Characteristics of hydrogen generation from ammonia by plasma membrane reactor

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Abstract

Ammonia is an excellent hydrogen carrier to solve the problems related to hydrogen transportation and storage in the hydrogen economy. In this study, pure hydrogen production was performed by a pulsed plasma membrane reactor equipped with a hydrogen separation membrane. Without the hydrogen membrane, the hydrogen conversion was 13 %. On the other hand, the hydrogen conversion of 21.9 % was attained by the plasma membrane reactor (PMR). The advantage of the PMR was to obtain pure hydrogen, which can apply to a fuel cell. The flow rate of hydrogen production by plasma decomposition of 100% ammonia was 20 mL/min.

1. Introduction

Greenhouse effect gases are emitted from various energy production sources such as coal fired power plants. In order to reduce the greenhouse effect gas, the key technology is establishment of the H_2 energy society, but there are some problem, for example, large energy loss in transportation and storage of hydrogen is a problem we cannot avoid.[1)]. To solve these problems, it proposed that hydrogen energy storage, carrier, and utilization system[2)-3)]. In the energy system, NH_3 is used as a H_2 energy carrier materials. NH_3 has a number of favorable characteristics, the primary one being its high capacity for H_2 storage, 17.6 wt%, based on its molecular structure. The secondary advantage is that NH_3 itself is carbon-free at the end users, although CO_2 emission on production of NH_3 is dependent on the source of energy.

In this research, an innovative H_2 production devices integrating plasma and hydrogen separation membrane has developed. The characteristics of NH_3 decomposition and H_2 production from NH_3 by the plasma membrane reactor was studied.

2. Mehtodology

Fig. 1 shows experimental setup of a plasma reactor with a hydrogen separation membrane (PMR). A raw gas controlled by the mass flow controller was supplied into the PMR. The gas was decomposed in atmospheric plasma generated by dielectric barrier discharge. The hydrogen concentration in the production gas was analyzed by gas chromatography (GC), and the flow rate was measured by the volume flow meter.

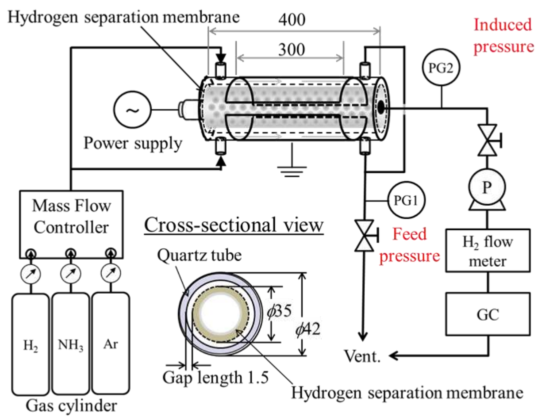

Fig. 1. Experimental setup for hydrogen production.

The PMR is consisting of the glass tube and the hydrogen separation membrane module made by Nippon Seisen Co., Ltd.. The palladium alloy membrane of 20 μm in thickness was elaborately welded inside a thin punched metal. The

PMR length was 400 mm, whereas the grounded electrode length was 300 mm. Two types of the reaction tubes were used, which gap length between the quartz tube and the electrode was 1.5 mm and 4.5 mm. Ground electrode was wrapped around the outer tube of the PMR.

Table 1 lists PMR conditions. The experimental conditions of hydrogen separation tests using H_2/Ar gas and hydrogen production tests using NH_3 was carried out. Repetition rate of the plasma power source was fixed to 10 kHz. To investigate the effect of the difference pressure between the feed pressure and exhaust pressure on separation of H_2, the feed pressure and induced pressure were changed.

Table 1. Experimental conditions.

	unit	
Plasma conditions		
Repetition rate, R_R	[kHz]	*10*
Power consumption	[W]	*100—400*
Pressure of supplied side, PG1	[kPa(G)]	*0—60*
Pressure of permeable side, PG2	[kPa(G)]	*−90—0*
H_2 separation experiments		
Hydrogen conc. (Ar base)	[%]	*10—100*
Flow rate	[L/min]	*0.5—2.0*
H_2 production experiments		
Ammonia conc.	[%]	*100*
Flow rate	[L/min]	*0.5—2.0*
Gap length	[mm]	*1.5, 4.5*

3. Results and discussions

3.1 Hydrogen separation characteristics of PMR

Permeation rate of the hydrogen separation membrane using a metal such as palladium alloys reported characteristic depended on the hydrogen partial pressure transmembrane. Its characteristics are represented by the following Richardson equation[4].

$$J = \phi / d \times (P_H^{0.5} - P_L^{0.5}) \qquad (1)$$

J is the hydrogen permeation flux [mol-H_2/s], ϕ is hydrogen permeability coefficient [mol-H_2/m・s・$Pa^{0.5}$], and d is the thickness of the hydrogen separation membrane [m].

Fig. 2 shows effect of the hydrogen permeation rate to hydrogen concentration in the feed gas. PG2 is a low pressure side as compared to the PG1. So, when PG2 gradually reduced in accordance with the Richardson equation, it is considered to increase hydrogen permeation rate by the hydrogen permeation flow rate was increased.

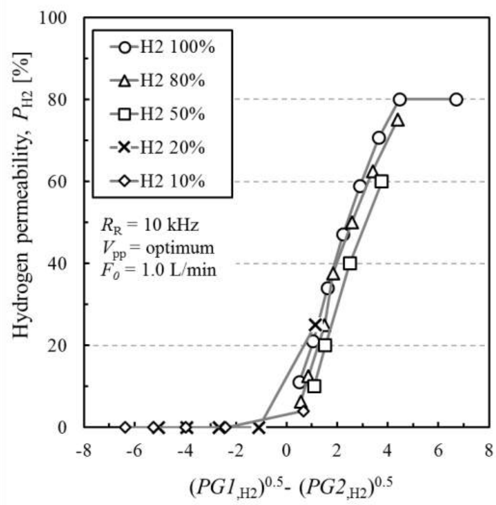

Fig. 2. The effect of hydrogen partial pressure.

