공학석사 학위논문

Improvement of hydrogen permeability with inert gas exposure in metallic membranes

불활성 기체 노출을 이용한

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Abstract

Improved hydrogen permeability with inert gas exposure in metallic membranes

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Hydrogen is a clean and efficient source of energy, and the hydrogen-based economy is now considered a potential solution for energy security and a sustainable future. Hydrogen production technology based on natural gas uses synthetic gas composed of hydrogen and carbon monoxide created through a catalytic reaction. Hydrogen production through natural gas reforming will continue in the near future. Among them, membrane technology is known as an effective method for ultra-high purity hydrogen purification. Hydrogen breaks down into atomic states on metal surfaces, moves space between metal lattices, and then passes through metallic membranes through a mechanism that bonds back into molecular states on the opposite surface. Hydrogen atoms are fixed in the space between metal surfaces and crystals during hydrogen permeation, resulting in low hydrogen permeability. Due to this mechanism, the metallic membrane has the advantage of high selectivity for hydrogen, but it is necessary to solve the problem of decreasing permeability during hydrogen permeation.

Therefore, by inserting an inert gas exposure process between hydrogen permeation tests, hydrogen atoms between metal lattices are removed to recover permeability. In the first step, a vanadium-nickel alloy membrane was used to explore the optimal conditions for hydrogen permeability recovery of inert gas exposure, and in the second step, the optimal gas exposure conditions were applied to recover the reduced hydrogen permeability of the Pd/V85Ni15/Pd membrane. When both argon and nitrogen gases were exposed at 0.8 MPa and 43 hours, the

degree of increase in permeability was large compared to the initial transmittance. Due to argon exposure, the hydrogen permeability of the metallic membrane increased by about 280% compared to the initial stage after the first exposure, and an improvement of 508% was achieved through the second exposure cycle. Since nitrogen is also non-reactive, it was confirmed that the recovery effect of hydrogen permeability was significant. In the case of nitrogen, it increased by 131% and 156%, respectively, after the first and second recovery cycles. Argon was more effective in recovery than nitrogen. In addition, the average hydrogen flow rate increased bymore than 1 cm^3/min (sccm) after the inert gas exposure cycle. Therefore, it was possible to switch from the batch process to a continuous process, and the experiment was conducted by changing the temperature of the process to 350, 400, 450, and 500 ℃. As a result, the metallic membrane showed high permeability at 400°C, and the overall hydrogen permeability pattern was also stabilized.

These results indicate that the inert gas exposure process mitigates the decreasing trend during the hydrogen permeation test and affects the improvement of the hydrogen permeability of the Pd/$V_{85}Ni_{15}$/Pd membrane. If the inert gas exposure can guarantee high hydrogen permeability through this study, it is believed that it can help increase the efficiency of the hydrogen separation process using a metallic membrane.

Keyword : Metallic membrane, Gas treatment, Hydrogen, Membrane technology

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1. Introduction

1.1. Study background

Our Earth is facing serious climate change and global warming associated with manmade CO_2. The human impact has affected patterns of precipitation changes, global glacial decline, and increased temperature on the Earth's surface. Humans have warmed the climate at an unprecedented rate in the past 2,000 years. Observed warming is due to emissions from human activities, with greenhouse gases. Among them, CO_2 has the largest contribution to warming. The total degree of warming is determined by past and future CO_2 emissions. Historical records of global surface temperatures show that human-induced long-term changes are clearly influenced by variability. Therefore, global efforts are needed to reduce greenhouse gases. The primary sources of greenhouse gas emissions in the United States are: transportation, and electricity production. More than 50% of the CO_2 generation is discharged from the source, and it comes from burning fossil fuels, mostly petroleum, coal and natural gas. Therefore, it is indispensable to reduce CO_2 emissions from fossil fuel combustion. The United Nations agreement at the Paris Climate Conference in 2015 highlighted the importance of reducing CO_2 emissions from fossil fuel combustion.

Hydrogen is a clean and efficient energy carrier, the transition to a hydrogen-based economy is a hot issue. It is also now widely regarded as a potential solution for the future of energy security and sustainability. There are three different industrial methods for producing hydrogen: water electrolysis, steam methane reforming (SMR), and coal and biomass gasification (Adhikari & Fernando, 2006). In water electrolysis, electricity is used to break H_2O molecules into H_2 and O_2. It does not need any purification step and CO_2 neutral which is environmentally friendly method. However, due to its high price to produce, electrolysis of water only accounts for about 4% of the global hydrogen production. In SMR, hydrogen is produced from natural gas, such as CH_4. CH_4 reacts with steam in high temperature (700-1000°C), high pressure conditions (4-20 bar) (Chen et al., 2017) and produces H_2, CO, and CO_2. H_2 is purified by removing CO_2 and other impurities from the mix gas stream in the final process. H_2 is produced by reacting various feedstocks such

as coal, biomass, or urban solid waste with steam or oxygen under high pressure and temperature, and may contain water vapor, a small amount of sulfur compounds (H_2S, COS), some ammonia, and other H_2, CO, and CO_2 through gasification of coal and biomass. The trace contaminant carbon dioxide reacts with H_2O to form more H_2 with CO_2 through the WGS reaction, and the last generated H_2 is purified. SMR and gasification are common methods of producing hydrogen which can meet the demand of large scale of industrial demand and economical ways. During the transition from a carbon-based (hydrogen fuel) economy to a hydrogen-based economy due to economic constraints, fossil fuel-based hydrogen production methods are considered essential and good temporary options to follow. Hydrogen production combined with carbon gas compounds is indispensable. The hydrogen production based on SMR or gasification needs purification step in the final stage. Because this production process provides a mixture of H_2 rich gases that require H_2 to be refined to a very high purity level (Sazali et al., 2020). Interest in ultra-purity hydrogen production has increased significantly in recent years and this has put pressure on the development of alternative methods of hydrogen purification.

Membrane separation technologies appear to be promising methods in gas separation applications. General objective of membrane is to guarantee hydrogen with industrially available purity. There are various types of membranes as shown in Table 1 (e.g. metallic membranes, silica membranes, zeolite membranes, carbon-based membranes, polymer membranes) which separate and purify pure hydrogen from a gas mixture such as CO, CO_2, O_2, N_2 for use as an energy source (Ockwig & Nenoff, 2007). Membrane separation technology is simple and easy to operate and the maintain. In addition, cost is low to separate and scale up (Bernardo et al., 2020). Membranes can be categorized based on materials: organic and inorganic membranes. Organic membranes are polymeric and biological. The gas transport mechanism through the polymer membrane may vary depending on the difference in pore size. The gas transport method in the porous polymer membrane is greatly influenced by the pore size and the size of the gas molecule. Inorganic membranes are classified into ceramic and metallic membranes. Ceramic membrane can permeate or selectively absorb hydrogen, however, ceramic materials has both mixed ionic conductivity and electronic conductivity leading to limited permeability and low stability (Julbe et al., 2001).

Dense metallic membranes have potentials to transport hydrogen with sorption-diffusion mechanism. It is attractive that hydrogen can permeate bulk metals with ensuring high purity of hydrogen.

Hydrogen purification using metallic membranes has a long history going back at least 1950s. The mechanism of hydrogen permeation through metallic membrane is different from porous membranes. Hydrogen permeation through metallic membranes is illustrated as a sorption-diffusion mechanism. Hydrogen diffusion occurs from a high pressure feed side to a low pressure permeate side in the following steps (Rahimpour et al., 2017; Shi, 2014).

- H_2 molecules move to the surface of the metallic membrane
- Reversible H_2 chemisorption on the metal surface
- Dissociation of H2 molecules into an atomic form at the membrane surface
- Diffusion of atomic hydrogen within metal lattice (generally rate limiting step)
- Association of atomic hydrogen at the metal surface
- Hydrogen molecular desorption from the surface of metal
- Transferring of H_2 molecules from the membrane surface to bulk flow

As shown in Figure 1, gaseous H_2 pass through metallic membranes by adsorption and desorption. First, hydrogen molecules adsorb and dissociate into atomic H on the metal surface when exposed to feed side with high pressure. H atoms subsequently diffuse to interstitial sites in the metal and recombine into molecular form on the other side of membrane where the pressure of hydrogen is low. Partial pressure difference across the membrane leads to net transport of hydrogen from feed stream to permeate stream (Sholl & Ma, 2006). Through this mechanism, metallic membranes can have high selectivity for hydrogen over other impurities compared to porous membranes which separate gas stream based on size distribution. Due to its high hydrogen permeability and theoretically infinite hydrogen selectivity, the operation of pure hydrogen and catalytic membrane reactors has been studied for a while (Uemiya et al., 1991).

Table 1 Issues in hydrogen permeation with membranes

Membrane type	Advantages	Disadvantages	References
Polymeric membrane	Polymeric membrane is easy to process and control	Physical properties of plasticization and aging can be obstacles to adopt in a large scale.	(Lamb et al., 2019; Park et al., 2017)
Ceramic membrane	In a silica-based ceramic membrane, when small gas molecules penetrate, the temperature increases and then increases with the activated transport mechanism.	The perovskite membrane is a major ceramic membrane, and the electron conductivity is very low at high temperatures, resulting in poor hydrogen permeability.	(Hashim et al., 2018; Yang et al., 2021)
Metallic membrane	Defect free, chemical and mechanically stable	In the presence of small amounts of impurities, it exhibits permeability decrease	(Yan et al., 2021)

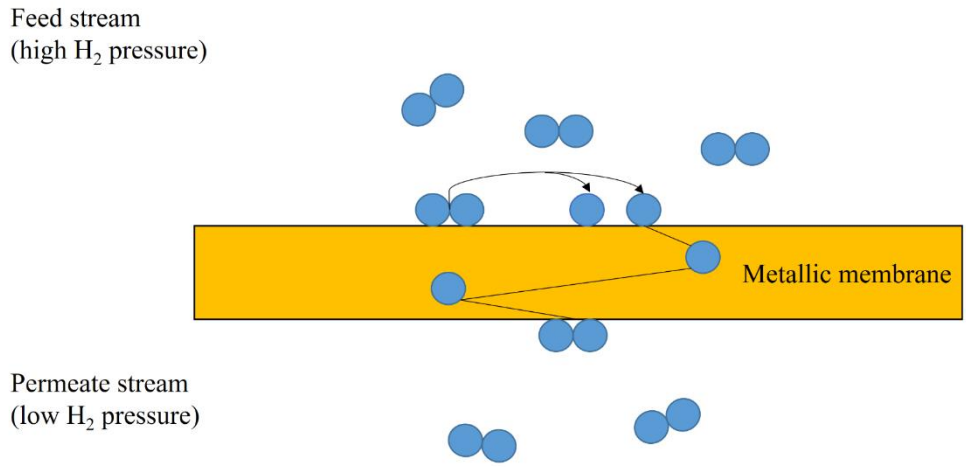

Figure 1 Schematic diagram of the mechanism of H_2 penetration across a metallic membrane.

The hydrogen flux (J_{H2}) of metallic membrane can be expressed as:

$$J_{H_2} = \frac{\varphi}{\delta}((P_{H_2}^{feed})^n - P_{H_2}^{permeate})^n) \qquad (1)$$

This equation is derived from Fick's law and Sieverts' law combining. The permeability (mol m^{-1} s^{-1} $Pa^{-1/2)}$ is φ, the membrane thickness is δ, and partial pressures of hydrogen in feed stream and permeate stream are expressed as $P_{H2,\ feed}$ and $P_{H2,\ permeate}$. The rate limiting step of metallic membrane hydrogen diffusion is bulk diffusion so that the exponential factor n is 0.5.

Each metal has its advantages and disadvantages. Palladium has been used with their high selectivity to separate hydrogen from gas mixtures (Graham, 1866). The Pd or Pd membrane exhibits high hydrogen permeability and chemical stability even in hydrocarbon gases, and after undergoing a deteriorated flux by hydrogen permeation test, the membrane recovers the flux by air treatment. Pure Pd can be an effective membrane at temperature above 300°C, but membrane cracking is common at lower temperatures (Wolf et al., 1994). This problem arises because Pd-H has two significantly different phases. At high temperatures, pure Pd membranes can be strongly poisoned by chemical impurities, especially sulfur-containing species (Kamakoti et al., 2005). These two difficulties be overcome by using metal alloys as membranes instead of pure Pd. In addition, high price of Pd is also an obstacle to adopt in large scale. The current price of palladium as of 2022 is $2,037.00 per ounce.

Group V metals such as vanadium, niobium and tantalum are also known as hydrogen permeable metals (M. D. Dolan et al., 2012). In general, the difference in hydrogen permeability is due to hydrogen s얌olubility. Group V metals are of great interest because of their high permeation rates. Their permeability increase as the temperature decreased (Kim et al., 2013) due to solubility. These metals are cheaper and more resistant to high temperatures than palladium. Nevertheless, the fabrication of these metallic membrane is difficult because exposure to hydrogen would lose flexibility in the presence hydrogen at room temperature. Because the absorbed hydrogen affects the physical and chemical properties of the host metal (Louthan Jr et al., 1972), group V metal embrittles when exposed to hydrogen (Ko et al., 2012). The poor surface properties of metals that reduce hydrogen transport (i.e., the production of surface oxide layers) are also another factor limiting their use.

Hydrogen embrittlement in group V metals is a major problem when these metals facing hydrogen. The main mechanism of this phenomenon has not been clearly understood. However, briefly, hydrogen concentration gradient makes hydrogen diffuse toward and accumulate at the stress concentrated region. The absorbed hydrogen affects the physical and chemical properties of the host metal (Louthan Jr et al., 1972). When the local hydrogen concentration reaches the threshold, a mechanical failure occurs on the surface of the metal membrane. To prevent hydrogen embrittlement, alloying is well known method by adjusting microstructure.

