Hydrogen production from ammonia by DBD pulsed plasma with hydrogen permeable membrane

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Abstract— An innovative energy storage and carrier system has proposed from our recent researches. We focused on development of hydrogen production devices using a dielectric barrier discharge pulsed plasma, which is a reactor for fuel cells in the innovative energy system. In this study, 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 conventional plasma reactor was 8.7 L/h, whereas that of the plasma membrane reactor was 21.0 L/h. 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. Since the rate-controlling step is the ammonia decomposition rate in the plasma, an improvement in hydrogen production is expected by investigating the optimum conditions for the plasma decomposition of ammonia.

Keywords— Hydrogen, Plasma reactor, Membrane reactor, Dielectric barrier discharge

I. INTRODUCTION

The introduction of a hydrogen economy has been an available strategy to control criminate change when hydrogen is produced without CO_2 emission. However, use of hydrogen has a large energy loss for its transportation and physical storages [1, 2]. Ammonia is a hydrogen storage material that may solve several problems related to the hydrogen transportation and storage in a hydrogen economy [3]. Therefore, an energy carrier and storage system using ammonia has been proposed [4]. For example, a system consisting of the hydrogen production by electrolysis of water, ammonia synthesis from hydrogen, and the hydrogen generation from ammonia, is recognized as a hydrogen carrier and storage system without CO_2 emission. However, the efficiently ammonia synthesis is currently difficult, though some researches have been performed ammonia synthesis studies at a low temperature and pressure [5, 6].

We have been developed an original deNO_x reactor using vacuum ultra violet (VUV) of 172 nm wavelength [7]. Recently, we found that nitric acid (HNO_3) was easily produced from NO_x by photochemical oxidation. HNO_3 is an available material for NH_3 production, because NH_3 can generate from HNO_3 by reduction at atmosphere pressure and a low temperature [8].

On the other hand, an original plasma membrane reactor for H_2 production from ammonia also has been developed. Using the plasma membrane reactor, pure hydrogen production for fuel cells was attained the flow rate of 21 L/h. These results have created a new hydrogen energy storage and carrier system consisting of the HNO_3 production reactor, the NH_3 production reactor, and the H_2 production reactor as shown in Figure 1 [9].

If the energy system shown in Figure 1 installs to the combustors, the cost of catalyst and ammonia would be reduced. Furthermore, excess electricity from renewable energy can use to drive each reactor; therefore hydrogen may be able to inexpensively produce. It is important for the establishment of the energy system to achieve high energy efficiency in each reactor.

In this paper, we focused on development of hydrogen production devices using a dielectric barrier discharge pulsed plasma, which is the reactor for fuel cells in the innovative energy system shown in Fig. 1 [10].

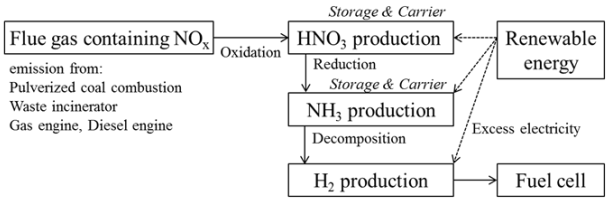

Fig. 1. An innovative energy storage and carrier system.

II. METHODOLOGY

Two different plasma reactors with and without a hydrogen separation membrane were prepared for the hydrogen production experiment. Fig. 2 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. Fig. 3 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. In the PMR, the hydrogen separation membrane module served as the high-voltage electrode of the PMR. The hydrogen separation membrane module was made by Nippon Seisen Co., Ltd. A palladium alloy membrane of 20 μm thickness was used as the membrane.

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To analyse the concentration of hydrogen generated at the reactor exit, a 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).

