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# Hydrogen Production Characteristics from Ammonia by Plasma Membrane Reactor

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## ABSTRACT

An innovative plasma membrane reactor (PMR) has been developed to produce $H_2$ from $NH_3$. The PMR is consist of atmospheric pressure plasma and the $H_2$ separation membrane, which can produce high-purity $H_2$ for fuel cells from $NH_3$. First, fundamental characteristics of $H_2$ separation of the PMR were examined by supplying $H_2$ gas. It verified that the PMR has excellent performance for $H_2$ separation at atmospheric pressure. Second, $NH_3$ decomposition and $H_2$ production characteristics of the PMR were investigated by supplying 100% $NH_3$ gas. The maximum $H_2$ conversion was 24%, whereas the plasma reactor without $H_2$ separation membrane was hydrogen conversion of 13%.  Purity of $H_2$ was about 100%, which can apply fuel cells. Stable $H_2$ production rate of 20 mL / min was observed.

**KEYWORDS:** Ammonia, Hydrogen, Atmospheric plasma, Hydrogen separation membrane, Dielectric barrier discharge

## 1. INTRODUCTION

The bottleneck of construction of hydrogen energy society is energy loss in the transportation and storage of $H_2$ [1]. In order to reduce energy loss, a new energy system using hydrogen carriers has been proposed [2]. Hydrogen carrier is available for transportation and storage of $H_2$. Among hydrogen carrier, $NH_3$ is promising, and research on $H_2$ production from $NH_3$ has been done in the world [3]. $NH_3$ has four advantages as an hydrogen carrier. (1) Liquefaction is easy. (2) The method of transportation and storage is established. (3) Carbon dioxide does not produce when $NH_3$ is converted to $H_2$ at end user side. (4) High energy density on a basis of weight and volume such as fossil fuels. In the hydrogen energy system using $NH_3$, a device for producing $H_2$ from $NH_3$ is required.

$H_2$ production from $NH_3$ by high electron energy of atmospheric pressure plasma is extremely promising. This is because that 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. We have elucidated the influence of applied voltage, $NH_3$ concentration, and $NH_3$ gas residence time on $H_2$ production [4]. The $H_2$ yield increased with an increase in higher applied voltage, gas residence time, and a decrease in $NH_3$ concentration. However, the $H_2$ yield saturated at high applied voltage because of $NH_3$ production from generated $H_2$. The reverse reaction has to reduce for high efficiency hydrogen production. In order to suppress the reverse reaction, an innovative plasma reactor combining a $H_2$ separation membrane (plasma membrane reactor: PMR) was designed [5]. The PMR can simultaneously perform $H_2$ production and $H_2$ separation, high purity $H_2$ is continuously produced.

The purpose of this research is to be clear hydrogen production characteristics of the plasma membrane reactor. $H_2$ separation characteristics and $H_2$ generation characteristics were investigated.

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## 2. EXPERIMENTAL

Fig.1 shows experimental setup for hydrogen production, which consists of a gas supply system, a high voltage pulse power supply for pulsed plasma, a plasma membrane reactor (PMR), and a gas chromatograph for measurement of hydrogen concentration. The PMR consisted of a glass tube and a hydrogen separation membrane module made by Nippon Seisen Co., Ltd. In this module, a palladium alloy (Pd-40%Cu) 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. Two types of quartz tubes with different outer diameters were used (Outer diameter = 42 mm or 48 mm, thickness = 2 mm). The electrodes had a coaxial configuration with quartz glass tubes as the dielectric material (see the sectional view in Fig.1).

Atmospheric pressure plasma was generated at the reaction gap by dielectric barrier discharge (DBD) with a high voltage pulse power supply (manufactured by Sawafuji Electric Co., Ltd.).

The flow rate of the test gas was adjusted by a mass flow controller with a gas blender (KOFLOC GB-3C and HORIBA SEC-E450). The produced $H_2$ gas flow rate was measured by a flow meter, and the $H_2$ concentration was measured by a capillary TCD gas chromatograph (INFICON GC-3000) at the exit of the PMR.

Table 1 lists experimental conditions of $H_2$ separation experiments and $H_2$ production experiments. In $H_2$ separation experiment, 100% $H_2$ gas or 0.5% $H_2$ gas (argon balance) was used as a test gas. In $H_2$ production experiment, 100% $NH_3$ gas was used. The effect of gas pressure at the PMR inlet ($P_{\mathrm{in}}$) and gas pressure at the PMR outlet ($P_{\mathrm{out}}$) on $H_2$ separation and production was investigated.