By increasing the amount of Ni, Al, Mo elements, it is possible to reduce the amount of C, Si, P, and S elements that affect the hydrogen embrittlement. For example, in case of Mn-B metal, when the C element content increases, the hydrogen embrittlement also increase (Zhang et al., 2014). V-Ni alloys are known to be the most promising because of its permeability and thermal stability (Nishimura et al., 1991). The effect of nickel as a second alloy element on the V-based membrane was investigated (M. Dolan et al., 2012). The V-based alloys with Ni content up to 15 at.% are studied (Bellini et al., 2018; Nishimura et al., 2002; Shim et al., 2013). These alloys maintain the BCC-structure up to the composition of $V_{85}Ni_{15}$, providing the best durability among BCC-metals. However, V-Ni alloy indicates a clear decrease in hydrogen diffusivity at hydrogen permeation condition as the Ni content increased, which leads to drastic decrease in total hydrogen permeability compared to pure vanadium membrane. In addition, the preparation method may have a serious impact on the final result. It has been found that cold rolling techniques to fabricate the membrane reduce hydrogen permeability by increasing particle size, while subsequent annealing recrystallization promotes large particle sizes containing fewer potentials, thereby improving hydrogen permeability (Song et al., 2010). In fact, defect traps increase the solubility of hydrogen due to an increase in diffusion activation energy while reducing permeability. However, palladium, an FCC metal, is not affected by durability because its permeability is not affected by changes in hydrogen solubility. It is common to deposit Pd on the double side of the metal alloy to improve thermal stability at high temperature (Conde et al., 2017).

When palladium is coated on the surface of the membrane, decrease in hydrogen flux appears to be related to the mutual diffusion between the palladium coated layer and the vanadium alloy

substrate, which affects the hydrogen permeation behavior (Edlund & McCarthy, 1995). It may lead to rapid decrease in hydrogen flux over time. A similar phenomenon was observed in other Pd-coated metal membranes. For example, it is reported that the mutual diffusion of Pd-coated Ti-Al membranes facilitated flux reduction and produced pinholes on the membrane surface at temperatures ranging from 500 °C to 700 °C (Zhang et al., 2011).

Air treatment on the metallic membrane can affect the membrane behavior. It is known that oxygen pretreatment can affect hydrogen permeability by activating the surface of Pd-Ag membrane and removing carbon-based pollutants on the surface (Pizzi et al., 2008).

In the process of oxidation and reduction of the metallic membrane, heat treatment in the air was able to observe higher hydrogen permeability than the initial hydrogen permeability (Fort et al., 1975; Keuler & Lorenzen, 2002). It also removes impurities from the surface by using air heat treatment on the fresh membrane, but also to recover deactivated membranes after the hydrogen permeation tests (Ali et al., 1994). This is because heat treatment in the air changes the properties of the membrane surface. It is observed that the surface roughness increases after heat treatment in the air, and the number of active sites for hydrogen dissociation increases (Wang et al., 2000). It is found that the oxidation time or temperature could affect the degree of improvement in penetration after oxygen treatment (Keuler & Lorenzen, 2002). The heat treatment in nitrogen and argon at 400 °C shows almost the same result as the heat treatment in air at 300 °C. These results show that the improvement of flux is largely dependent on both temperature and ambient atmosphere (Mejdell et al., 2008). However, there is another research that extremely high pressure of high molecular weight gases inhibits hydrogen flux. High molecular weight non-reactive gases cause subsequent hydrogen flux degradation when exposed to the metal membrane at high pressure. These effects were observed for N_2, Ar and CO_2 at 3.0 MPa and 500 °C, and a significant reduction in hydrogen flux within 24 hours was recovered only to 60% (Lundin et al., 2017). Therefore, the recovery of the reduced hydrogen flux in the metal membrane must be accompanied by an appropriate conditions of gas treatment. Processing conditions can have a significant impact.

1.2. Research objective

Numerous studies have been conducted on various metals as candidates for hydrogen permeation membranes. Among them, the $V_{85}Ni_{15}$ membrane, which has relatively high price competitiveness, was selected as a substrate to confirm hydrogen permission.

The $V_{85}Ni_{15}$ membrane without Pd sputtering showed low permeability due to the oxide layer on the surface. Therefore, a thin Pd layer was deposited to improve the hydrogen flux. In this study, to recover the reduced hydrogen permeability during hydrogen permeation, hydrogen permeation experiments were conducted with Ar and N_2 exposure processes in order to have a greater effect than air treatment. To find the ideal transmission continuous process conditions, the temperature change of the Pd sputter membrane alloy was also explored. The relative hydrogen permeability results before and after the inert gas process have been described in detail. The purpose of this study is not only to devise a process of recovering reduced hydrogen permeability through this study, but also to design a process capable of stably using a Pd sputtered membrane for hydrogen permeation.

2. Materials and methods

2.1 Membrane preparation

There are two types of membranes used in the experiment (Figure 2). Both are based on V-Ni alloy membranes, one is a naked V-Ni alloy membrane, and the other is a membrane with Pd sputtering on both sides. V-Ni alloy membrane was made using high purity V (>99.9%) and Ni pellets. V and Ni were mixed and melted on a water-cooled copper hearth using an Ar arc melter in the proportion of 85 wt% V+ 15 wt% Ni. Arc-melted V-15Ni alloy ingots were prepared and heat treated at 1350 ℃ in pure-argon atmosphere for 12hours to ensure compositional homogeneity. A total ingot was cut into sheet-shape and polished on both sides using a 2000 grit abrasive paper. The final thickness of the tested membranes was measured 270-280 μm.

Pd thin films (100 nm) were prepared on both sides of the V alloy substrate using an electron-beam evaporator (KOREA VACUUM TECH., LTD, KVE-E2004L). The Pd pellets (Taewon Scientific Co., 99.99%) were placed in a tungsten crucible and subjected to e-beam evaporation. A constant e-beam voltage of 7.5 kV and current of 70 mA was applied to maintain a deposition rate of 0.5 Å/s. The base pressure of the chamber during deposition was maintained around 10^{-6} Torr.

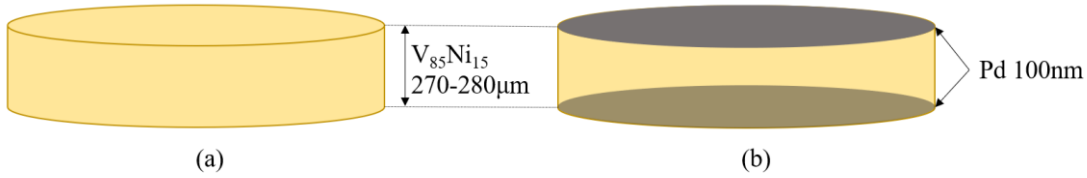

Figure 2 Fabricated metallic membrane diagrams: (a)$V_{85}Ni_{15}$ and (b) Pd coated $V_{85}Ni_{15}$ (Pd/$V_{85}Ni_{15}$/Pd)

2.2 Gas permeation test cycles

A gas permeation equipment used in the experiment is largely divided into two parts between metallic membrane. The feed stream side is connected to three different gases. In all stages of the permeation experiments, gases with 99.999% purity (Hanmi gas, Korea) were used. Each gas was injected into the cell using a mass flow controller (MFC; F-201CV, Bronkhorst). The metallic membranes were fixed with 7 mm internal diameter circular Cu gaskets, resulting in an active surface of 38.48 mm^2. Three thermocouples were used to raise the temperature, and metal leads outside helped maintain the temperature. The permeate stream side was connected to a mass flow meter (MFM; F-110C, Bronkhorst) to measure the stream of the gas that penetrated the metallic membrane. Ar connected to the permeate stream side is used to prevent pressure difference between membranes. The hydrogen flux measurement setting was similar to (Mejdell et al., 2008). Each membrane was placed in the apparatus and heated with a thermocouple located inside the cell. The overall process of the membrane experiment is shown in Figure 3. A preliminary leak test was conducted on both sides of the membrane using inert gas at room temperature to confirm that the membrane did not leak. Hydrogen permeability was measure at 350 °C with pure H_2 gas (purity of 99.999%) for 5 hours at 0.4 MPa with no sweep gas. Subsequent inert gas treatments were conducted after permeability check. The membrane cells were filled with Ar or N_2 on the feed side and Ar on the permeate side at 350 °C. The flux is regenerated by air treatment (Lundin et al., 2017), therefore the main component of air, N_2, was selected. Ar was chosen because it is a non-reactive gas similar to N_2. Inert gas treatments were conducted to find out optimal recovery treatment conditions. Inert gas pressure used both 0.4 MPa which is equal to the hydrogen pressure and 0.8 MPa which is higher than the hydrogen pressure, and the exposure time differed from 19 hours and 43 hours. If the pressure swing becomes large, there is a possibility of mechanical defects in the membrane, so the maximum exposure pressure was limited to 0.8 MPa, which is twice the hydrogen exposure pressure. After the treatment, the hydrogen permeability was checked again (Figure 4).

Pd coated membranes were tested under optimal condition which was determined in

preliminary V-Ni alloy membrane. The impact of Ar and N_2 was tested in each membrane. After 3 cycles of inert gas treatments, both Ar-treated alloy membrane and N_2-treated alloy membrane were tested in continuous process. A constant flow of H_2 was fed to the feed side using MFC. As before, hydrogen was adjusted to 0.4 MPa, and continuous flow was fed at 2 cc/min. This series of continuous process was repeated at 350, 400, 450 and 500℃.

Hydrogen permeability (Φ) was evaluated using the following equation (Collins & Way, 1993; Keurentjes et al., 2004):

- $\Phi = \frac{J \cdot L}{{P_1}^n - {P_2}^n}$ (mol m-1 s-1 Pa-1/2) (1)

Where J: hydrogen flux (cc/min), P_1: feed pressure (Pa), P_2: permeate pressure (Pa), L: membrane thickness (m), A: area of membrane and n: rate limiting step. Typically, a rate limiting step of metallic membrane permeation is the bulk diffusion, so the n-value was approximately 0.5 in these tests.

In addition, if the Pd membrane with increased permeability due to inert gas treatment may ensure a minimum flow rate for a continuous process, the process can be converted to continuous process. Therefore, in a previous semi-batch process that checks the hydrogen flow rate on the permeate side every 10 minutes without additional hydrogen injection for 5 hours, it can be converted into a continuous process that checks the hydrogen flow rate through with continuous hydrogen injection for 5 hours. In this process, the permeate valve was kept opened and checked spontaneously.

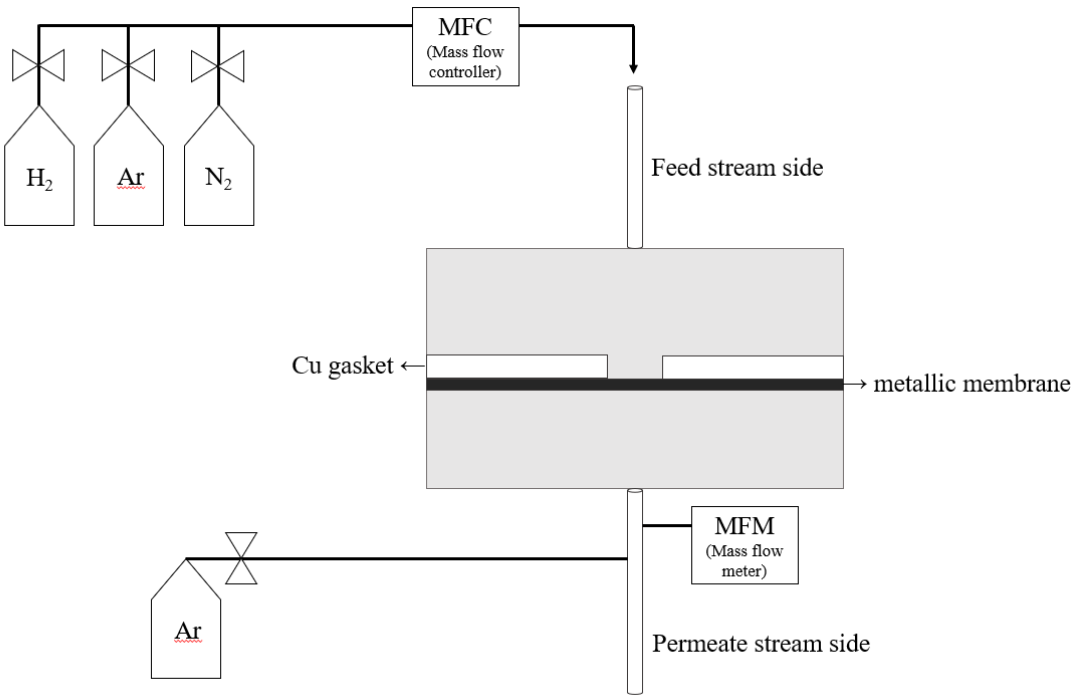

Figure 3. Schematic diagram of metallic membrane cell permeation

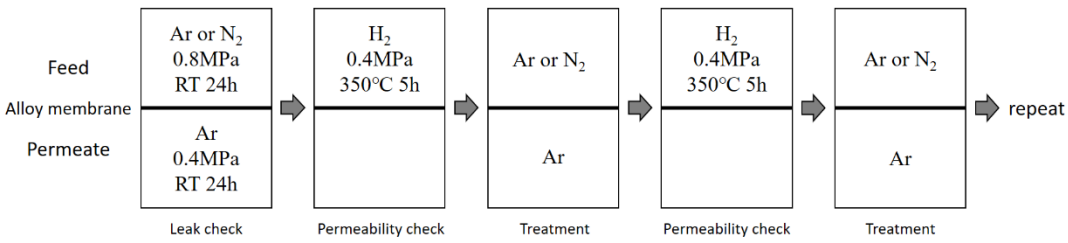

Figure 4 Scheme of hydrogen permeation and inert gas treatment cycles

3. Results and discussion

3.1 Optimal inert gas treatment condition

Hydrogen permeability was measured every 10 minutes during 5-hour permeation test. Hydrogen permeability change of $V_{85}Ni_{15}$ alloy membrane for 5 days was illustrated in Figure 5. After preliminary leak test, a hydrogen permeation experiment for 5hours was conducted. Then the feed side left hydrogen intact and the permeate side ventilated. Overall trend line graph showed that the hydrogen permeability decreases over time for 5 days. To illustrate the tendency of the permeability of membrane itself, permeation flux values were calculated.