Generally, the hydrogen separation membrane of palladium alloy is reported to require a high temperature of 350 ºC - 400 ºC to decomposition and permeation of hydrogen[5]. However, in this study reaction field temperature didn't increase until the above operating temperature, hydrogen permeation occurred. It is considered to have occurred hydrogen permeation by obtaining H radicals to dissociate H-H bonds between H_2 by electron energy of the plasma even at a low temperature. Moreover, it was found that it decreased hydrogen permeation rate according to the hydrogen concentration in the feed gas decreased. However, since in the hydrogen concentration of 10% of the result the hydrogen permeation was occurred in the conditions that the value of ($PG1_{H2}^{0.5} - PG2_{H2}^{0.5}$) was greater than or equal to zero, $PG1_{H2}^{0.5}$ - $PG2_{H2}^{0.5}$ was considered to be a parameter about hydrogen permeation.

3.2 H_2 generation characteristics from the NH_3 by NMR

Fig. 3 shows comparison of H_2 conversion between the PMR and the PR. For comparison existing plasma reactor that did not have a built-in hydrogen separation membrane (hereinafter called, PR) are also plotted experimental results. The hydrogen conversion rate by using the PMR (*d* = 4.5 mm) was able to improve to 21.9%. Compared with the results of PR, which is improved approximately 9%. It is considered to precede the decomposition reaction of NH_3. Moreover, when the separation membrane permeate gas was measured by gas chromatography, it was confirmed that almost 100% of the hydrogen gas.

Fig. 4 shows H_2 permeable rate for NH_3 decomposition by the PMR. Focusing to the gap length of the PMR, when power consumption was raised to 400 W from 300 W on the PMR (*d* = 4.5 mm), hydrogen permeation flow rate was dramatically increased from 7 mL to 20 mL. By contrast, dramatic increase in the hydrogen permeation rate on the PMR (*d* = 1.5 mm) wasn't observed. Looking at the change in the reactor hydrogen concentration, H_2 permeable rate was raised on the PMR (*d* = 4.5 mm) from 10.1 % to 12.4 %. Contrastingly, H_2 permeable rate was raised on the PMR (*d* = 1.5 mm) from 8.8 % to 11.0 %. From Fig. 3, the partial pressure of the hydrogen separation membrane inside and outside is found to significantly affect. So In the hydrogen concentration 11.0%−12.4%, hydrogen permeation is considered to have dramatically increased.

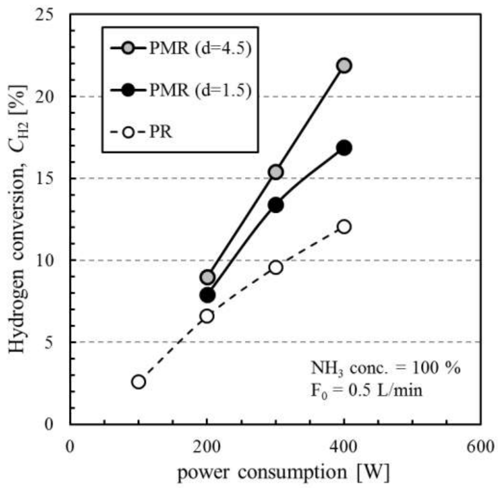

Fig. 3. H_2 conversion by the PMR and the PR.

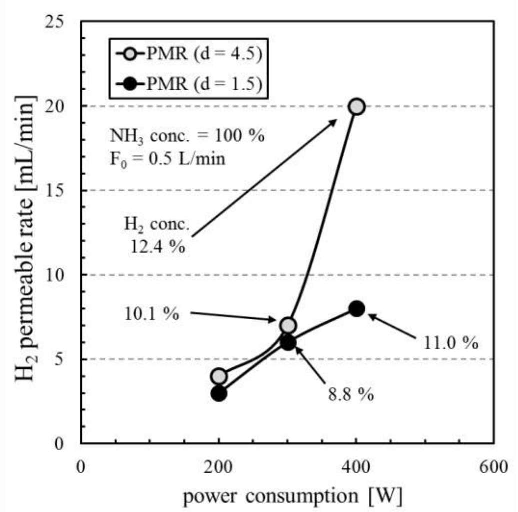

Fig. 4. Effect of the gap length, *d*, on H_2 permeable rate.

3.3 Hydrogen separation mechanism by the PMR

In a conventional H_2 separation membrane use, it well know that high temperature of about 400 ºC is required to generate and absorb H atoms onto the membrane[6-7]. However, in the PMR, it is presumed to be occurred hydrogen permeation by proceeding reactions (1)−(4). By the these mechanism, the PMR is performed hydrogen separation without heating.

(1) NH_3 decomposition by plasma
(2) H radical adsorption to the membrane surface

(3) Membrane permeation of H radicals
(4) Recombination between H radical

4. Conclusion

In this study, as a new method for producing high purity hydrogen efficiently from ammonia, the development of the plasma membrane reactor (PMR) which combines atmospheric pressure plasma and the hydrogen separation membrane was performed. The maximum hydrogen conversion rate was 13% when using a typical plasma reactor. By contrast, With PMR the hydrogen conversion rate was able to improve to 21.9%. Moreover, purity hydrogen obtained by transmitting separation membrane was about 100%, and it stably obtained a feed rate of 20 mL/min.

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