

Development of a hydrogen purifier with Pd-based composite membrane

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Abstract—A hydrogen purifier equipped with Pd-Cu-Ni/PNS membranes has been developed to purify low-grade hydrogen and supply it to processes requiring high-purity hydrogen. The purifier does not include any purge system to flush out hydrogen from the membrane module to prevent membrane embrittlement because there is no α - β phase transition below the critical point of the Pd-H system, making the purifier simple. The hydrogen purifier was tested with three different grades of hydrogen, 90, 99 and 99.9%, to determine the effects of the grade of feed hydrogen on the hydrogen permeation behavior. A lower grade required a lower recovery ratio of the purifier to obtain a given relative hydrogen permeation flux. It was confirmed that the purifier can provide high-purity hydrogen to a gas chromatograph (GC) for carrier and make-up gases. A 75-day durability test provided evidence that the hydrogen purifier could be useful for extended periods as needed for commercial processes.

Key words: Hydrogen, Purifier, Membrane Module, Pd Based Membrane, Composite Membrane

INTRODUCTION

The demand for high purity hydrogen has increased rapidly for several industrial processes, such as chemical synthesis, hydrogenation, semiconductor manufacturing and fuel cells. Hydrogen can be purified through several techniques, such as pressure swing adsorption (PSA), cryogenic distillation, getters, or membrane separation. Hydrogen purification processes are compared in Table 1. PSA, getters, and cryogenic distillation processes are commercially available processes, but they are energy-intensive and complicated [1-4]. Membrane-related processes are promising technologies for the production of high-purity hydrogen. Hydrogen separation membrane technologies offer a number of potential advantages relative to current hydrogen separation technology: (1) lower capital cost; (2) small physical space requirements; (3) fewer moving parts; (4) higher hydrogen recovery rates; (5) ability to produce hydrogen at a steady rate; (6) ability to produce high-purity hydrogen; (7) potential for integration with hydrogen generation technologies so that reforming, shifting and purification can be carried out in a single compact membrane reactor system, with improved thermal efficiency by eliminating the need to cool and reheat gases for gas clean-up and shift reactions [4-7].

Palladium and its alloys have come to occupy an important position in hydrogen separation from gaseous mixture because of their high hydrogen permeability, chemical compatibility and excellent hydrogen selectivity [8-11]. As shown in Table 2, several com-

panies such as Johnson Matthey, ATI Properties, Parker and Japan Pionics currently supply commercial hydrogen purifiers equipped with Pd-based membranes with various capacities of hydrogen purifications. In addition, there have been numerous attempts to apply these membranes used in various types of the membrane reactors [12]. The equipment from these companies includes a purge system to flush out hydrogen from the membrane module to prevent membrane embrittlement, because there is α - β phase transition below the critical point of the Pd-H system, i.e., 565 K at 1.97 MPa.

This study shows a new hydrogen purifier consisting of Pd-based composite membranes and a new designed module. Novel Pd-Cu-Ni/PNS composite membranes and their module [13] were installed in a hydrogen purifier, and the effects of operating and feed gas conditions on the hydrogen permeation behavior were studied. The permeated gas from the hydrogen purifier was analyzed by a gas chromatograph (GC) to investigate whether the membranes could be applied to processes demanding high-purity hydrogen. Extended 75-day durability tests were carried out. Since there is no the α - β phase transition in the membrane at temperatures below the critical points of the Pd-H system, the purifier does not need a purge system, unlike commercial systems where this is a must to prevent membrane embrittlement at temperature below the critical points.

EXPERIMENTAL DETAILS

1. Hydrogen Purifier Design and Operation

The dotted rectangle in Fig. 1 provides a perspective view of a hydrogen purifier, including valves and instrument for controlling pressure, temperature, retentate flow-rate and permeate pressure.