The averaged-permeability of the first day was 4.61×10^{-9} mol/m s $Pa^{1/2}$. It decreased to 3.26×10^{-9} mol/m s $Pa^{1/2}$ with no inert gas treatment. Between each hydrogen tests, the membrane kept exposed to hydrogen. Permeability value maintained to 3.28×10^{-9} mol/m s $Pa^{1/2}$ in the third day. Permeability of $V_{85}Ni_{15}$ membrane initially increases to about 30 hours, then gradually decreases. Therefore, it decreased to 3.08×10^{-9} mol/m s $Pa^{1/2}$, 2.54×10^{-9} mol/m s $Pa^{1/2}$, and 2.79×10^{-9} mol/m s $Pa^{1/2}$ in 4th , 5th day, and 6th day, respectively. In 4 days of using, relative hydrogen permeability was around 66% of initial permeability. When the surface of the feed side membrane is exposed to hydrogen, hydrogen atoms cannot pass through the metal alloy by moving the metal lattice. Generally, it is known that the hydrogen trapping phenomenon occurs for the alloy membranes. If sufficient driving force is not continuously provided, hydrogen atoms located between the metal lattice are not moving. As the number of metal lattices filled with hydrogen atoms increases, the rate of movement decreases and the overall permeability decreases. However, it is possible to provide a driving force to remove atoms between the lattice by removing hydrogen and injecting inert gas between the hydrogen permeation tests.

The possible mechanism is that the pressure gradient which was made with feed side inert gas makes the hydrogen atoms move to permeate side and metal lattices empty. And in the process, the gas that makes the pressure difference may not react with the metal membrane to be effective. Therefore, the inert gas affects the recovery. When comparing the initial permeability and the

subsequent permeability by calculating them as relative permeability (Figure 5), it can be confirmed that the trend gradually decreases over time. In the continuous hydrogen permeation process, the hydrogen permeability did not recover to a similar level as the first time, and only about 70% was achieved. In addition, the flux of the entire process decreased over time.

When the operation sequence was different that inert gas treatments were inserted between hydrogen permeation test, the results changed (Figure 6). After initial permeability measurement, treatment was performed with Ar and N_2 then hydrogen permeation experiments were conducted again. Inert gas treatment was conducted with 0.4 MPa for 43hours. Compared to initial value, Ar-treated membrane showed 133% increase while N_2-treated showed 90% of initial value after 1st cycle of treatment. According to Figure 5, if hydrogen is continuously used, the permeability decreases to the initial level of 77% on 4th day, but if inert gas treatments with N_2 and Ar are used, the permeability remained similar to the initial level or increased more. Ar was much more effective than N_2. Relative hydrogen permeability shows higher value with both types of gas treatment than without any treatments. It can be assumed that on the metal membrane surface N_2 decomposition. N atoms are intercalated and bound into the vacancy of the vanadium surface (Zou et al., 2018). However, Ar can be assumed to have impact on hydrogen atoms in the V alloy because there is no interaction between vanadium and Ar even if it is inserted into an empty space. To determine the optimal condition of recovery, further experiments were implemented with variation of time and pressure.

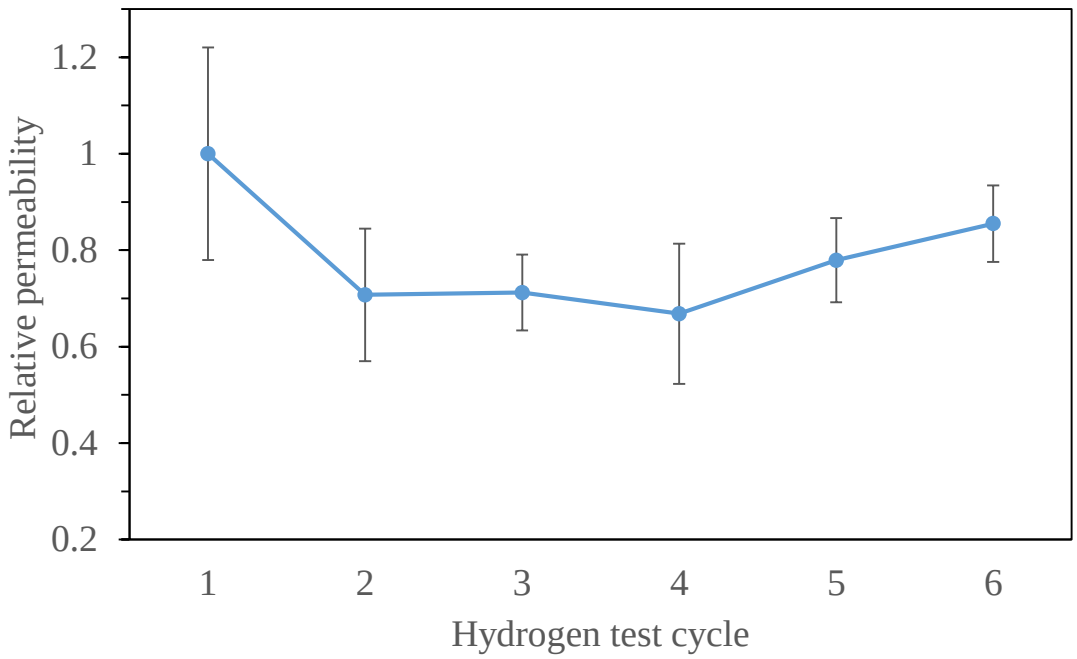

Figure 5 Hydrogen permeability of V-Ni alloy membrane for 5 days. Hydrogen permeation flux was measured for 5 hours in each day. Between measurements, feed side was filled with hydrogen gas and permeate side was ventilated.

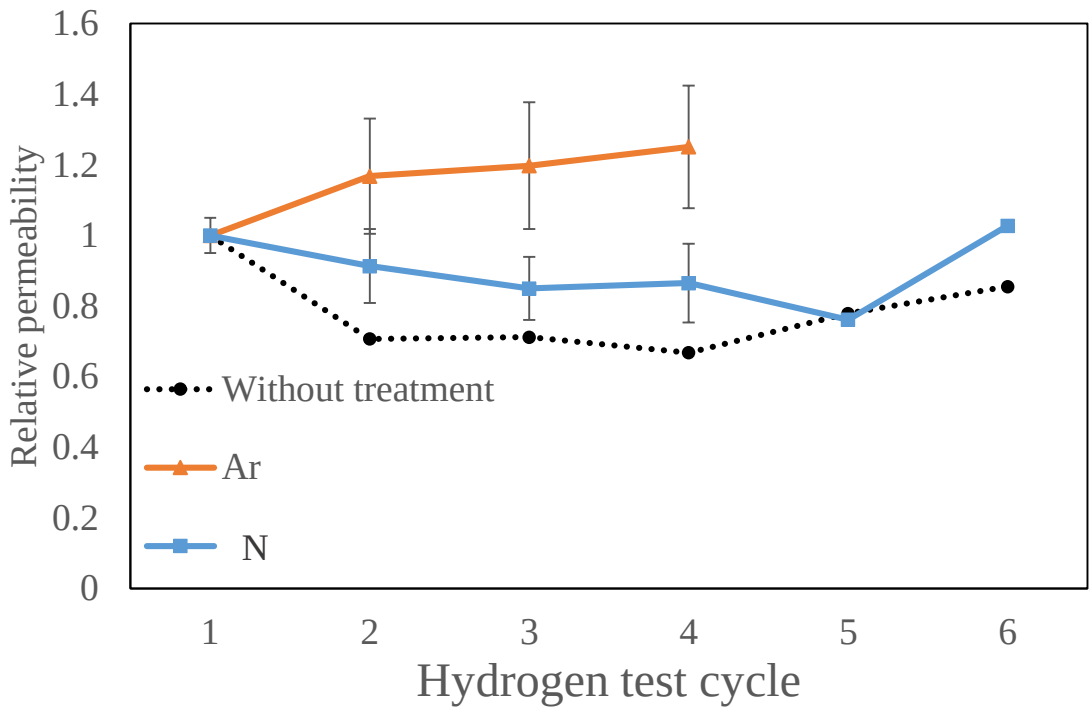

Figure 6 Comparison of relative permeabilities between initial membrane and after inert gas treatments with 0.4 MPa Ar and N_2 for 43h.

To find out the overall long term tendency of metallic membrane, the hydrogen tests were conducted with single membrane. During the test, the inert gas treatments were accompanied by different conditions of argon exposure. In the preliminary tests using argon, it showed that the degree of recovery of hydrogen permeability varies significantly depending on the inert gas treatment conditions. Results of relative hydrogen permeability when treated under argon treatment conditions in a 58-day long-term experiment (Figure 7).

Between each blue bars, argon treatment was performed under certain conditions, and the orange lines were obtained by continuing to expose hydrogen without gas treatment. The initial hydrogen permeability was set to 1, and the relative permeability of the other permeabilities were calculated. Most relative hydrogen permeabilities were higher than 80% with Ar gas treatment. Moreover, subsequent permeabilities were higher than the initial one with specific treatment conditions. Argon treatment under different conditions was performed before and after each permeability was conducted. However, as shown in the trend of hydrogen permeability over the initial 10 days, when the argon exposure time was 1 day, it did not affect the permeability and continued to decrease. When the exposure time is 19 hours, the permeability was 67% at the beginning. However, the reduced permeability rose and recovered to 115% when the argon exposure was extended to 67 hours. The permeability consecutively decreased to 86%, 89%, 77%, and 79% with 19 hours. After 10 days, exposure time was prolonged to 67 hours which showed significant impact on the permeability. Degraded membrane continuously enhanced its hydrogen flux, and reached the value similar to the initial one and even higher. It can be assumed that with argon treatment permeability has increased as more metal lattices can be involved in hydrogen migration. The permeability, which rose to 137% due to argon gas treatment, decreased to 0.75 as in Figure 7 when continuously performing the hydrogen transmission process. This means that even if an inert gas is treated from the ultimate point of view, it cannot prevent the metal lattice from being saturated and decreasing permeability. It can only be expected that the role of inert gas is to free the hydrogen atoms located in the lattice so that the gas can move during the next hydrogen experiment. Relative hydrogen permeability increased to 99% with 67 hours of continuous Ar exposure. When hydrogen exposure was continuously carried out under the same

argon conditions, the degree of permeability similar to the initial one continued to appear. This can be used for stable hydrogen separation of argon operation. When hydrogen exposure was long between 30 and 40 days, hydrogen permeability undoubtedly decreased. However, it recovered after argon exposure, and this pattern was the same between 40 and 50 days. In conclusion, hydrogen permeability degradation is reversible. It can be seen that it is effective in improving hydrogen permeability only when a sufficient exposure time is guaranteed. Hence, when a new approach with inert gas cycles was proposed in metallic membranes, the membrane permeability itself did not decrease to the degree that cannot be used in the process, rather it showed recovery and consistent value in long term process.

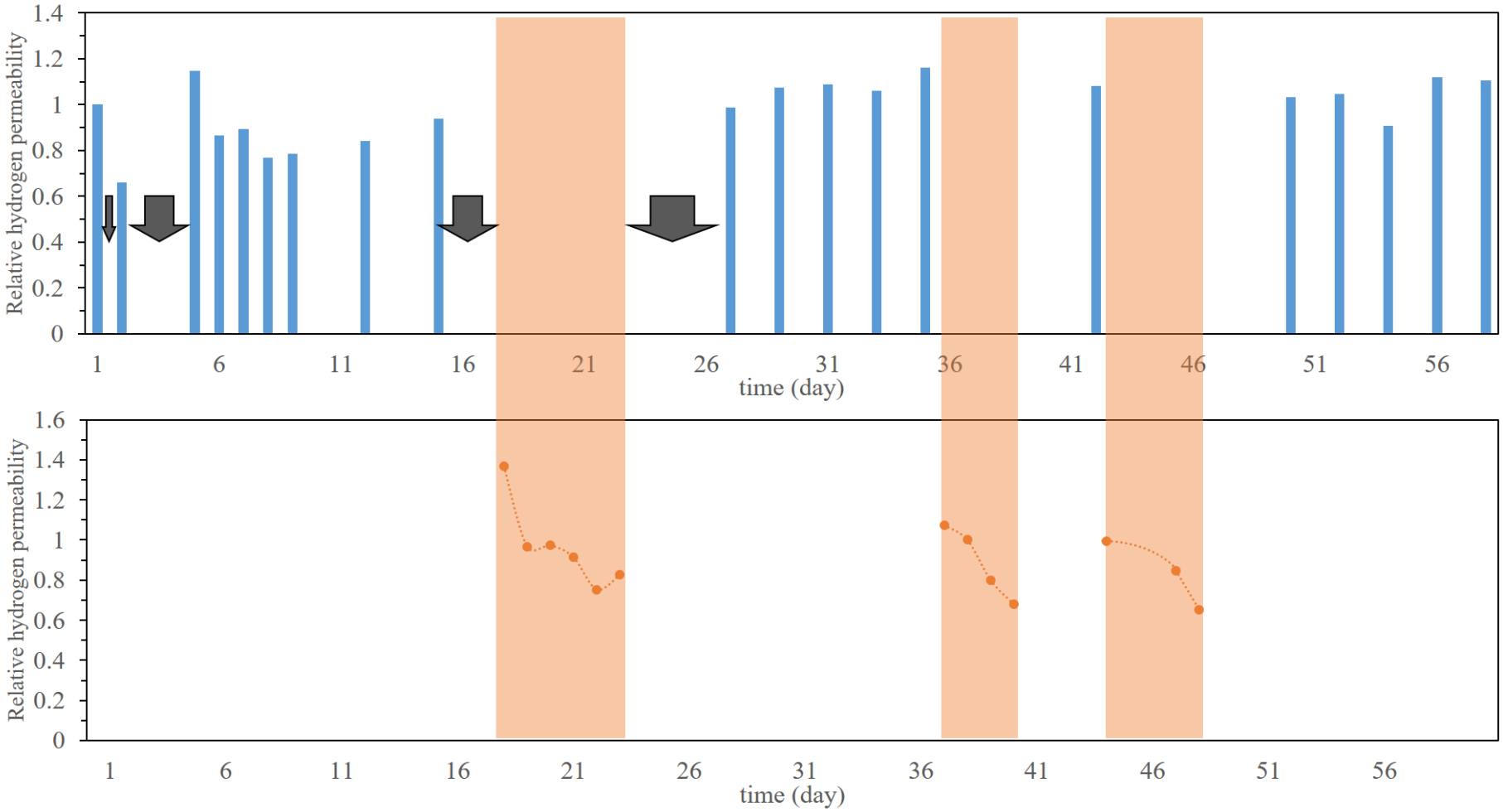

Figure 7 Relative hydrogen permeability result with long-term experiments

Condition parameters are categorized into two main groups including exposure time and pressure. To study how the different parameter in the treatment procedure affected the permeability recovery and activation, some of the membranes were examined with certain conditions with Ar and N_2. The process was conducted for 5 hours. During the hydrogen permeation, feed side was filled with hydrogen only and no additional gas injection. The hydrogen flow rate was confirmed by opening the valve on the permeate side every 10 minutes, and the results were shown as average.

