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 H2 from NH3. The PMR is consist of atmospheric pressure plasma and the H2 separation membrane, which can produce high-purity H2 for fuel cells from NH3. First, fundamental characteristics of H2 separation of the PMR were examined by supplying H2 gas. It verified that the PMR has excellent performance for H2 separation at atmospheric pressure. Second, NH3 decomposition and H2 production characteristics of the PMR were investigated by supplying 100% NH3 gas. The maximum H2 conversion was 24%, whereas the plasma reactor without H2 separation membrane was hydrogen conversion of 13%. Purity of H2 was about 100%, which can apply fuel cells. Stable H2 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 H2 [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 H2. Among hydrogen carrier, NH3 is promising, and research on H2 production from NH3 has been done in the world [3]. NH3 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 NH3 is converted to H2 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 NH3, a device for producing H2 from NH3 is required.

H2 production from NH3 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, NH3 concentration, and NH3 gas residence time on H2 production [4]. The H2 yield increased with an increase in higher applied voltage, gas residence time, and a decrease in NH3 concentration. However, the H2 yield saturated at high applied voltage because of NH3 production from generated H2. The reverse reaction has to reduce for high efficiency hydrogen production. In order to suppress the reverse reaction, an innovative plasma reactor combining a H2 separation membrane (plasma membrane reactor: PMR) was designed [5]. The PMR can simultaneously perform H2 production and H2 separation, high purity H2 is continuously produced.

The purpose of this research is to be clear hydrogen production characteristics of the plasma membrane reactor. H2 separation characteristics and H2 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 H₂ gas flow rate was measured by a flow meter, and the H₂ concentration was measured by a capillary TCD gas chromatograph (INFICON GC-3000) at the exit of the PMR.

Table 1 lists experimental conditions of H₂ separation experiments and H₂ production experiments. In H₂ separation experiment, 100% H₂ gas or 0.5% H₂ gas (argon balance) was used as a test gas. In H₂ production experiment, 100% NH₃ gas was used. The effect of gas pressure at the PMR inlet (P_in) and gas pressure at the PMR outlet (P_out) on H₂ separation and production was investigated.

<table>
<thead>
<tr>
<th>Plasma conditions</th>
<th>[kHz]</th>
<th>10</th>
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</thead>
<tbody>
<tr>
<td>Repetition rate, R_R</td>
<td>[W]</td>
<td>100−400</td>
</tr>
<tr>
<td>Power consumption</td>
<td>[kPa (G)]</td>
<td>0−60</td>
</tr>
<tr>
<td>Pressure of supplied side, Pin</td>
<td>[kPa (G)]</td>
<td>−95−0</td>
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<tr>
<td>Pressure of permeable side, P_out</td>
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</table>

| For H₂ separation experiments         |                |               |
| H₂ concentration (diluted by Ar)      | [%]            | 10−100        |
| Flow rate of H₂ or H₂/Ar, F₁         | [L/min]        | 0.5−2.0       |

| For H₂ production experiments         |                |               |
| NH₃ concentration                     | [%]            | 100           |
| Flow rate of NH₃                      | [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:

$$P_{H2} [%] = F_{H2} / (F_0 \times [H_2]_0) \times 100$$  \hspace{1cm} (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 pressure difference at in/out of the H$_2$ separation membrane [6]. The correlation is given by the following Richardson equation:

$$J = \phi / d \times (P_{H}^{0.5} - P_{L}^{0.5})$$  \hspace{1cm} (2)

where $J$ [mol-H$_2$·s$^{-1}$] is the H$_2$ permeation flux, $\phi$ [mol-H$_2$·m$^{-1}$·s$^{-1}$·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$_2$)](image)

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 ºC [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 H2 separation. In other words, the PMR can reduce the temperature for H2 separation of Pd alloy membrane.

3.2 H2 production characteristics by PMR from NH3
H2 production experiments using 100% NH3 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 H2 production. Figure 3a shows effect of total power consumption on H2 yield, which was compared with previous data obtained by a plasma reactor without H2 separation membrane (PR). The H2 yield $Y_{H2}$ [%] was redefined as follows:

$$Y_{H2} = \left(\frac{F_0 \times [H_2]_{out}}{100 + F_{P_{H2}}} \times (F_0 \times 1.5) \times 100\right)$$

where $F_0$ [L/min] is the supplied NH3 gas flow rate, $[H_2]_{out}$ is the H2 concentration at the reactor outlet, and $F_{P_{H2}}$ [L/min] is the measured H2 flow rate.

It found that the maximum H2 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 H2 yield comparing with the PR. This is because that equilibrium in reaction (4) moves to right side by H2 separation during H2 production in plasma.

$$2NH_3 \leftrightarrow 3H_2 + N_2$$

Figure 3b shows effect of power consumption on H2 permeable rate as a function of the gap length. The flow rate of H2 production was greatly increased at the power consumption of 400W in the gap length of 4.5 mm. The behavior related to H2 separation characteristics that the H2 separation rate is increased with an increase in hydrogen concentration.

4. CONCLUSIONS
Hydrogen separation characteristics and hydrogen production characteristics of the innovative plasma membrane reactor (PMR) were investigated. First, H2 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 H2 separation membrane generally required the temperature of 350°C - 450°C.
Second, it found that pure H\textsubscript{2} can be continuously produced by the PMR. The maximum H\textsubscript{2} conversion was 24.4\%.

**REFERENCES**