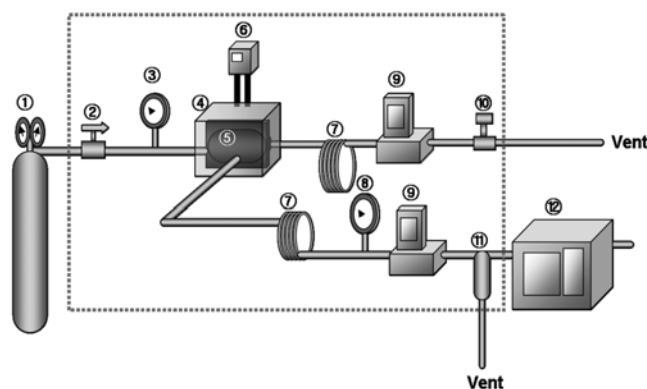
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Table 1. Comparison hydrogen purification processes [12]

	Cryogenic distillation	Getter	Pd-based membrane
Method	Adsorption at ultra-low temperature	Adsorption impurities using Getter	Hydrogen permeation
Material	Liquid nitrogen, Activated carbon	Zirconium-based catalyst	Pd-based membrane
Operating temperature [°C]	–196	200	300-500
Recovery ratio [%]	95	99	95
Pressure drop [atm]	Very low	Very low	2-10 (Pressurization)
Capacity (Nm ³ /h)	50-500	0.1-100	0.1-30
Strong points	Easy maintenance, Large capacity oriented	Simplicity, High recovery ratio	Low capital and maintenance costs, High selectivity
Weak points	Not suitable for small capacity	High Getter cost	High pressure drop

Table 2. List of the companies offering palladium-based membrane [12]

Company	Nationality	Product (s)
Johnson Matthey	USA	Palladium Alloy Diffusion Cell/Hydrogen Purifier
ATI Properties, Inc. (Wah Chang)	USA	Palladium-based Metal Membrane
Parker Hannifin Corp.	USA	Parker Balston [®] Hydrogen Generator
Idatech	USA	ElectraGen XTR Module
MRT Ltd.	Canada	HydRec [™] (Membrane Reformer)
Japan Pionics	Japan	Hydrogen Diffusion Purifier

**Fig. 1. Schematic of a hydrogen purifier: used to supply gas to the GC.**

- | | |
|--|----------------------------|
| 1. H ₂ -N ₂ mixture gas cylinder | 7. Cooling coil |
| 2. On-off valve | 8. Permeate pressure gauge |
| 3. Feed pressure gauge | 9. Flow meter |
| 4. Furnace | 10. Metering valve |
| 5. Membrane module | 11. Check valve |
| 6. Temperature controller | 12. Gas chromatograph |

The membrane module equipped with two Pd-Cu-Ni/PNS composite membranes was developed in a previous study [13]. The feed side pressure is controlled with a pressure regulator equipped on the gas cylinder, and pressure can be read accurately from the pressure gauge equipped on the hydrogen purifier. A controllable check-valve sets and maintains the permeate side pressure. The temperature is controlled with a temperature controller equipped with a K-type thermocouple. Two digital flow meters measure the permeate and retentate gas flow rates. A metering valve on the retentate side facilitates

control of the retentate flow rate. To prevent the digital flowmeters from being damaged by hot gases from the membrane module, cooling coils are installed upstream of the digital flow meters to cool the hot gases.

2. Hydrogen Purifier Operation

To determine the effects of the grade of feed hydrogen on the hydrogen permeation behavior, the hydrogen purifier was operated with three grades of hydrogen, 90, 99 and 99.9%, prepared by diluting high purity hydrogen with high purity nitrogen. As indicated in Fig. 1, the hydrogen purifier was tested as a gas supplier for a gas chromatograph (GC) to determine whether it could be used in a commercial process demanding high-purity hydrogen. Feed gas was 99% H₂+1% N₂, and the feed, permeate and retentate gases were analyzed by the GC (Agilent 6890N) equipped with an HP-MOL-SIV column and a thermal conductivity detector (TCD) using the permeate gas as both carrier and make-up gas. A long-term durability test was carried out for 75 days. The gases were from the Korean gas company, Deokyang Energen Corp. The hydrogen purifier operated at a temperature of 723 K. The permeate side pressure was maintained at 0.476 MPa (70 psi) by means of a controllable check-valve. The flowrates of the permeate and retentate gases were measured at different feed pressures for the three different grades of hydrogen. The retentate flowrate was controlled by the metering valve, and the feed flowrate was calculated by summing the permeate and retentate flowrates. The measurements clarified the effects on hydrogen permeation behavior of the recovery ratio (R) defined as:

$$R = \frac{\text{Permeate flowrate (ml min}^{-1}\text{)}}{\text{Feed flowrate (ml min}^{-1}\text{)}} \quad (1)$$

The feed flow rate was changed from 400 ml min⁻¹ to 1,500 ml min⁻¹ to adjust the recovery ratio.



Fig. 2. Photograph of the hydrogen purifier.

RESULTS AND DISCUSSION

1. Configuration of Hydrogen Purifier

A photograph of the assembled hydrogen purifier appears in Fig. 2. The dimensions are 425 mm long, 165 mm wide and 460 mm high, being similar in size to a desk-top computer. As shown in Fig. 1, there is no purge system, unlike a commercial system where this is a must to prevent membrane embrittlement at temperature below the critical points of the Pd-H system, i.e., 565 K at 1.97 MPa. Thin palladium membranes easily suffer from hydrogen embrittlement, particularly due to the α - β phase transition at temperatures below the critical points of the Pd-H system [14,15]. The difference in the specific volumes of the lattices of the α and β phases is up to 10% [16], so that the phase transitions are accompanied by generation of defects, causing fatal fracture of thin palladium membranes [17]. Pd alloys such as Pd_{1-x}Ag_x and Pd_{1-x}Cu_x can withstand repeated temperature cycling with less distortion than pure Pd [18,19]. However, phase transition still occurs in Pd-Ag and Pd-Cu alloy membranes [20,21]. To prevent the generation of defects due to hydrogen embrittlement when hydrogen purifiers are turned off, whether deliberately or due to external events such as power outages, commercial hydrogen purifiers have purge systems to remove hydrogen from the purifier when the temperature exceeds the critical point of the Pd-H system. Typically, nitrogen is introduced in an attempt to flush out any hydrogen from the hydrogen purifier. To reduce the purging time, Johnson Matthey has disclosed a V-purge system equipped with a vacuum pump [22]. In a previous study, we carried out α - β phase transition tests in the temperature range below the critical