The effects of argon exposure time were measured at 19, 43, 67, and 91 hours, respectively (Figure 8). The experiment was conducted while the argon pressure was fixed at 0.8 MPa. When Ar was exposed to a metal membrane having an initial average permeability of 3.37×10^{-8} mol/m s $Pa^{1/2}$ for 19 hours and then hydrogen permeability was measured again for 5 hours, it was 2.23×10^{-8} mol/ m s $Pa^{1/2}$, which was not recovered rather reduced. However, it can be seen that after 49 hours of exposure, it increased to 3.62×10^{-8} mol/m s $Pa^{1/2}$. And the permeability of 3.86×10^{-8} mol/m s $Pa^{1/2}$, 3.33×10^{-8} mol/m s $Pa^{1/2}$ was measured after exposure for 67 hours and 91 hours, respectively. Compared to the initial permeability, 19 hours of exposure achieved 66%, while 107%, 114% and 98% were achieved after 43 hours, 67 hours, and 91 hours of exposure, respectively. Ar must be exposed for at least 43 hours to obtain results similar to initial permeability. However, if the exposure time is too long, the recovery process is relatively long compared to the permeation process, therefore 43 hours was determined as the optimal recovery time. The mechanism of decrease in hydrogen flux has not been well discovered yet. However, thermal treatment in air has been used to remove poisoning species from fresh membranes. Similarly, argon gas also had comparable or much more significant impact on the metallic membrane with prolonged exposure.

The effect of argon exposure pressure was measured at 0.4 MPa and 0.8 MPa. Since the hydrogen injection pressure was 0.4 MPa, cracks were observed in the metallic membrane if the pressure difference was greater than 0.8 MPa. Therefore, the experiment was conducted by setting the maximum pressure to 0.8 MPa. The initial hydrogen permeability of the pressure experiment was 1.09×10-8 mol/m s $Pa^{1/2}$. After exposure to 0.4MPa, it was 3.81×10^{-9} mol/m s $Pa^{1/2}$, and when

argon of 0.4MPa was repeatedly exposed, the increase was 4.42×10^{-9} mol/m s $Pa^{1/2}$, which was not recovered a lot. However, when the argon exposure pressure increased to 0.8 MPa, the transmittance was consistently increased to 1.11×10^{-8} mol/m s $Pa^{1/2}$, 1.17×10^{-8} mol/m s $Pa^{1/2}$. Comparing the relative permeability, 0.4 MPa achieved 35% and 41% compared to the initial stage. This is a lot lower than the number of consecutive hydrogen penetration operations. Rather, 0.4 MPa had little effect as the relative permeability was much higher when continuous hydrogen test was performed. However, if the argon pressure increased to 0.8 MPa, it was possible to achieve 102%, 107%. Using as high pressure as possible on a line where the membrane does not break is effective in restoring permeability by applying force for the hydrogen atom to move.

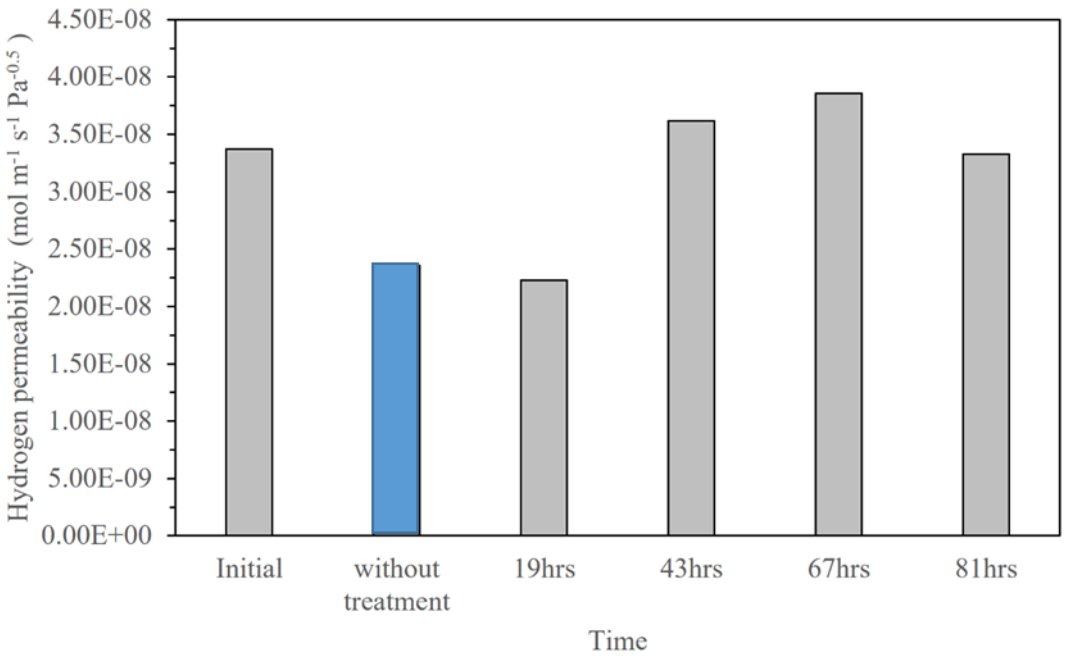

Figure 8 Permeabilities after inert treatment with Ar. Exposure time duration was differentiated 19-91 hours. (0.8 MPa of pressure)

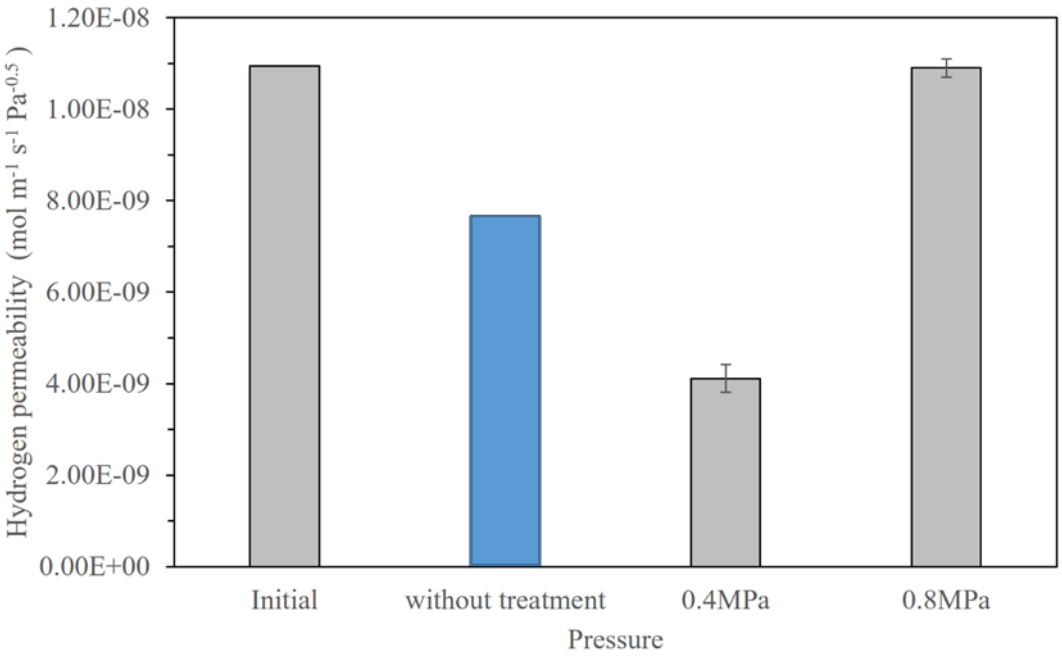

Figure 9 Permeabilities after inert treatment with Ar. Exposure pressure ranging from 0.4 MPa to 0.8 MPa (43 hours exposure time).

This is the result of time and pressure when exposure treatment was performed with nitrogen. (Figure 10, Figure 11). V-Ni membrane was treated with nitrogen with different time and pressure. As Ar- treated membrane, N_2- treated membrane was also tested with after 19, 43 hours of exporsure with 0.8 MPa pressure (Figure 10). In the previous treatment, if the time is long, the recovery effect is great, but the effect is insignificant compared to time, so the efficiency has decreased. Therefore, 67 and 91 hours were not applied to nitrogen treatment. V alloy membrane initial permeability was 6.29×10^{-9} mol/m s $Pa^{1/2}$. With nitrogen treatment at 0.8 MPa for 19 hours, the permeabilities were 5.43×10^{-9} mol/m s $Pa^{1/2}$, 5.49×10^{-9} mol/m s $Pa^{1/2}$, consecutively. Calculating the relative permeability, it was 86% and 87% compared to the initial permeability, which was more effective than the argon exposure experiment under the same conditions. However, when the exposure time was prolonged to 43 hours, the results trend were different. Hydrogen permeability values were 6.00×10^{-9} mol/m s $Pa^{1/2}$ in consecutive permeation tests and its relative permeability was 95%. As more hydrogen atoms are removed between the metal lattice, hydrogen permeability recovery occurs well. However, increasing permeability trend with increasing exposure time was stronger in Ar treatment compared to N_2 treatment. Compared to argon which made the permeability increase even after the hydrogen tests, N_2 had the effect of just restoring the initial level. It can be assumed that argon molecule (40 u) is even heavier than nitrogen molecule (28 u) so that the impact of Ar was greater. This is because heavier physical force can be applied.

Figure 11 shows the repeated permeation results with pressure variation. For the same reason as the argon pressure difference experiment, the maximum applied pressure was limited to 0.8 MPa. The metallic membrane with the initial 6.26×10^{-9} mol/m s $Pa^{1/2}$ decreased to 4.00×10^{-9} mol/m s $Pa^{1/2}$ when the metallic membrane was exposed to nitrogen with 0.4 MPa after the hydrogen permeation experiment. At this time, the time was used by adopting 43 hours, which showed high efficiency in the previous experiment. After that, even if the experiment was repeated under the same conditions, the permeability of 4.29×10^{-9} mol/m s $Pa^{1/2}$ was shown. Converting the value into relative permeabilities were 63% and 68%. However, when the exposure pressure increased to 0.8MPa, the permeability recover to 6.12×10^{-9} mol/m s $Pa^{1/2}$ and 5.09×10^{-9} mol/m s

$Pa^{1/2}$. It could be concluded that relative permeabilities were 97% and 81%, respectively. Similarly, in the nitrogen pressure variation experiment, the higher the pressure, the greater the effect of permeability recovery. However, the effect of the pressure value was different. Since the hydrogen exposure pressure is 0.4 MPa, if the difference from this value increases, the load applied to the metallic membrane increases, which makes significant influence. Like argon, nitrogen was found to be effective in recovery as the exposure pressure was greater.

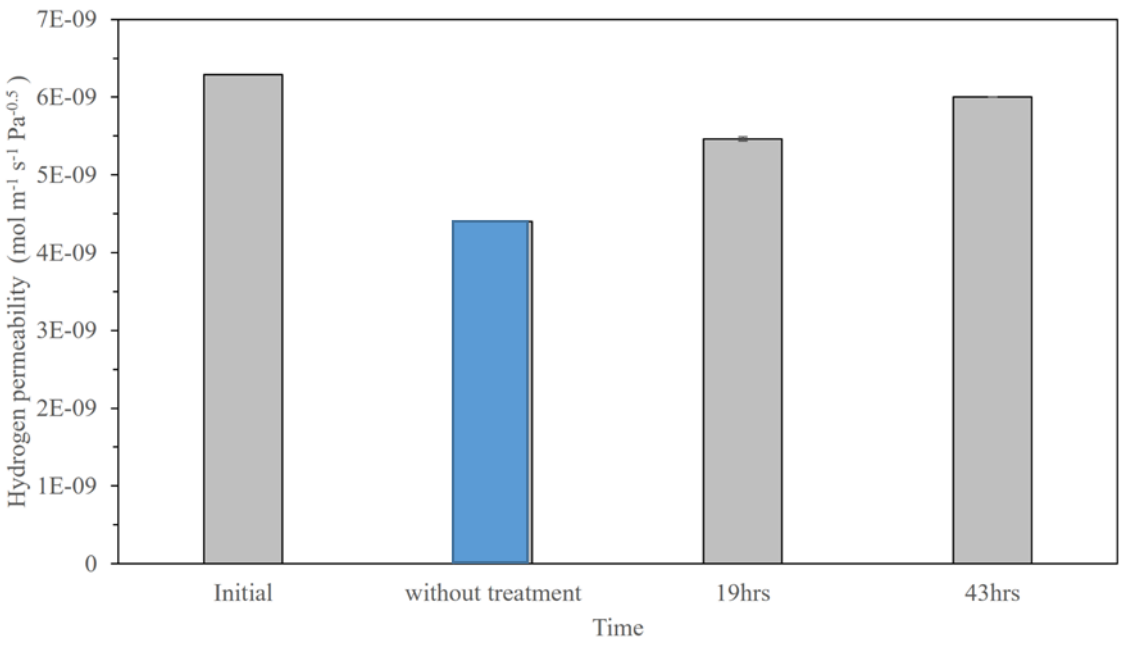

Figure 10 Permeabilities after inert treatment with N_2 Exposure time duration was differentiated 19-43 hours. (0.8 MPa of pressure)