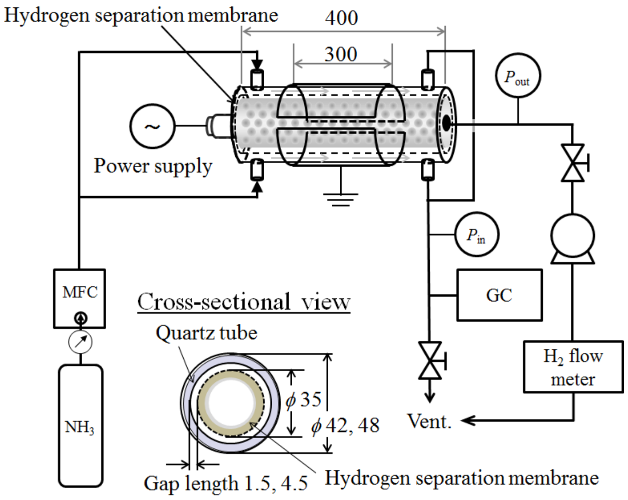

Fig. 1 Experimental setup for hydrogen separation and production by plasma membrane reactor.

Table 1 Experimental conditions

| | | |
|---|---|---|
| Plasma conditions | | |
| Repetition rate, $R_R$ | [kHz] | 10 |
| Power consumption | [W] | 100−400 |
| Pressure of supplied side, *Pin* | [kPa (G)] | 0−60 |
| Pressure of permeable side, $P_{\mathrm{out}}$ | [kPa (G)] | −95−0 |
| For $H_2$ separation experiments | | |
| $H_2$ concentration (diluted by Ar) | [%] | 10−100 |
| Flow rate of $H_2$ or $H_2$/Ar, $F_0$ | [L/min] | 0.5−2.0 |
| For $H_2$ production experiments | | |
| $NH_3$ concentration | [%] | 100 |
| Flow rate of $NH_3$ | [L/min] | 0.5−2.0 |
| Gap length | [mm] | 1.5 or 4.5 |

## 3. RESULT AND DISCUSSION

### 3.1 $H_2$ Separation Characteristics of PMR (Influence of Differential Pressure)

First, the $H_2$ separation characteristics of PMR were investigated by using 100% $H_2$ gas. The $P_{in}$ was varied in the range of 0 to 60 kPa(G) by changing the secondary cylinder pressure of the supplied $H_2$ gas shown in Fig.1. The $P_{out}$ was also changed from 0 to -90 kPa(G) by adjusting the valve before the suction pump. By changing the differential pressure between $P_{in}$ and $P_{out}$, the dependence of $H_2$ permeability on the differential pressure at the outlet of the $H_2$ separation membrane was investigated. The $H_2$ permeability, $P_{H2}$ [%] was defined by the following equation:

$$P_{H2}\ [\%] = F_{H2} / (F_0 \times [H_2]_0) \times 100 \qquad (1)$$

where $F_{H2}$ [L/min] is the $H_2$ permeation flow rate at the $H_2$ separation membrane outlet, $F_0$ [L/min] is the supply gas flow rate, $[H_2]_0$ is the $H_2$ concentration in the supply gas.

Fig. 2 shows the change of $F_{H2}$ with respect to the differential pressure ($P_{in} - P_{out}$). At the $P_{in} = 0$, the $F_{H2}$ increased with an increase in the differential pressure. Smith reported that the behaviour of $H_2$ permeation flux of $H_2$ separation membrane depends on $H_2$ partial pressure and difference pressure at in/out of the $H_2$ separation membrane [6]. The correlation is given by the following Richardson equation:

$$J = \phi / d \times (P_H^{0.5} - P_L^{0.5}) \qquad (2)$$

where $J$ [mol-$H_2 \cdot s^{-1}$] is the $H_2$ permeation flux, $\phi$ [mol-$H_2 \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-0.5}$] is the $H_2$ permeability coefficient, and $d$ [m] is the $H_2$ separation membrane thickness. $P_H$ and $P_L$ [Pa] are $H_2$ partial pressure of the $H_2$ separation membrane inlet side and outlet side.

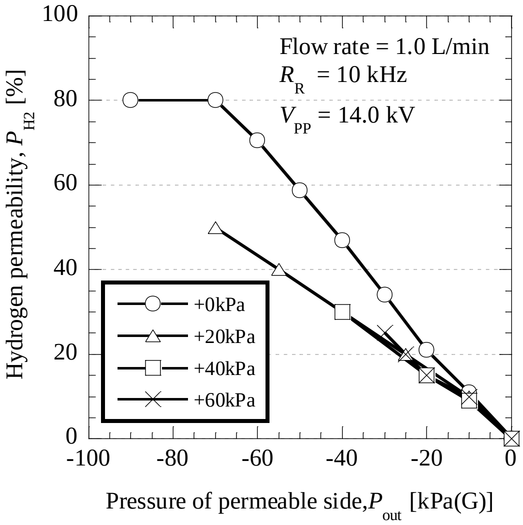

Fig. 2 Hydrogen separation characteristics of the plasma membrane reactor (Supplied gas:100% $H_2$)

According to equation (2), $H_2$ permeability, $P_{H2}$, proportionally increased with a decrease in $P_{out}$ under a constant $P_{in}$. On the other hand, at a constant $P_{out}$, $P_{H2}$ decreased with an increase in $P_{in}$. This is because that $H_2$ production was affected by $P_{in}$. Under pressurized plasma condition, plasma is unstable; therefore, $H_2$ production was decreased. Compared to atmospheric pressure plasma, pressured plasma decreases the density of generated electrons e, so it is considered that the H radical concentration generated also decreases. [7].