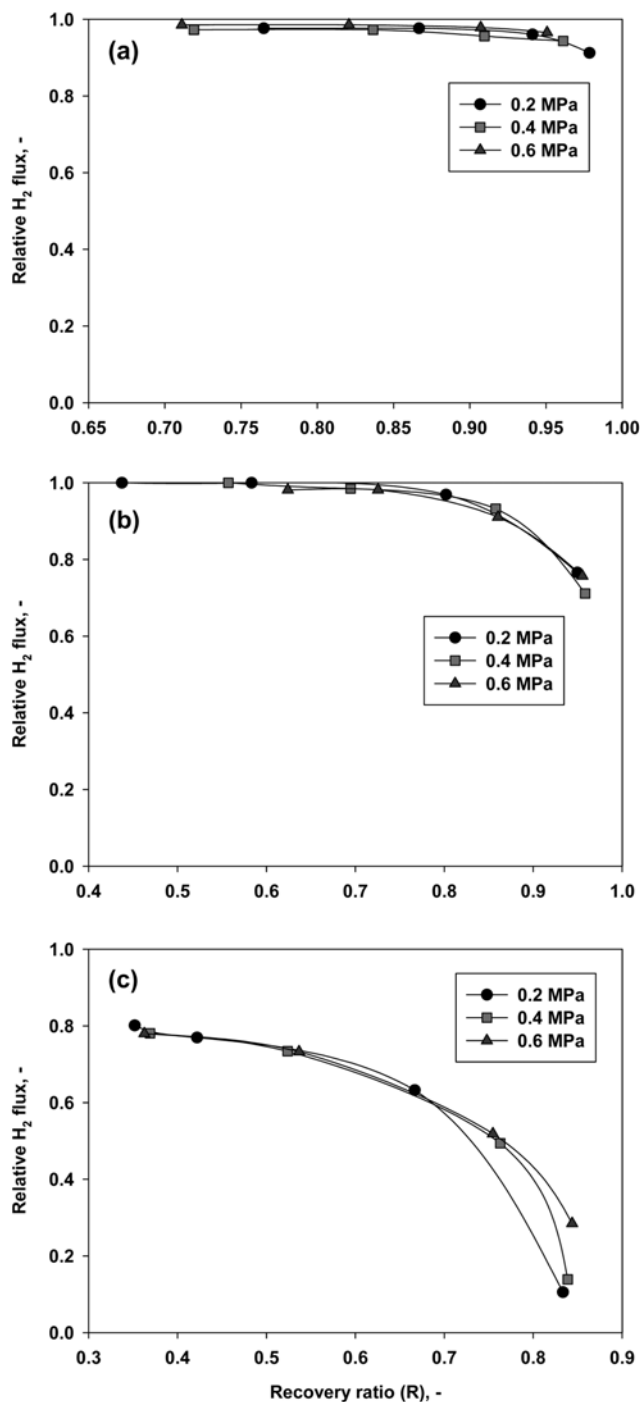


Fig. 3. Effect of recovery ratio according to feed hydrogen partial pressure on hydrogen permeation flux: (a) 99.9% hydrogen; (b) 99.0% hydrogen; (c) 90% hydrogen; diluted with high purity nitrogen; Relative H₂ flux is the maximum value when considering only dilution effect.

point and showed that there was no phase transition [13,23]. For this reason, we have not needed to provide a purge system to prevent membrane embrittlement for our hydrogen purifier. Therefore, it was possible to design and build a simple hydrogen purifier.

2. Effects of Feed Condition and Recovery Ratio

Fig. 3 shows the effect of recovery ratio on the hydrogen perme-

ation behavior for the three different purities of hydrogen diluted with nitrogen. It was possible to increase the hydrogen permeation flux by decreasing the recovery ratio, i.e., by increasing the feed velocity. As the hydrogen concentration of the feed decreased, the effect of recovery ratio on the permeation flux increased. While the recovery ratio had little effect on the permeation flux for a feed gas concentration of 99.9%, it was impossible to reach the ideal value

when the feed gas was 90% H_2 . This is because polarization affects hydrogen permeation behavior for lesser-purity hydrogen. It means that the high rate of hydrogen removal from the adjacent layer to the membrane causes the hydrogen-depleted concentration polarization effect. The hydrogen-depleted concentration polarization effect resulting from insufficient mass transport in the gas phase makes the hydrogen partial pressure difference on the adjacent layer