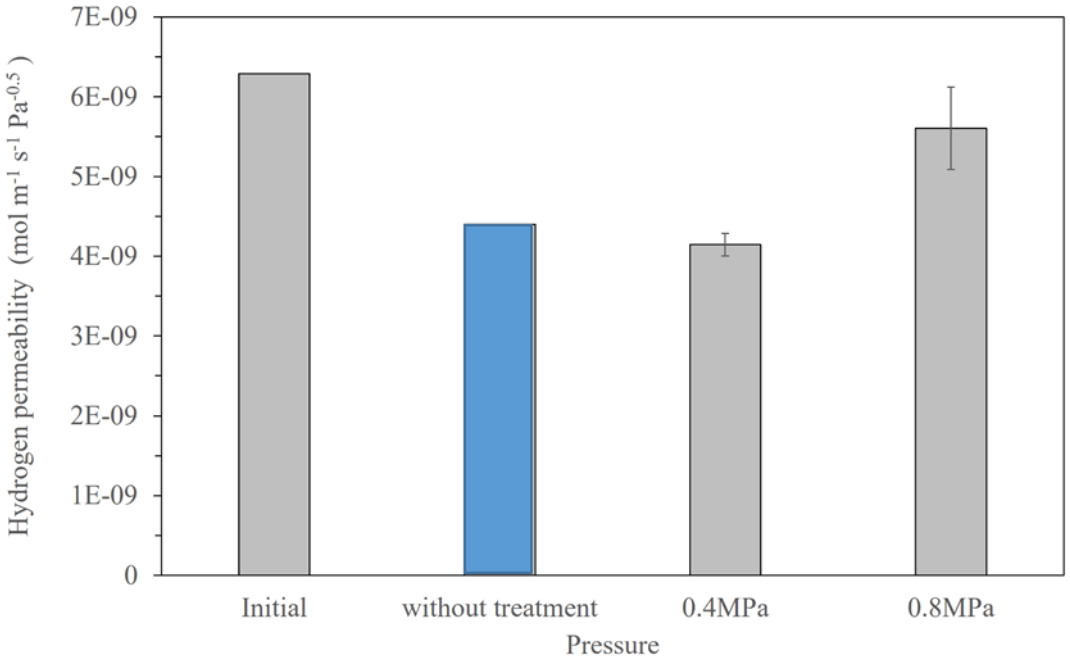

Figure 11 Permeabilities after inert treatment with N_2. Exposure pressure ranging from 0.4 MPa to 0.8 MPa (43 hours exposure time).

Similar permeability decay and recovery has been reported with metallic membrane. The membrane was exposed to air for 500 hours, after which the flux recovered to initial permeability (Lundin et al., 2017). The membrane is exposed to air at 350 °C, and then stabilized hundreds of hours after recovering its initial value. If the exposure gas changed to inert gas, the results of experimental analysis were shown in Table 2. After using Ar and N2, the relative permeability recovery efficiency results were analyzed based on the initial permeability.

As a result of the repeated experiment, the degree of permeability recovery increased as the inert gas pressure increased and the exposure time increased. In the case of argon, the permeability after treatment increased compared to the initial permeability, and enhancement was also shown. All experimental results showed that the increase effect was consistent in the metallic membranes. In the present study, after an initial rapid decline over 5 hours, the flux recovered to an around 90% of initial value after 43 h. The permeability recovery with Ar increased up to 133% with 0.8 MPa, 43 hours, and with N_2, recovered 97% with same conditions. If the pressure difference between feed side and permeate side is large, the force of the hydrogen atom located between the surface metal atoms becomes greater. Therefore, as more hydrogen atoms are removed, it can be estimated that the permeability is high and stable in the next hydrogen experiment.

Unlike the vanadium metallic membrane, which generally suffers from an embrittlement problem, the metallic membrane used in this study were robust enough to be used in practical hydrogen separation applications if the inert gas experimental conditions were kept constant. The cause of the embrittlement is that the process is operated at a low temperature, and at a temperature of 350°C or higher, it was robust without embrittlement. Except the case of the inert gas treatment pressure should not exceed 0.8 MPa. The higher the pressure in the inert gas treatment, the more effective it is, so it is efficient to apply the pressure as high as possible.

There is no leakage during the long-term test. The membrane used in this study endured repeated hydrogen experiments and gas exposure without being destroyed. As a result of the repeated experiment, both argon and nitrogen showed maximum efficiency when treated at 0.8 MPa and 43 hours. Therefore, further experiments with Pd coated membrane were conducted at

0.8 MPa of inert gas for 43 hours.

Table 2 Experimental result based on experimental condition differences; bolded conditions are the most effective conditions in each inert gas

no	Gas	Pressure (Mpa)	time (hr)	Efficiency compared to previous permeability (%)
1	N_2	0.4	43	65.5 (63-68)
2	N_2	0.8	19	86.5 (86-87)
3	**N_2**	**0.8**	**43**	**91.4 (89-95)**
4	Ar	0.4	43	38 (35-41)
5	**Ar**	**0.8**	**43**	**112 (101-133)**
6	Ar	0.8	67	114
7	Ar	0.8	91	99

3.2 Permeability test of Pd coated membrane

The high permeability of BCC V metal has been acknowledged for a long time, however pure form of BCC metals makes crack rapidly on the surface when exposed to hydrogen due to the high hydrogen solubility. Therefore, alloying with other metals can be a solution, but this can largely induce permeability decrease. Metallic membrane sample surfaces were coated with Pd to promote H_2 dissociation so that the influence of bulk alloy properties could be minimized.

When the Pd-coated membrane experiment is conducted for 5 hours, the hydrogen permeability was initially measured to be 2.74×10^{-7} mol/m s $Pa^{1/2}$ and 8.72×10^{-7} mol/m s $Pa^{1/2}$. Compared to the naked $V_{85}Ni_{15}$ membrane of 1.65×10-6 mol/m s Pa1/2, it was significant that thin Pd coating made noticeable increase. Compared to the results of literatures, pure V shows 3.00×10^{-7} mol/m s $Pa^{1/2}$ (Steward, 1983) and Ni has 7.80×10^{-11} mol/m s $Pa^{1/2}$ permeability. To prevent vanadium embrittlement, the permeability is 3.50×10^{-8} mol/m s $Pa^{1/2}$ with palladium both sides coating (Dolan et al., 2018). When vanadium and nickel are alloyed, the permeability is decreased to 5.00×10^{-8} mol/m s $Pa^{1/2}$ with Pd coating (Nishimura et al., 2002). Palladium coating is effective when used alone, but alloyed palladium has also potent of hydrogen permeation characteristics. Pd-Cu alloy coating is efficient in hydrogen permeation test with 6.00×10^{-8} mol/m s $Pa^{1/2}$ permeability (Yang et al., 2007). It showed that the membranes used in this study had comparable permeability value (Table 2).

However, during the overall 5 hours hydrogen permeability check, the Pd coated membrane decreased drastically and converged to almost zero at the end of the experiment (Figure 12). The permeability of the initial Pd coated membrane was 1.26×10^{-6} mol/m s $Pa^{1/2}$. Compared to non-coated membrane, its initial permeability was 1.65×10^{-6} mol/m s $Pa^{1/2}$. Pd coating had 76 times effect at initial stage. During experiment, the hydrogen flux showed repetitive fluctuation and decreasing trend. Non-Pd membrane also indicated fluctuation during the test, but decreasing trend was not observed. After 5 hours, the value converged to zero.

Drastic decrease in hydrogen flux over time at high temperatures seems to be related to interdiffusion between palladium coating layers and V alloy substrates. The decrease in hydrogen

flux seems to be related to the mutual diffusion between the palladium coated layer and the vanadium alloy substrate, which affects the hydrogen permeation behavior (Edlund & McCarthy, 1995). Similar permeability decay and regeneration with air have been reported in Pd-based membranes in the past. The fact that permeability is restored after air exposure shows that air exposure is a surface phenomenon that restores hydrogen adsorption and dissociation rates. This deterioration over time may be due to the rearrangement of the external Pd layer due to Pd magnetic diffusion.

In addition, palladium phase transition with hydrogen made membrane permeability decrease drastically, compared to naked vanadium-nickel alloy. In the case of membranes without Pd coating, inert gases such as Ar and N_2 indicated hydrogen permeability recovery similar to initial value or even higher than initial one. Therefore, inert gas exposure is assumed to be effective in metallic membrane surfaces, so that similar procedures were conducted in Pd coated membrane.

Table 3 Comparison of hydrogen permeability between reported and experimental results

Metal	H_2 permeability (mol/m s $Pa^{1/2}$)	Temperature(°C)	References
V	3.00×10^{-7}	400	(Steward, 1983)
Pd	1.60×10^{-8}	400	(Morreale et al., 2003)
Ni	7.80×10^{-11}	500	(Phair & Donelson, 2006)
$Pd/V_{85}Ni_{15}/Pd$	5.0×10^{-8}	300	(Nishimura et al., 2002)
$Pd_{60}Cu_{40}/V_{85}Ni_{15}$	6.00×10^{-8}	300	(Yang et al., 2007)
$PdAg_{24}$	1.3×10^{-8}	400	(Nayebossadri et al., 2019)
Pd/V/Pd	3.5×10^{-7}	340	(Dolan et al., 2018)
Pd/V	1.65×10^{-7}	500	(Cooney et al., 2014)
$V_{85}Ni_{15}$	1.16×10^{-9}		
$Pd/V_{85}Ni_{15}/Pd$	2.74×10^{-7}	350	Present work
$Pd/V_{85}Ni_{15}/Pd$	8.72×10^{-7}		

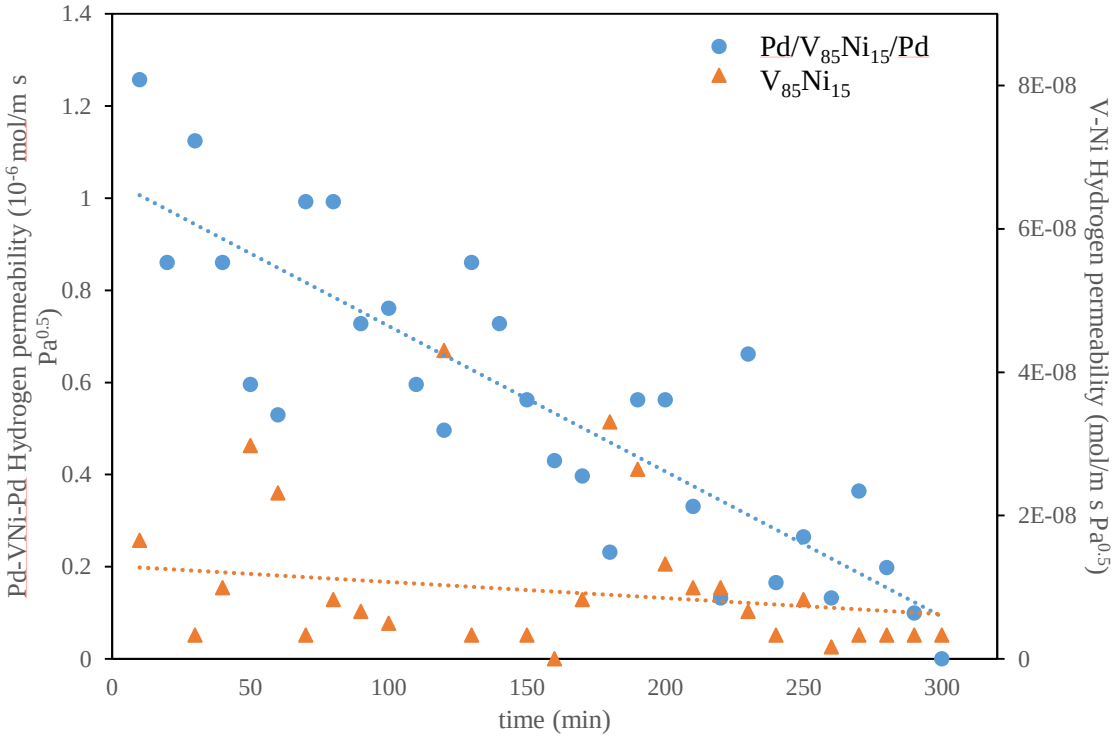

Figure 12 Comparison of hydrogen permeabilities between Pd/$V_{85}Ni_{15}$/Pd and naked $V_{85}Ni_{15}$ alloy membrane for 5 hours.

As the effect of recovery and enhancement was much more significant with inert gases than air in vanadium nickel alloy membrane. It can be assumed that similar effect can be found Pd coated one. Air purge at 500 °C, which lasted for about 1 hour, is found to cause pore opening on the surface of the Pd film. These processes create up to 30% more surface area especially in the air-treated palladium membrane (Roa & Way, 2005). The previous vanadium membrane permeation indicated that the permeation showed greater permeabilities with inserted inert gas treatment than air treatment reported in literature (Dolan et al., 2018).

Therefore, inert gas treatment condition was applied under optimal conditions (Figure 12). Optimal condition was inert gas using at 0.8 MPa, 350°C for 5 hours. The two membranes showed initial permeability of 2.24×10^{-7} mol/m s $Pa^{1/2}$, 7.12×10^{-7} mol/m s $Pa^{1/2}$. And treated at a pressure of 0.8 MPa for 43 hours using Ar and N_2, respectively. Like vanadium membranes, the treatment effect was greater in palladium coating membranes when inert gas was argon. After 1st cycle with argon, the permeability increased to 6.27×10^{-7} mol/m s $Pa^{1/2}$ which is 280% of initial value. Meanwhile, the nitrogen treated membrane increased to 9.29×10^{-7} mol/m s $Pa^{1/2}$, but the ratio between the initial value is 130%. 3rd permeation values which were results of after the second were 1.14×10^{-6} mol/m s $Pa^{1/2}$ and 1.11×10^{-6} mol/m s $Pa^{1/2}$ with Ar and N2, respectively. Calculating relative permeability compared to initial values, argon- treated membrane had 508% increase, nitrogen-treated membrane had 155% increase. Both palladium-coated membranes increased with inert gas exposure compared to initial permeability. However, the degree of increase was much greater than that of the non-Pd coated membrane.