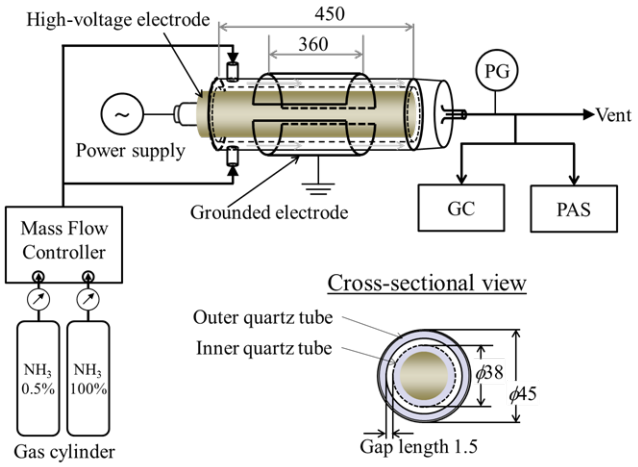

Fig. 2. Configuration of the plasma reactor (PR).

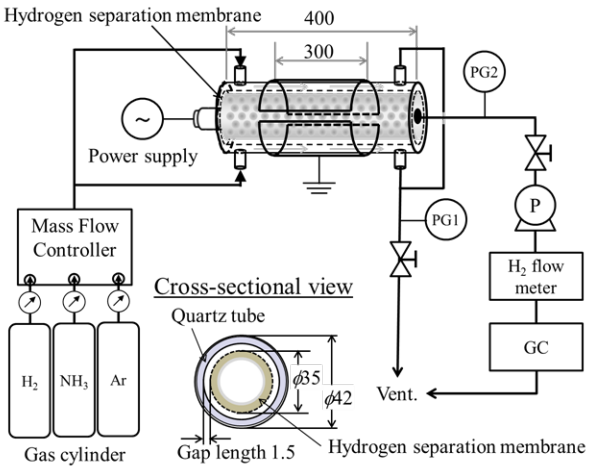

Fig. 3. Experimental setup for hydrogen production by plasma membrane reactor (PMR).

III. Results And Discussion

A. Hydrogen production characteristics of 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.

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

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. 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.

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

$$NH_2 + H \rightarrow NH_3 \qquad (2)$$
$$NH + 2H \rightarrow NH_3 \qquad (3)$$

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

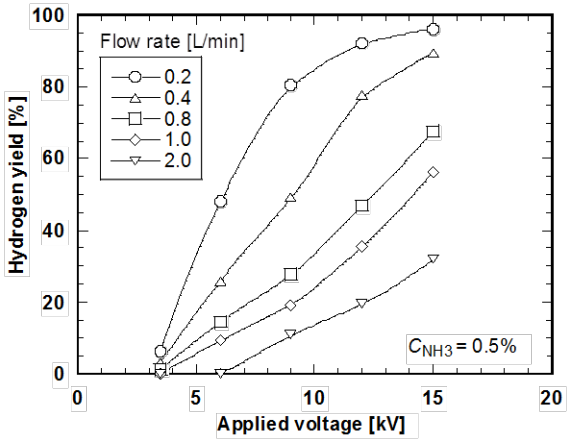

Fig. 4. Effect of Vpp on hydrogen yield as a parameter of flow rates of 0.5% ammonia gas

B. Hydrogen separation performance of the PMR

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. Fig. 5 shows the hydrogen separation characteristics of the PMR as variables of induced pressure (PG2 in Fig. 3) and feed pressure (PG1 in Fig. 3). 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. Its surface temperature was 408 K, which was measured by a radiation thermometer (Hioki 3460-50).

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 [11]. 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 [12].

Hydrogen permeation in the PMR is estimated from a solution diffusion mechanism [13], as follows:

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

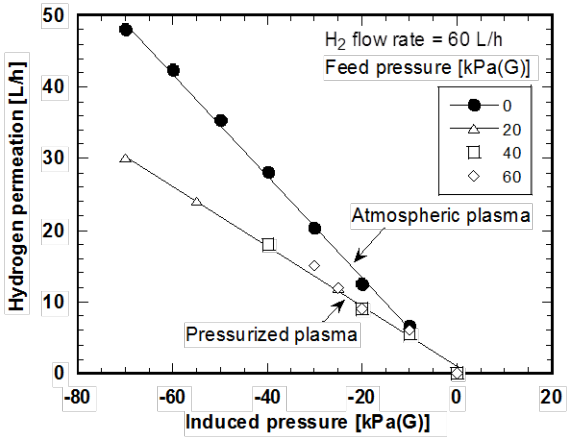

Fig. 5. Hydrogen separation characteristics of PMR for pure hydrogen supply.