Generally, a $H_2$ separation membrane made of a palladium alloy can separate $H_2$ at a temperature of 350°C - 450 °C [8]. Figure 2 shows that sufficient $H_2$ permeability can be performed by the PMR without membrane heating. This is the advantage of the PMR. Though the temperature of the $H_2$ separation membrane module heated up to 201 °C by Joule heat, external heating is not required for $H_2$ separation. In other words, the PMR can reduce the temperature for $H_2$ separation of Pd alloy membrane.

### 3.2 $H_2$ production characteristics by PMR from $NH_3$

$H_2$ production experiments using 100% $NH_3$ gas were carried out. Two types of PMRs having different gap length (d = 1.5 mm or 4.5 mm) were examined to be clear effect of the gas residence time in the PMR on $H_2$ production. Figure 3a shows effect of total power consumption on $H_2$ yield, which was compared with previous data obtained by a plasma reactor without $H_2$ separation membrane (PR). The $H_2$ yield $Y_{H2}$ [%] was redefined as follows:

$$Y_{H2} = (F_0 \times [H_2]_{out} / 100 + Fp_{H2}) / (F_0 \times 1.5) \times 100 \tag{3}$$

where $F_0$ [L/min] is the supplied $NH_3$ gas flow rate, $[H_2]_{out}$ is the $H_2$ concentration at the reactor outlet, and $Fp_{H2}$ [L/min] is the measured $H_2$ flow rate.

It found that the maximum $H_2$ yield of the PR and PMR(d = 4.5) was 13.0 % and 24.4 %, respectively. It is clear that the PMR has advantage in $H_2$ yield comparing with the PR. This is because that equilibrium in reaction (4) moves to right side by $H_2$ separation during $H_2$ production in plasma.

$$2NH_3 \rightleftarrows 3H_2 + N_2 \tag{4}$$

Figure 3b shows effect of power consumption on $H_2$ permeable rate as a function of the gap length. The flow rate of $H_2$ production was greatly increased at the power consumption of 400W in the gap length of 4.5 mm. The behavior related to $H_2$ separation characteristics that the $H_2$ separation rate is increased with an increase in hydrogen concentration.

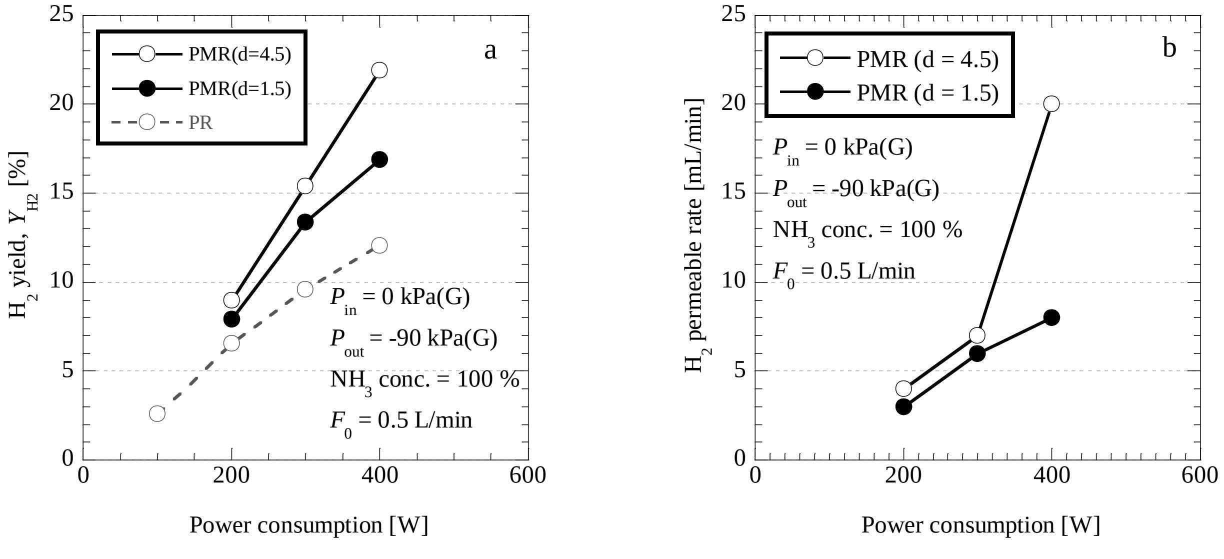

Fig. 3 $H_2$ production characteristics from $NH_3$ by PMR. (a: $H_2$ yield, b: $H_2$ permeable rate)

## 4. CONCLUSIONS

Hydrogen separation characteristics and hydrogen production characteristics of the innovative plasma membrane reactor (PMR) were investigated.

First, $H_2$ permeability of the PMR proportionally increased with a decrease in $P_{out}$ under a constant $P_{in}$ without external heating. This is the advantage of the PMR, because $H_2$ separation membrane generally required the temperature of 350°C - 450 °C

Second, it found that pure $H_2$ can be continuously produced by the PMR. The maximum $H_2$ conversion was 24.4 %.

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