While the non-Pd membrane showed an average recovery of about 100%, the Pd membrane showed a continuous increase in permeability after inert gas exposure. Immediately after the first treatment, the increase in permeability was greater than that of the non-Pd membrane. This means that the inert gas treatment effect is greater in Pd-coated V-Ni membrane than in naked V-Ni membrane. In case of air treatment, there are more studies which subject is Pd coated membrane. Pd is easily oxidized and active metal. It can form an oxide film on its surface with just heating. And it is possible to increase hydrogen permeation by treating it with inert gas with maximizing the action of the oxide film on the surface. In case of air exposure, the formation of palladium

oxide is promoted due to the air exposure. The formation of palladium oxide reduces the size of the original Pd crystallite to nano-size, possibly increasing the volume of grain on the surface. More particle boundaries will enable more surface diffusion of H_2.

In particular, air purge is found to be effective in restoring membrane activity in poisoned membranes during exposure to gas flows containing hydrogen sulfide. The lattice changes observed in the metal film exposed to air may also have some effect on the increase in H2 flux. The X-ray diffraction pattern showed the production results of palladium oxide during air treatment of the Pd film. As a result, nano-sized grains can modify the hydrogen transport mechanism through the membrane by introducing much more surface diffusion of H_2, and slow solid-state diffusion between membranes by generating more transport routes (Roa & Way, 2005). Argon made much faster increase when comparing the increase rate. The initial permeability was one-third that of the N_2 treated membrane, but the permeability became similar after gas treatments.

Unlike vanadium-nickel alloy membrane, the reason for the increase in hydrogen permeability in the palladium coated membrane is because of the phase transition of Pd. Pure Pd membranes show phase transitions between alpha (α) and beta (β) phases due to changes in temperature and hydrogen pressure. Hydrogen is dissolved in Pd to form an α-phase palladium hydride. As the hydrogen concentration increases in Pd, the phase is separated from the α phase, causing a rapid increase in the H/Pd ratio and expansion of the crystal lattice. Therefore, if the hydrogen permeation test is conducted again after the inert gas treatment, the hydrogen concentration increases and the crystal lattice expands, increasing the hydrogen permeability.

Pd absorbs a large amount of hydrogen and is accompanied by large lattice expansion, and the system becomes a hydride phase called a β phase. As shown in Figure 14, β phase can store more hydrogen in the lattice than the α phase. It can be assumed that hydrogen in the metal lattice is removed as it transitions from β to α phase due to inert gas treatment. In addition, when the H atom is absorbed into the Pd lattice, the Pd lattice expands due to lattice distortion around the H atom (Dekura et al., 2019). Therefore, after lattice expansion and hydrogen removal, it can be

possible to create conditions that allow hydrogen to pass through faster the next hydrogen experiment. The inert gas pressure was opposite to the hydrogen pressure, which can cause rapid phase transition when hydrogen is exposed to the Pd surface again. An increase in feed side pressure with inert gas injection will lead to an improvement in surface rate (adsorption/absorption) on the feed side and then surface resistance will become less important compared to bulk diffusion in the metal layer, which is probably why hydrogen permeability increases after a higher pressure inert gas exposure process.

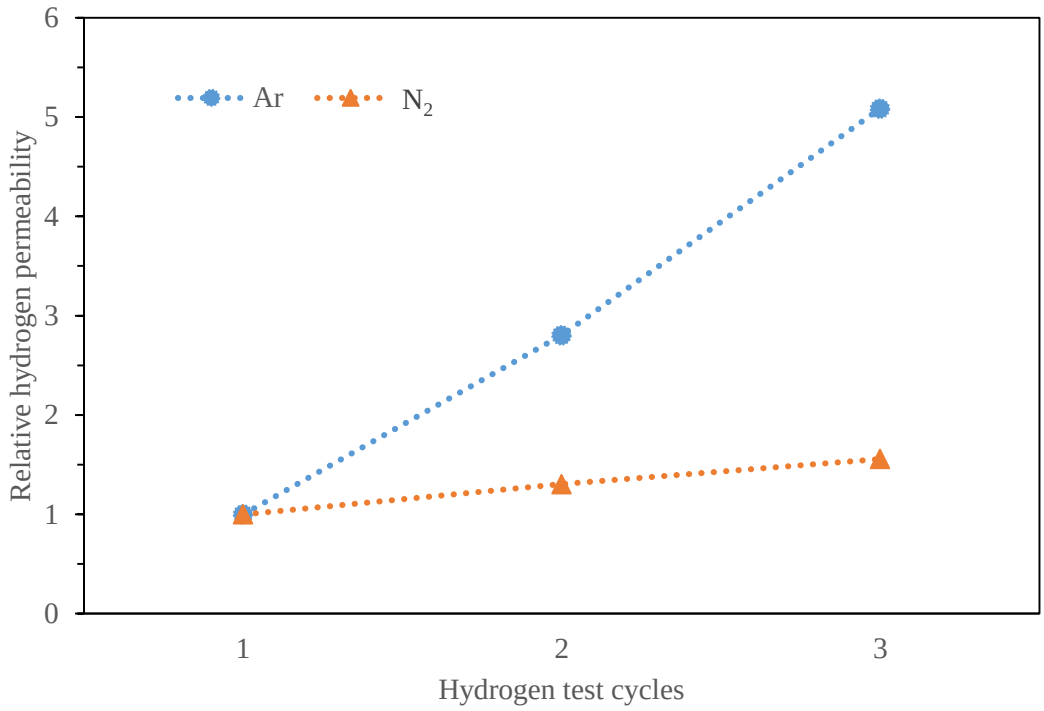

Figure 13 Hydrogen permeability through the Pd coated membranes with inert gases treatments

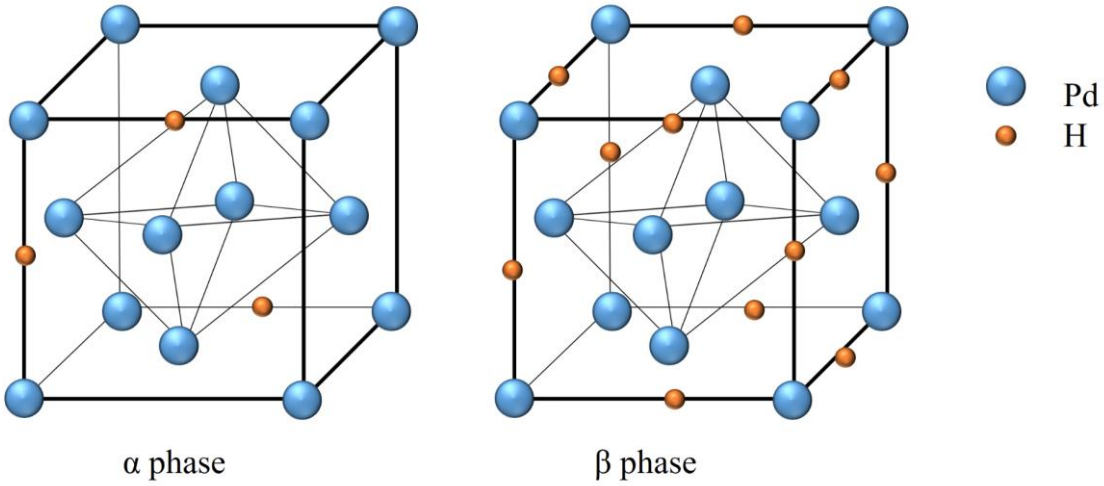

Figure 14 H/Pd is the number of absorbed H atoms per Pd atom (Akiba et al., 2015)

Detection limit of mass flowmeter is 1 cc/min. Therefore, to operate the membrane reactor in a continuous way, the hydrogen flux should exceed that specific value. After 2nd treatment with inert gases (i.e. Ar, N_2), the metallic membrane's hydrogen flux exceed the minimum value. In the previous process, the process is similar to semi-batch process. During the 5-hour hydrogen permeation test, there was no additional hydrogen injection on the feed side, and the valve of the permeate side was opened every 10 minutes to check the hydrogen flux. In this process, argon connected to the bottom side was used for hydrogen removal and purification. However, if the process is changed to a continuous process, the hydrogen valve on the feed side is continuously supplied while being opened for 5 hours during the hydrogen experiment. Hydrogen supplied to feed side travels through two paths. One is through the Pd-coated metallic membrane to the permeate side, and the other is to ventilate hydrogen that has not passed through the membrane.

In that result, hydrogen flux of argon treated metallic membrane was illustrated in Figure 15. The first measured hydrogen flux was 2.09 cc/ min. When measured by continuous flow of hydrogen for 5 hours, the permeation was also partially reduced at the beginning. However, rather than rapidly decreasing like the no inert gas treated membrane in Figure 12, it saturates after a certain portion of reduction and converges to 1.45 cc/min. The membrane surface was expected to be saturated with higher permeability than before inert gas treatments. For this reason, the permeability converged to the higher value even in the continuous process.

Until now, hydrogen exposure tests have been conducted at 350℃. Due to the characteristic of gas diffusion, as the temperature increases, the diffusion rate increases and a larger amount of hydrogen can penetrate during the same time period. However, since the metallic membrane, which is currently the subject of the experiment, was coated with palladium on a vanadium nickel alloy substrate, the diffusion between the palladium film and the substrate increases as the temperature increases. Moreover, there is a study about the argon gas treated membrane at 700 ℃ shows no difference in recovery of decreased hydrogen flux compared to non-treated membrane. Therefore, it was valuable that to which temperature does the inert gas exposure process have an active effect.

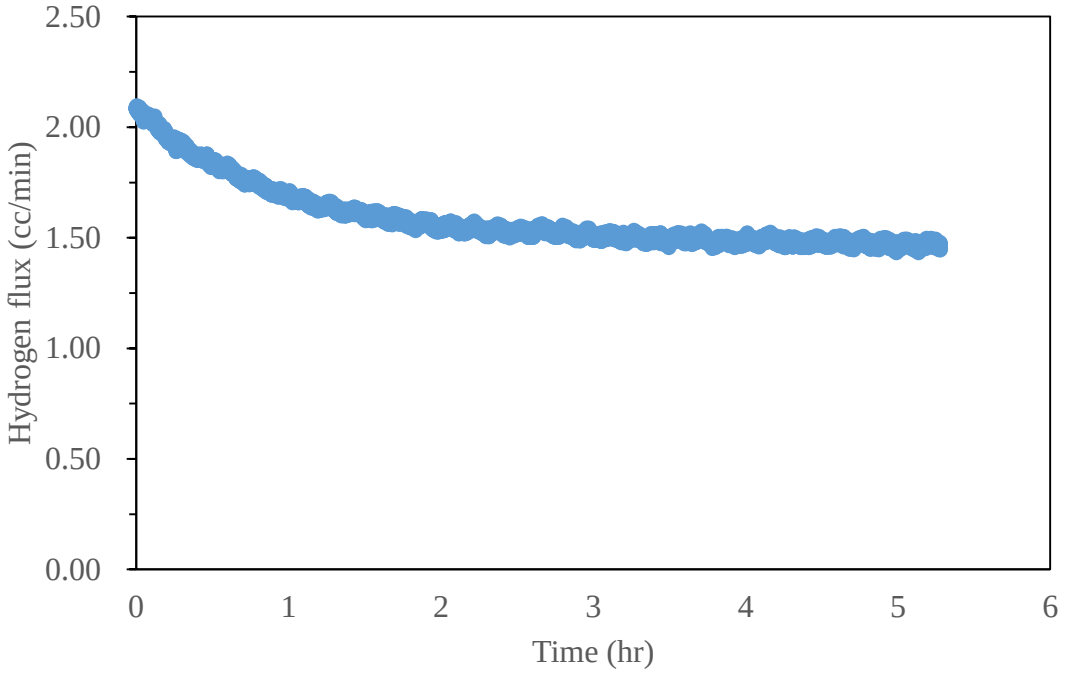

Figure 15 Continuous hydrogen flux result of Argon treated Pd coated vanadium nickel alloy membrane

After inert gas exposure twice, argon membrane and nitrogen membrane showed significantly stable value. Each membrane reached the minimum value of continuous process at 350℃ and was modified exposure temperature. The hydrogen permeation results with different temperature were illustrated in Figure 16 and Figure 17. Inert gas exposure was conducted in 0.8 MPa, 43 hours with difference in temperature. Between the hydrogen permeation tests, the membrane reactor was heated up to 400, 450, 500 ℃ and inert gas was injected in the feed side. After the recovery process, the reactor was cooled down to 350 ℃ where the hydrogen permeation temperature is.

When comparing the hydrogen flux result with relative flux, it doubled with argon exposure at 400 ℃. However, the treatment temperature increased much more at 450℃, the flux did not decrease anymore. It showed only 83% of the previous result. T이he hydrogen flux got decreased even the inert gas treatment temperature was much higher. Moreover, the stability got worse resulting that the fluctuation during the hydrogen test expanded at 500 ℃. Inert gas treatment with argon in a continuous process was a lot more effective at 400 ℃.

In case of nitrogen, the result trend was different. When the treatment temperature increased to 400, 450, 500 ℃, the permeation flux showed 114%, 107%, 107% of 350 ℃ permeation result, respectively. However, fluctuation of full time scale in hydrogen tests was significantly similar with argon exposure. Fluctuation reduced and permeation became stable at 400 ℃. Afterwards, as the treatment temperature rises to 500 ℃, the ups and downs are repeated during the hydrogen permeation for 5 hours. When the argon exposure temperature is 700 ℃, the permeability reduction phenomenon in the metallic membrane is not affected (Edlund & McCarthy, 1995). However, the temperature of the inert gas treatment and hydrogen permeation test at 350 ℃ had different impact on the membrane. According to other study (M. D. Dolan et al., 2012), the permeability through Pd-coated $V_{85}Ni_{15}$ membrane has a weak dependence on temperature. However, in this study, when the Pd coated V alloy membrane treated with argon, the permeabilities varied depending on the temperature. Temperature can have impact on arrangement of the metallic membrane component so that further study may reveal the

relationship between diffusion in composite metals and permeation recovery with temperature difference. Different expansion by inert gases causes structural components to mechanically collide (contraction, compression) with each other. This in turn can affect the solubility and diffusion of hydrogen in the micro-volume of the membrane alloy. However, the Pd membrane can be delaminated from the substrate with temperature swing (inert gas temperature ↔ hydrogen permeation temperature, 350°C) so that the permeability showed decreased with increasing treatment temperature.