C. Hydrogen production performance of the PMR

Hydrogen production experiments were conducted in the PMR using the 100% ammonia gas at various flow rates. Feed pressure and induced pressure were 0 and 70 kPa(G), respectively. Fig. 6 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.

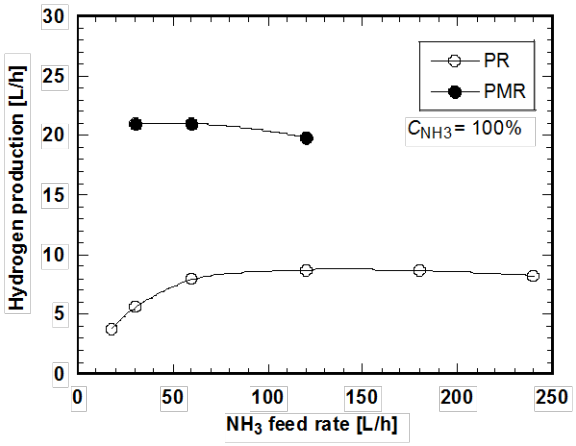

Fig. 6. Hydrogen production performance of the PMR and PR

IV. Conclusion

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 plasma reactor (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 0.5% 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, a plasma membrane reactor (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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REFERENCES

[1] Eberle U, Felderhoff M, Schueth F., Chemical and physical solutions for hydrogen storage, Angew Chem. Int. Edit., Vol.48, 6608–6630, 2009.

[2] Lan, R, Irvine, J. T. S. and Tao, S., Ammonia and Related Chemicals as Potential Indirect Hydrogen Storage Materials, Int. J. Hydrogen Energy, Vol. 37, No. 2, pp 1482-1494, 2012.

[3] Green Jr L., An ammonia energy vector for the hydrogen economy, Int. J. Hydrogen Energy, Vol.35, 355–359, 1982.

[4] Kojima Y., J. Jpn. Inst. Energy, Vol.93 No.5, pp.378–385, 2014. (in Japanese)

[5] Pickett C.J., Talarmin J., Electrosynthesis of ammonia, Nature, Vol.317, 652–653, 1985.

[6] Skodra A., Stoukides M., Electrocatalytic synthesis of ammonia from steam and nitrogen at atmospheric pressure, Solid State Ionics, Vol.180, 1332–1336, 2009.

[7] Kambara S., Hayakawa Y., Masui M., Hishinuma N., Kumabe K., Moritomi H., Removal of nitric oxide by activated ammonia generated by vacuum ultraviolet radiation, Fuel, Vol.94, pp.274–279, 2012.

[8] Crumpton W. G., Isenhart T. M., Hersh C. M., Determination of Nitrate in Water Using Ammonia Probes and Reduction by Titanium (III), Water Pollution Control Federation, Vol. 59, No. 10, pp. 905–908, 1987.

[9] Watanabe, M., Kambara, S., Hydrogen energy storage system originated from nitrogen oxides in flue gas, Proc. 10th Conf. on Sustainable Development of Energy, Water and Environment Systems, SDEWES2015.1054, 1-6, Dubrobnik (Croatia), 2015.

[10] Kambara S., Hayakawa Y., Inoue Y., Tomonori M., Hydrogen production from ammonia by a plasma membrane reactor, J. Sustainable Dev. Energy, Water & Env. Systems, in print, 2015.

[11] Sieverts, A. and Krumbhaar, W., Solubility of Gases in Metals and Alloys, Berichte der Deutschen Chemischen Gesellschaft, Vol.43, pp 893-900, 1910.

[12] Yun, S. and Oyama, S. T., Correlations in Palladium Membranes for Hydrogen Separation: A Review, J. Membrane Sci., Vol. 375, Nos. 1-2, pp. 28-45, 2013.

[13] Yoshida, H., Okuno, K., Naruse, Y. and Kashiwai, T., Metallurgical Considerations on Pd, Pd-alloy and their Metal-Hydrogen Systems, Fusion Science and Technology, Vol. 8, No. 2P2, pp. 2388-2394, 1985.