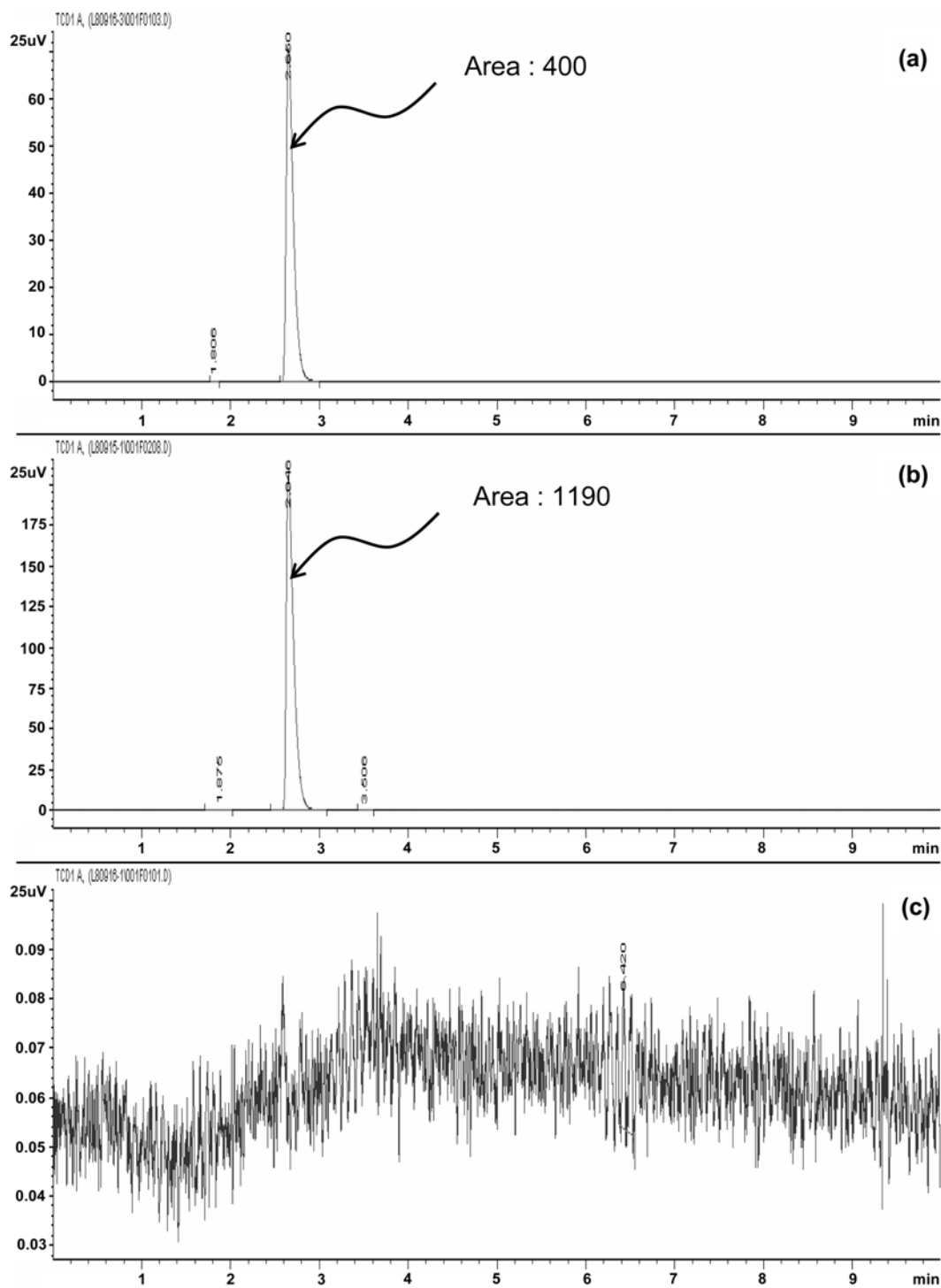


Fig. 4. The nitrogen analysis with gas chromatograph: (a) feed gas; (b) retentate; (c) permeate; feed gas was 99% H_2 +1% N_2 ; recovery ratio was 67%; carrier and make-up gases were the permeated hydrogen; feed and permeate side pressures were 0.6 and 0.48 MPa respectively.

to the membrane lower than the mean pressure difference, which consequently results in reduced hydrogen flux. Some studies have reported the polarization effect when using mixture gases of hydrogen and inert-gas like this study [24,25].

Peters et al. [24] showed that a large reduction in hydrogen flux was observed for a 50% H₂+50% N₂ mixture relative to pure H₂. They attributed the flux reduction to build-up of a hydrogen-depleted concentration layer adjacent to the membrane due to limited mass transport in the gas phase. He et al. [25] found that increasing the gas feed velocity helped to polarization, although the effect could not be eliminated. From the viewpoint of economics, determining the recovery ratio is very important when operating the hydrogen purifier with low-grade H₂. This means that a significant amount of hydrogen can be wasted to obtain high enough permeation flux. To obtain an appropriate permeation flux, the recovery ratio, temperature and transmembrane pressure difference can be controlled. There will be a trade-off between these three operational variables to operate under optimum economic conditions. Further study is needed to determine the most effective operating conditions to optimize the hydrogen permeation flux.