Another possible theory is that palladium phase morphology depending on the temperature. At intermediate temperatures, the relative amounts of α and β phase are expected to vary in a membrane (Elkina & Meldon, 2002). Since the solubility of hydrogen in the alpha phase is quite high, the dissolved hydrogen concentration gradient will be abnormally large. However, if a phase transition phenomenon occurs due to a temperature change, the tendency of hydrogen dissolution may change. The improvement of hydrogen flux at around 400°C was attributed to lattice expansion associated with crystal transition from α to β phases (Okazaki et al., 2006). However, at sufficiently high temperatures, only the α phase prevails, so the permeability decreases again. This phenomenon may occur similarly when palladium is coated on metal substrate.

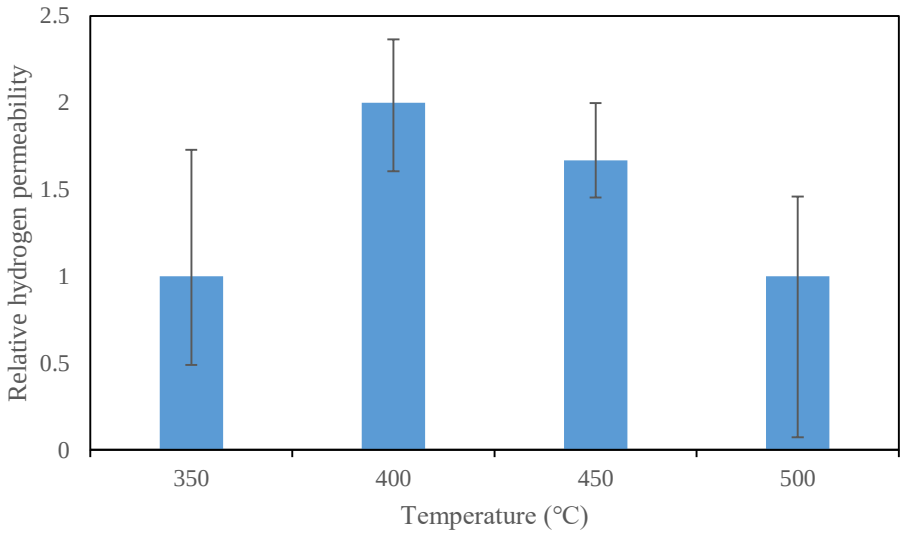

Figure 16 Continuous hydrogen permeation flux with Ar exposure at different temperatures

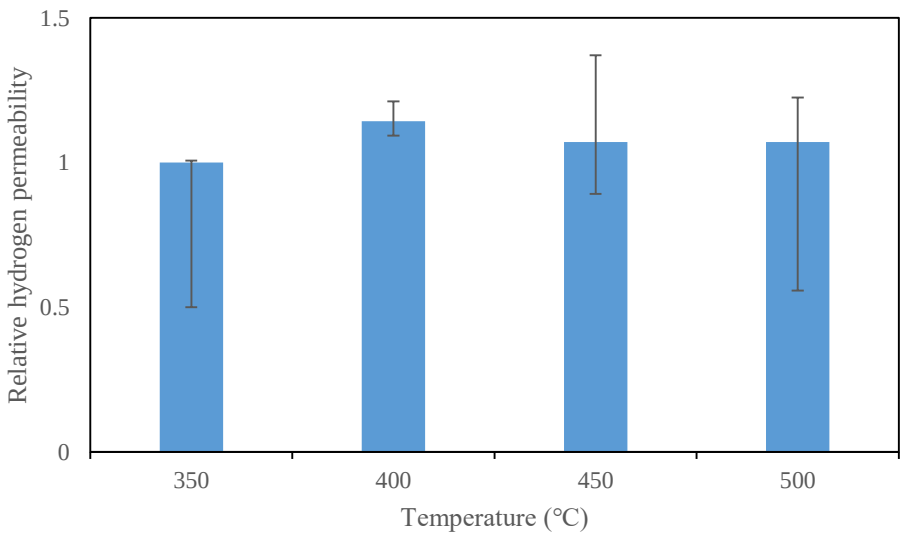

Figure 17 Continuous hydrogen permeation flux with N2 exposure at different temperatures

Figure 18 shows the change in X-ray diffraction pattern with inert gas treatment. Each gas treated membranes were the membranes after Figure 15, Figure 16. It is assumed that inter-diffusion between Pd coating and V-Ni substrate may occur in the membrane because inert gas treatment was performed up to 500°C.

Before gas treatments and hydrogen permeation tests, the membrane pattern showed consistent with Pd peaks. This means that palladium coating using deposition was properly performed. However, changes occur when the membrane is exposed to high temperatures with argon and nitrogen. A particularly noticeable change is that a new peak occurs at around 62°. And this is much more maximized when treated with nitrogen. The approximate location is similar to the peak shown in V-doped NiO materials (Park et al., 2013). After nitrogen treated at high temperature, sputtered Pd can be delaminated much faster than with argon treatment.

It can be seen that nitrogen causes a greater change in membrane surface characteristics because small peaks were illustrated when nitrogen treatment is performed among the two inert gas treated membranes. Neither argon nor nitrogen is reactive, but argon is a little more reactive than nitrogen, making it easier to maintain inert conditions. Therefore, inert condition on the metal film has a significant effect on maintaining the Pd coating of the membrane. In addition, many small peaks appeared when nitrogen treatment was performed. This is presumed to be due to the uneven surface and the removal of palladium hydride. And as the temperature increases, the phase transition phenomenon of palladium hydride is minimized, resulting in a change in the relative hydrogen permeability.

And as the temperature increases, the phase transition of palladium hydride is minimized, resulting in a change in the relative hydrogen permeability. One possible hypothesis is that as the temperature increases, there is little movement from β phase to α phase, resulting in slow hydrogen permeation during the next hydrogen experiment.

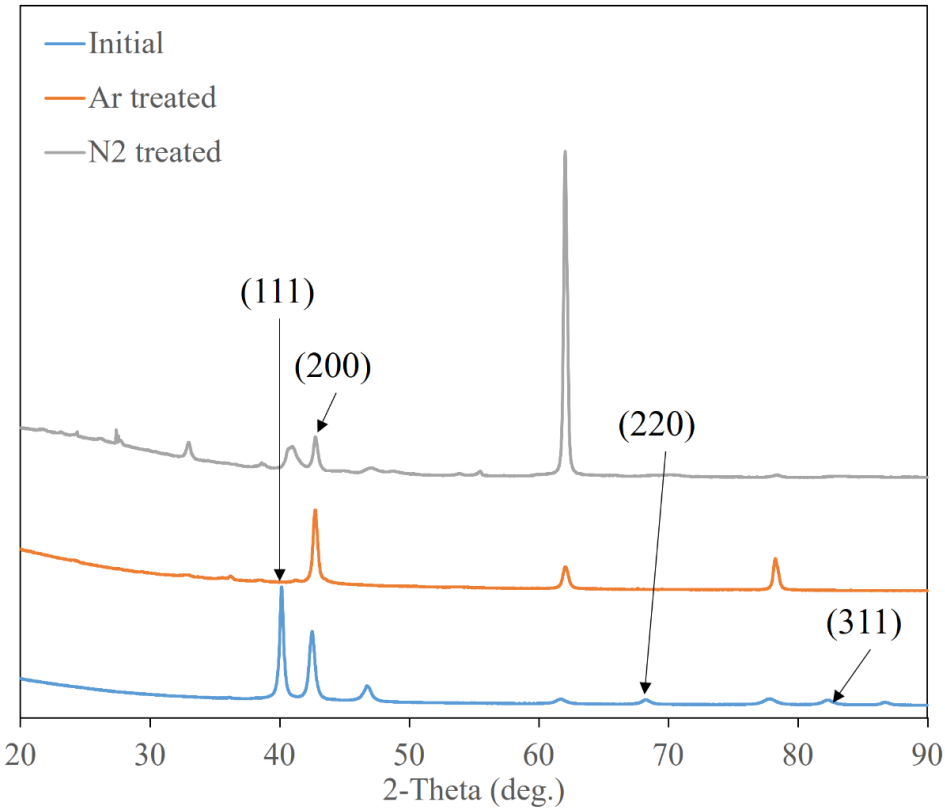

Figure 18 Change in X-ray diffraction patterns of Pd coated membrane as the function of inert gas treatment. Membranes were heated under inert gas atmosphere.

4. Conclusion

In this study, the impact of metallic membrane exposure to inert gas was evaluated using permeation tests. The objective was to propose a new approach to increase their permeability and recovery. Hydrogen transport in metallic membranes occurs through various sorption- diffusion mechanisms, which include the dissociation of hydrogen molecules, the diffusion between metal lattices in the form of atom and the association of atomic hydrogen into molecular form. The lattice gaps in the hydrogen perm-selective metals only allow hydroge It can be assumed to pass through, and the selectivity of metallic membrane to hydrogen is therefore theoretically infinite. However, in practice, metallic membranes permeability decreases during hydrogen tests. Such phenomenon was observed both with vanadium-nickel alloy membrane and Pd coated alloy membrane in this study. In particular, Pd coated membrane permeability decreased 100 times after 5 hours of hydrogen permeation experiment. Therefore, recovery of permeability is necessary to use the metallic membrane in a long-term perspective.

In this research, a new process which consisted of exposing the metallic membrane to an inert gas between hydrogen experiments was proposed and tested. Results showed that both argon and nitrogen treatment could contribute to hydrogen permeability over 90% recovery. However, both types of membranes were much more effective when the gas was argon. Further experiments were conducted to determine the optimal gas treatment conditions and gas exposure time and pressure appeared to a have a significant impact on the treatment performance. For both nitrogen and argon, the greater the exposure pressure and the longer the exposure time, the better the permeability recovery. Based on these results, 43 hours was considered the optimal exposure time, and increasing treatment time over 43 hours did not significantly increase recovery. Experiments tended to show that increasing the pressure gradient between the inert gas pressure (feed side) and the atmospheric pressure (permeate side) increased the recovery. However, increasing the pressure gradient between the feed side and the permeate side also increases the risk of cracks. Therefore, an inert gas exposure pressure was recommended as large as possible, but it should not exceed 0.8 MPa in this study.

As a result of applying inert gas treatment to Pd coated substrates with the previous optimal conditions, the permeability recovery phenomenon by inert gas was significant. Similarly, this impacts were also more effective in argon gas. This is assumed to be due to the phase transition of palladium. In addition, the Pd membrane with increased permeability with inert gas treatment may ensure a minimum flow rate for a continuous process. In this process, the permeability changed significantly due to temperature. It showed a different pattern from previous studies, and structural mechanical research seems to be needed. In addition, as a result of XRD analysis, argon and nitrogen can cause changes in the Pd coating of the membrane. In particular, nitrogen contributes more to the production of irreversible palladium hydride.

In conclusion, inert gas treatments appears to be a promising approach to increase metallic membrane hydrogen permeability and recovery. Further study is, however, recommended to evaluate the effect of gas temperature on the treatment efficiency.

References

Adhikari, S., & Fernando, S. (2006). Hydrogen membrane separation techniques. *Industrial & Engineering Chemistry Research*, *45*(3), 875-881.

Akiba, H., Kobayashi, H., Kitagawa, H., Kofu, M., & Yamamuro, O. (2015). Glass transition and positional ordering of hydrogen in bulk and nanocrystalline palladium. *Physical Review B*, *92*(6), 064202.

Ali, J. K., Newson, E., & Rippin, D. (1994). Deactivation and regeneration of Pd Ag membranes for dehydrogenation reactions. *Journal of Membrane Science*, *89*(1-2), 171-184.

Bellini, S., Liang, X., Li, X., Gallucci, F., & Caravella, A. (2018). Non-ideal hydrogen permeation through V-alloy membranes. *Journal of Membrane Science*, *564*, 456-464.

Bernardo, G., Araújo, T., da Silva Lopes, T., Sousa, J., & Mendes, A. (2020). Recent advances in membrane technologies for hydrogen purification. *International journal of hydrogen energy*, *45*(12), 7313-7338.

Chen, J., Yan, L., Song, W., & Xu, D. (2017). Methane steam reforming thermally coupled with catalytic combustion in catalytic microreactors for hydrogen production. *International journal of hydrogen energy*, *42*(1), 664-680. https://doi.org/https://doi.org/10.1016/j.ijhydene.2016.12.114

Collins, J. P., & Way, J. D. (1993). Preparation and characterization of a composite palladium-ceramic membrane. *Industrial & Engineering Chemistry Research*, *32*(12), 3006-3013.

Conde, J. J., Maroño, M., & Sánchez-Hervás, J. M. (2017). Pd-Based Membranes for Hydrogen Separation: Review of Alloying Elements and Their Influence on Membrane Properties. *Separation & Purification Reviews*, *46*(2), 152-177. https://doi.org/10.1080/15422119.2016.1212379

Cooney, D. A., Way, J. D., & Wolden, C. A. (2014). A comparison of the performance and stability of Pd/BCC metal composite membranes for hydrogen purification. *International journal of hydrogen energy*, *39*(33), 19009-19017.

Dekura, S., Kobayashi, H., Kusada, K., & Kitagawa, H. (2019). Hydrogen in Palladium and Storage Properties of Related Nanomaterials: Size, Shape, Alloying, and Metal-Organic Framework Coating Effects. *ChemPhysChem*, *20*(10), 1158-1176. https://doi.org/https://doi.org/10.1002/cphc.201900109

Dolan, M., McLennan, K., & Way, J. D. (2012). Diffusion of atomic hydrogen through V–Ni alloy membranes under nondilute conditions. *The Journal of Physical Chemistry C*, *116*(1), 1512-1518.

