. So it was clear that hydrogen conversion decreased with an increase of ammonia concentration.

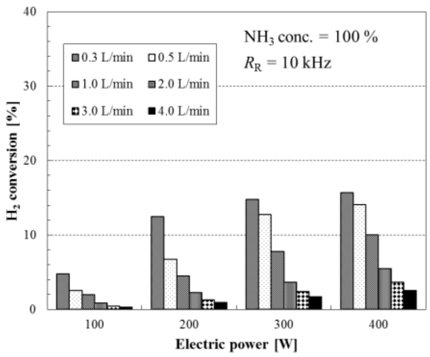

Fig. 6 Effects of electric power and flow rates on hydrogen conversion.

Figure 7 shows comparison between low concentration and high concentration on hydrogen production. In figure 7, hydrogen production increased with an increase of ammonia concentration. Based on figure 2, figure 6 and figure 7, high concentration ammonia had high performance about hydrogen production, but there was a problem of unreacted ammonia because of low performance about hydrogen conversion.

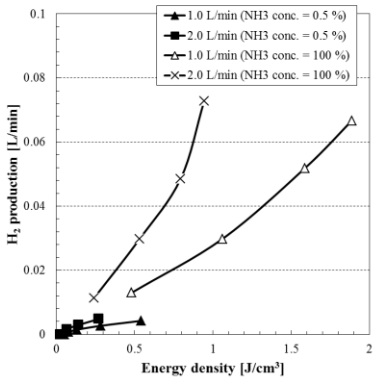

Fig. 7 Comparison between low concentration and high concentration on hydrogen production.

C. Reviewing of hydrogen production energy efficiency

Until now, we investigated characteristics of hydrogen production using low and high concentration ammonia gases. In this section, we calculated hydrogen production energy efficiency in each condition to evaluate the usefulness of this device.

Figure 8 shows comparison between low concentration and high concentration on maximum hydrogen energy efficiency. In figure 8, energy efficiency at high concentration ammonia was 800 times higher than it at low concentration ammonia. So it was clear that high concentration ammonia was superior to low concentration ammonia from a practical application perspective.

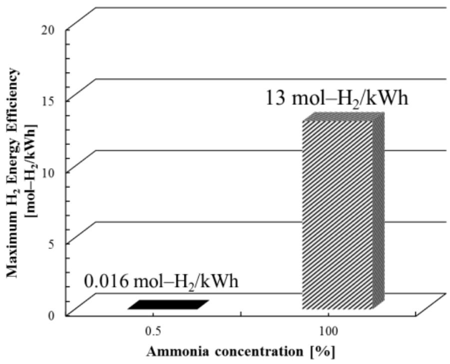

Fig. 8 Comparison between low concentration and high concentration on maximum hydrogen energy efficiency.

IV. Discussion

In figure 2, ammonia was decomposed by atmospheric plasma and generated hydrogen in this device. From this result, we thought that the bond between N and H of ammonia was dissociated by plasma's electronic energy, so hydrogen generated.

In figure 3 and figure 4, unknown species (N_2H_2, N_2H_4)

which earlier study reported were not found in this device. But we found new chemical specie (m/z = 29; ex. NNH). From these results, we thought that NNH converted nitrogen soon because NNH has a short half–life. Thus, mass balance in this paper was composed by hydrogen, nitrogen and unreacted ammonia.

In figure 5, there was a different trend between hydrogen conversion and hydrogen production at low concentration ammonia. From this result, we thought that ammonia input per unit time is related to an alteration in hydrogen production. In fact, hydrogen production could improve at high concentration ammonia (figure 7). But hydrogen conversion was reduced to less than a quarter. In other words, it was clear that there was unreacted ammonia which ammonia didn’t convert to hydrogen. On the other hand, we found that high concentration ammonia was superior to low concentration ammonia in terms of hydrogen production energy efficiency (figure 8). We estimated that these results are related to state of atmospheric plasma.

Figure 9 shows comparison between low concentration and high concentration on state of the plasma reactor. In figure 9, plasma firing state at low concentration ammonia (a) was very radiant and we could see white lines, while it at high concentration ammonia (b) was not more radiant than (a). In particular, we focused attention on white lines at (a). This is called streamer discharge. Because Argon plasma was very stable and electronic energy was high, energy that was spent by ammonia gas spread three–dimensionally. Thus, low concentration ammonia got high numerical value for hydrogen conversion, but it become clear to be the manufacturing method that was non–efficiency.

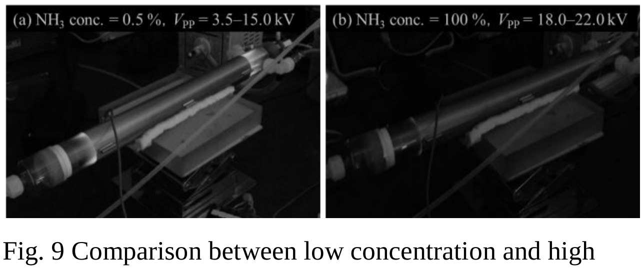

Fig. 9 Comparison between low concentration and high concentration on state of the plasma reactor.

V. CONCLUSION

This research’s objective is development of world first hydrogen production devices integrating both ammonia and atmospheric plasma reactor to spread hydrogen energy economy. In this paper, the following conclusions were obtained.

A) Ammonia was decomposed by atmospheric plasma and generated hydrogen in this device. And this device can produce hydrogen at low temperature without catalyst and carbon dioxide. Because 100 % hydrogen conversion was attained, so this device is expected new process for hydrogen production.

B) In terms of hydrogen conversion, low concentration ammonia was superior to high concentration ammonia. But in terms of hydrogen production, there was a trend different from hydrogen conversion.

C) Hydrogen production energy efficiency at high concentration ammonia was 800 times higher than it at low concentration ammonia. So it was clear that high concentration ammonia was superior to low concentration ammonia from a practical application perspective.

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