3. Application to a Gas Chromatograph as a Gas Supplier

We have investigated whether the hydrogen purifier could be applied to processes demanding high-purity hydrogen. Generally, gas analysis must have high accuracy so that high-purity gases are used as span gases. In case of a GC, carrier and make-up gases of high purity are required to analyze samples and avoid analysis errors. Hydrogen is widely used as a GC carrier and make-up gas, especially with thermal conductivity detectors (TCD), because of its very high conductivity compared with other gases. In our experiments the permeated gas was introduced to the GC as a carrier and make-up gas. The gas fed to the hydrogen purifier was a mixture of 99% H₂+1% N₂. The feed and permeate side pressures were 0.6 and 0.48 MPa respectively, and it was found to be possible to operate the GC with the permeated hydrogen. Fig. 4 shows the three different areas of nitrogen peaks between the feed, retentate and permeate gases. The recovery ratio was 67%, i.e., 33% of the hydrogen remained in the retentate so that the nitrogen in the retentate was concentrated by a factor of three. As a result, the nitrogen area for the

retentate was almost three times larger than that of the feed side. As shown in Fig. 4(c), we could not find any nitrogen peak for the permeated hydrogen gas, meaning that impurities in the permeate from the purifier were undetectable.

4. Durability of the Hydrogen Purifier

The present membranes and membrane module of the hydrogen purifier were tested continuously for 75 days at 723 K. Hydrogen permeation fluxes were obtained at a transmembrane pressure difference of 0.25-0.6 MPa over this period. As shown in Fig. 5, the hydrogen permeation flux could be controlled by varying the transmembrane pressure difference, and the permeation flux was maintained constant over the extended period. The durability test of the hydrogen purifier showed that there was negligible interdiffusion between membrane films and the porous nickel supports (PNS) at 723 K. Furthermore, the results show that the silver interlayer between the membranes and the metallic frame of the module provided good adhesion between the palladium alloy film and the nickel unit cell body.

CONCLUSIONS

A hydrogen purifier was developed with a membrane module equipped with Pd-Cu-Ni/PNS membranes. No purge system was provided, unlike commercially available membrane systems where purging is required to prevent membrane embrittlement. This omission was possible because we had verified that there was no α - β phase transition below the critical point of the Pd-H system, and it made the hydrogen purifier simple. The recovery ratio is an important operating factor when the feed gas is low grade of hydrogen. For a mixture of 99% H₂+1% N₂, the present hydrogen purifier was used to provide high-purity hydrogen to a gas chromatograph. The trials were successful with negligible nitrogen passing through the membrane. A 75-day test showed that the hydrogen permeation flux remained constant, verifying that there was no damage to the membrane module over the extended period.

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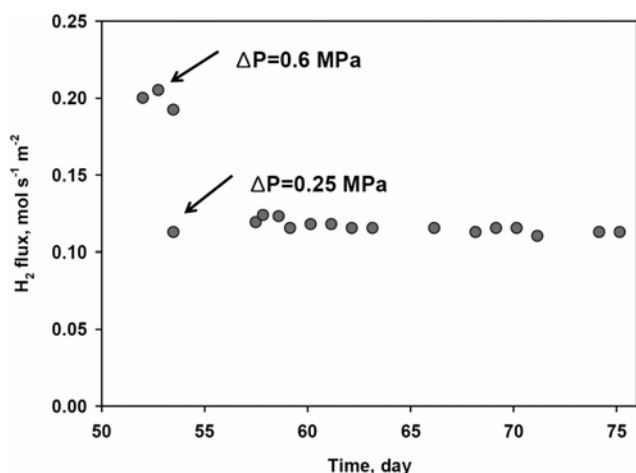


Fig. 5. Durability of hydrogen purifier: at an operating temperature of 723 K.

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