Dolan, M. D., McLennan, K. G., & Way, J. D. (2012). Diffusion of Atomic Hydrogen through V–Ni Alloy Membranes under Nondilute Conditions. *The Journal of Physical Chemistry C*, *116*(1), 1512-1518. https://doi.org/10.1021/jp208691x

Dolan, M. D., Viano, D. M., Langley, M. J., & Lamb, K. E. (2018). Tubular vanadium membranes for hydrogen purification. *Journal of Membrane Science*, *549*, 306-311.

Edlund, D. J., & McCarthy, J. (1995). The relationship between intermetallic diffusion and flux decline in composite-metal membranes: implications for achieving long membrane lifetime. *Journal of Membrane Science*, *107*(1-2), 147-153.

Elkina, I. B., & Meldon, J. H. (2002). Hydrogen transport in palladium membranes. *Desalination*, *147*(1-3), 445-448.

Fort, D., Farr, J., & Harris, I. (1975). A comparison of palladium-silver and palladium-yttrium alloys as hydrogen separation membranes. *Journal of the Less common metals*, *39*(2), 293-308.

Graham, T. (1866). XVIII. On the absorption and dialytic separation of gases by colloid septa. *Philosophical transactions of the Royal Society of London*(156), 399-439.

Hashim, S. S., Somalu, M. R., Loh, K. S., Liu, S., Zhou, W., & Sunarso, J. (2018). Perovskite-based proton conducting membranes for hydrogen separation: A review. *International journal of hydrogen energy*, *43*(32), 15281-15305.

Julbe, A., Farrusseng, D., & Guizard, C. (2001). Porous ceramic membranes for catalytic reactors — overview and new ideas. *Journal of Membrane Science*, *181*(1), 3-20. https://doi.org/https://doi.org/10.1016/S0376-7388(00)00375-6

Kamakoti, P., Morreale, B. D., Ciocco, M. V., Howard, B. H., Killmeyer, R. P., Cugini, A. V., & Sholl, D. S. (2005). Prediction of hydrogen flux through sulfur-tolerant binary alloy membranes. *Science*, *307*(5709), 569-573.

Keuler, J. N., & Lorenzen, L. (2002). Developing a heating procedure to optimise hydrogen permeance through Pd–Ag membranes of thickness less than 2.2 μm. *Journal of Membrane Science*, *195*(2), 203-213.

Keurentjes, J. T., Gielens, F. C., Tong, H., Van Rijn, C., & Vorstman, M. A. (2004). High-flux palladium membranes based on microsystem technology. *Industrial & Engineering Chemistry Research*, *43*(16), 4768-4772.

Kim, K. H., Park, H. C., Lee, J., Cho, E., & Lee, S. M. (2013). Vanadium alloy membranes for high hydrogen permeability and suppressed hydrogen embrittlement. *Scripta materialia*, *68*(11), 905-908. https://doi.org/https://doi.org/10.1016/j.scriptamat.2013.02.028

Ko, W.-S., Jeon, J. B., Shim, J.-H., & Lee, B.-J. (2012). Origin of hydrogen embrittlement in vanadium-based hydrogen separation membranes. *International journal of*

hydrogen energy, *37*(18), 13583-13593.

Lamb, K. E., Dolan, M. D., & Kennedy, D. F. (2019). Ammonia for hydrogen storage; A review of catalytic ammonia decomposition and hydrogen separation and purification. *International journal of hydrogen energy*, *44*(7), 3580-3593.

Louthan Jr, M., Caskey Jr, G., Donovan, J., & Rawl Jr, D. (1972). Hydrogen embrittlement of metals. *Materials Science and Engineering*, *10*, 357-368.

Lundin, S.-T. B., Patki, N. S., Fuerst, T. F., Wolden, C. A., & Way, J. D. (2017). Inhibition of hydrogen flux in palladium membranes by pressure–induced restructuring of the membrane surface. *Journal of Membrane Science*, *535*, 70-78.

Mejdell, A., Klette, H., Ramachandran, A., Borg, A., & Bredesen, R. (2008). Hydrogen permeation of thin, free-standing Pd/Ag23% membranes before and after heat treatment in air. *Journal of Membrane Science*, *307*(1), 96-104.

Morreale, B. D., Ciocco, M. V., Enick, R. M., Morsi, B. I., Howard, B. H., Cugini, A. V., & Rothenberger, K. S. (2003). The permeability of hydrogen in bulk palladium at elevated temperatures and pressures. *Journal of Membrane Science*, *212*(1-2), 87-97.

Nayebossadri, S., Speight, J. D., & Book, D. (2019). Hydrogen separation from blended natural gas and hydrogen by Pd-based membranes. *International journal of hydrogen energy*, *44*(55), 29092-29099.

Nishimura, C., Komaki, M., & Amano, M. (1991). Hydrogen permeation characteristics of vanadium-nickel alloys. *Materials Transactions, JIM*, *32*(5), 501-507.

Nishimura, C., Komaki, M., Hwang, S., & Amano, M. (2002). V–Ni alloy membranes for hydrogen purification. *Journal of alloys and compounds*, *330*, 902-906.

Okazaki, J., Tanaka, D. A. P., Tanco, M. A. L., Wakui, Y., Mizukami, F., & Suzuki, T. M. (2006). Hydrogen permeability study of the thin Pd–Ag alloy membranes in the temperature range across the α–β phase transition. *Journal of Membrane Science*, *282*(1), 370-374. https://doi.org/https://doi.org/10.1016/j.memsci.2006.05.042

Park, H. B., Kamcev, J., Robeson, L. M., Elimelech, M., & Freeman, B. D. (2017). Maximizing the right stuff: The trade-off between membrane permeability and selectivity. *Science*, *356*(6343), eaab0530. https://doi.org/doi:10.1126/science.aab0530

Park, H. W., Na, B.-K., Cho, B. W., Park, S.-M., & Roh, K. C. (2013). Influence of vanadium doping on the electrochemical performance of nickel oxide in supercapacitors [10.1039/C3CP52498A]. *Physical Chemistry Chemical Physics*, *15*(40), 17626-17635. https://doi.org/10.1039/C3CP52498A

Phair, J. W., & Donelson, R. (2006). Developments and Design of Novel (Non-

Palladium-Based) Metal Membranes for Hydrogen Separation. *Industrial & Engineering Chemistry Research*, *45*(16), 5657-5674. https://doi.org/10.1021/ie051333d

Pizzi, D., Worth, R., Giacinti Baschetti, M., Sarti, G. C., & Noda, K.-i. (2008). Hydrogen permeability of 2.5μm palladium–silver membranes deposited on ceramic supports. *Journal of Membrane Science*, *325*(1), 446-453. https://doi.org/https://doi.org/10.1016/j.memsci.2008.08.020

Rahimpour, M., Samimi, F., Babapoor, A., Tohidian, T., & Mohebi, S. (2017). Palladium membranes applications in reaction systems for hydrogen separation and purification: A review. *Chemical Engineering and Processing: Process Intensification*, *121*, 24-49.

Roa, F., & Way, J. D. (2005). The effect of air exposure on palladium–copper composite membranes. *Applied surface science*, *240*(1-4), 85-104.

Sazali, N., Mohamed, M. A., & Salleh, W. N. W. (2020). Membranes for hydrogen separation: A significant review. *The International Journal of Advanced Manufacturing Technology*, *107*(3), 1859-1881.

Shi, F. (2014). *Reactor and process design in sustainable energy technology*. Elsevier.

Shim, J.-H., Ko, W.-S., Kim, K.-H., Lee, H.-S., Lee, Y.-S., Suh, J.-Y., Cho, Y. W., & Lee, B.-J. (2013). Prediction of hydrogen permeability in V–Al and V–Ni alloys. *Journal of Membrane Science*, *430*, 234-241.

Sholl, D. S., & Ma, Y. (2006). Dense metal membranes for the production of high-purity hydrogen. *MRS bulletin*, *31*(10), 770-773.

Song, G., Kellam, M., Liang, D., & Dolan, M. (2010). Influence of processing conditions on the microstructure and permeability of BCC V–Ni membranes. *Journal of Membrane Science*, *363*(1-2), 309-315.

Steward, S. (1983). *Review of hydrogen isotope permeability through materials*.

Uemiya, S., Sato, N., Ando, H., Kude, Y., Matsuda, T., & Kikuchi, E. (1991). Separation of hydrogen through palladium thin film supported on a porous glass tube. *Journal of Membrane Science*, *56*(3), 303-313.

Wang, D., Clewley, J., Flanagan, T. B., Balasubramaniam, R., & Shanahan, K. (2000). Enhanced rates of hydrogen absorption resulting from oxidation of Pd or internal oxidation of Pd-Al alloys. *Journal of alloys and compounds*, *298*(1-2), 261-273.

Wolf, R. J., Lee, M. W., & Ray, J. R. (1994). Pressure-composition isotherms for nanocrystalline palladium hydride. *Physical review letters*, *73*(4), 557.

Yan, E., Cheng, J., Zhang, K., Chen, Y., Huang, R., Ge, X., Chu, H., Zou, Y., Zhang, H., Xu, F., & Sun, L. (2021). A novel Nb-based hydrogen purification membrane

without catalytic palladium overlayer. *Journal of alloys and compounds*, *875*, 160103. https://doi.org/https://doi.org/10.1016/j.jallcom.2021.160103

Yang, J., Nishimura, C., & Komaki, M. (2007). Effect of H2S on hydrogen permeation of Pd60Cu40/V–15Ni composite membrane. *Journal of alloys and compounds*, *446*, 575-578.

Yang, M., He, F., Zhou, C., Dong, F., Yang, G., Zhou, W., & Shao, Z. (2021). New perovskite membrane with improved sintering and self-reconstructed surface for efficient hydrogen permeation. *Journal of Membrane Science*, *620*, 118980.

Zhang, D., Fan, Y., Xu, N., & He, Y. (2011). Effect of intermetallic diffusion between Pd and Ti–Al alloy on the performance of Pd/Ti–Al alloy composite membranes. *Journal of Membrane Science*, *377*(1), 221-230. https://doi.org/https://doi.org/10.1016/j.memsci.2011.04.052

Zhang, Y., Zhou, C., Hui, W., & Dong, H. (2014). Effect of C content on hydrogen induced delayed fracture behavior of Mn-B type steels. *J. Iron Steel Res*, *26*(5), 49-55.

Zou, T., Zhang, P., Zhao, J., Zheng, P., & Chen, J. (2018). First principles study of vacancy-solute complexes in vanadium. *Journal of alloys and compounds*, *763*, 861-866. https://doi.org/https://doi.org/10.1016/j.jallcom.2018.06.037

초 록

수소는 깨끗하고 효율적인 에너지원으로, 현재 수소 기반 경제는 에너지 안보와 지속 가능한 미래를 위한 잠재적인 해결책으로 여겨지고 있다. 천연가스를 기반으로 하는 수소 생산 기술은 촉매 반응을 통해 만들어진 수소와 일산화탄소 등으로 구성된 합성가스를 매개로 한다. 전 세계적으로 천연가스 개질을 통한 수소 생산은 가까운 미래에도 지속될 것이다. 그 중 멤브레인 기술은 초고순도 수소 정제를 위한 효과적인 방법으로 알려져 있다. 수소는 금속 표면에서 원자 상태로 분해되어 금속 결정 사이의 공간을 이동한 후, 반대쪽 표면에서 다시 분자 상태로 결합하는 메커니즘을 통해 금속 분리막을 투과하는데, 수소의 투과 과정 중 금속 표면과 결정 사이의 공간에 수소 원자가 포집되고 금속 수소화물이 생성되어 수소 투과도가 낮아지는 것으로 알려져 있다. 이러한 메커니즘에 의해 금속막은 수소에 대한 선택성이 높은 장점이 있지만 수소 투과 진행 중 투과도 저하 현상 문제를 해결해야한다. 따라서 H2 투과 사이 불활성 기체 노출 공정을 삽입해 금속 격자 사이 수소원자를 제거하여 투과도를 회복하고자 하였다. 첫 번째 단계에서는 바나듐-니켈 합금막을 사용하여 비활성 기체 노출의 수소 투과도 회복 공정의 최적의 조건을 탐색했고, 두 번째 단계에서는 Pd/V85Ni15/Pd 막의 감소된 수소 투과성을 회복하기 위해 최적 기체 노출 조건을 적용하여 투과도 회복 정도를 확인했다. 아르곤, 질소 기체 모두 0.8 MPa, 43시간 노출 시켰을 때의 투과도가 초기 투과도 대비 증가 정도가 크게 나타났다. 아르곤 노출로 인해 금속막은 1차 노출 후 초기 대비 약 280%의 수소 투과도가 증가하였으며, 2차 노출 사이클로 508%의 개선을 달성하였다. 질소도 비반응성을 가지므로 수소 투과도 회복 효과가 유의미함을 확인했다. 질소의 경우 1·2차 회복 사이클 이후 각각 131%, 156% 증가했다. 아르곤은 질소보다 회복에 더 효과적이었다. 또한

비활성 기체 노출 사이클 이후 평균 수소 유량이 1 cm^3/min (sccm)보다 증가했다. 따라서, 기존의 회분식 공정에서 연속 공정으로 전환이 가능했고, 공정의 온도를 350, 400, 450, 500 ℃로 변화하여 실험을 진행했다. 그 결과, 금속막은 400 ℃에서 높은 투과성을 보였으며, 전체 수소 투과 양상도 안정화 되었다. 이러한 결과는 비활성 가스 노출 공정이 수소 투과 시험 중 감소 추세를 완화하고 Pd/V85Ni15/Pd 멤브레인의 수소 투과도 향상에 영향을 미침을 나타낸다. 이 연구를 통해 비활성 기체 노출이 높은 수소 투과도를 보장할 수 있다면, 금속막을 이용한 수소 분리 공정의 효율성을 높이는데 도움이 될 수 있을 것으로 사료된다.