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Pd-Cu alloy membrane deposited on alumina modified porous nickel support (PNS) for hydrogen separation at high pressure

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Abstract−This study reports on the hydrogen permeation properties of Pd-Cu alloy membranes at high pressures. A 7 μm thick Pd-Cu alloy membrane was prepared on an alumina-modified porous nickel support (PNS) by our developed magnetron sputtering and Cu-reflow method at 700 °C for 2 hours. The membrane was mounted in a stainless steel permeation cell with a gold-plated stainless steel O-ring. Helium leak testing confirmed that the membrane and membrane module were free of defects. Permeation tests were then conducted using hydrogen at temperatures in the range from 678 to 816 K with a transmembrane pressure difference of 1-20 bars, which showed that the membrane had a hydrogen permeation flux of 1.06 mol m^{-2} s^{-1} at a temperature of 816 K and a pressure difference of 20 bars. EDX analysis was carried out after hydrogen permeation test at 816 K and showed that there was no intermetallic diffusion between the Pd-Cu layer and PNS because the alumina layer inhibited it effectively.

Key words: Hydrogen, Separation, Pd-based, High-pressure Permeation

INTRODUCTION

Coal gasification is a rapidly emerging technology with potential applications in combined-cycle power generation and the production of liquid fuels, chemicals and hydrogen. The production of hydrogen for transport and distributed power applications requires extensive post-gasification processing, including cleaning, shift conversion and gas separation to produce high purity hydrogen. However, the combination of a hydrogen-selective membrane with a water-gas shift catalyst in a single catalytic membrane reactor would allow a high degree of CO conversion, despite the low equilibrium constant of the reaction at high temperature, since the continuous removal of hydrogen in the reactor provides a favorable equilibrium shift based on the equilibrium of reaction (1).

$$CO+H_2O \leftrightarrow CO_2+H_2 \tag{1}$$

Three different types of membranes, based on the hydrogen transport mechanism, have been investigated recently: molecular, atomic, and ionic (proton) transport. Among these, atomic transport membranes, the so-called dense metallic membranes, have a very long history and have already been commercialized. Among the several kinds of dense metallic membranes, Pd-based membranes are believed to be commercialized and offer potential advantages for hydrogen separation at elevated temperature and pressure differences [1].

Composite structures consisting of an ultra-thin membrane film and porous substrate can successfully reduce the material costs and provide high hydrogen permeation rates. The materials which have been employed commercially for porous substrates include ceramics, glass and metals such as stainless steel (PSS), Inconel, nickel [1] and Hastelloy [2]. For practical applications, porous metals have the advantage of facilitating scale-up to commercial units. However, atomic interdiffusion of metals between the thin Pd/Pd alloy layer and the metal components occurs during high-temperature processing. To inhibit atomic interdiffusion, a ceramic layer must be introduced as a diffusion barrier. The common methods of forming an interdiffusion barrier layer include coating a thin ceramic layer such as ZrO_2, TiO_2, Al_2O_3 and SiO_2 [2]. In the case of hydrogen derived from coal technologies, hydrogen separation membranes are expected to operate with a hydrogen partial pressure of at least 50 psi on the permeate side and ΔP values in the range of 100-300 psi (6-20 bars) are to be expected [3].

This study was undertaken to optimize the modification of a porous nickel support (PNS) with alumina sol to avoid defect generation when making Pd-Cu alloy composite membranes by means of magnetron sputtering, followed by Cu-reflow, and to construct a membrane module for high pressure operation in order to apply Pd-based membranes to coal gasification. The PNSs were fabricated by means of the method developed by the Korea Institute of Energy Research (KIER) involving nickel powder pressing and sintering [4-6]. The PNSs were modified with an alumina sol coating to inhibit interdiffusion, as well as decrease the surface roughness and pore size. A gold coated stainless steel O-ring was employed in the membrane module for operation at high pressure (~21 bars). Hydrogen permeation and helium leak tests were employed to test the performance of the Pd-Cu alloy membrane and membrane module.

EXPERIMENTAL

1. Membrane Preparation

The preparation of the Pd-Cu alloy composite membrane consisted of the modification of PNS and sputtering of Pd and Cu, followed by Cu-reflow at 700 °C under vacuum (~10^{-3} bar). The entire membrane preparation process is shown in Fig. 1. PNSs developed

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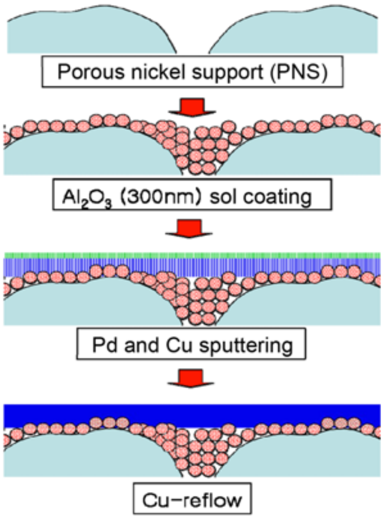

Fig. 1. Schematic of preparation of Pd-Cu alloy composite membrane.

by KIER were used as the substrates for the Pd-Cu alloy composite membranes [4-6]. The difference between the present study and previous studies is that the PNSs in this study were not modified by polishing but by alumina sol coating. This alumina sol coating method can provide the PNS with the thermal stability required to inhibit the intermetallic diffusion between the Pd-Cu alloy layer and nickel substrate at high temperature (>450 °C) [2]. Aluminum oxide sol was prepared using precursors with a mean particle size of 300 nm. To prepare the aluminum oxide sol, 0.05 g of boehmite powder (Sasol) and 0.5 g of aluminum oxide powder (Aldrich) were added to 20 mL of deionized water and then dispersed by ultrasonic agitation for 10 min to prepare the aluminum oxide sol. The PNS was coated with the aluminum oxide sol by means of a deep coating method. After drying at ambient temperature, it was calcined at 700 °C for 2 hours in a vacuum furnace (~10^{-3} bar).

A Pd-Cu alloy membrane was prepared by sputtering Pd and Cu on the PNS followed by the Cu-reflow method. The detailed fabrication methods are described in previous papers [7,8]. After Pd-Cu deposition by sputtering, Cu-reflow and Pd-Cu alloy formation was performed at 973 K for 2 hours. During Cu-reflow, the muffle furnace was evacuated to ~10^{-3} bar by supplying a 5%H_2/Ar mixture gas. The temperature was increased to 973 K at a rate of 7 K/min and the mixture gas was continuously introduced during the Cu-reflow. The thickness of the Pd-Cu alloy film was found to be 7 μm by SEM analysis (Fig. 2).

2. Permeation Measurements

Permeation testes were conducted with pure hydrogen and nitrogen at temperatures in the range of 678 to 816 K and at feed side pressures in the range of 200 to 2,100 kPa (2-21 bars). The permeate side was at ambient pressure. The permeation apparatus consists of a membrane module, furnace, temperature controller, pressure gauge/controller and mass flow controller. The membrane module designed to be operated at high pressures consisted of two stainless steel frames and a stainless steel O-ring made with ID 3 mm tube. On the O-ring, two small holes were formed to withstand the high pressure operation. Gases were introduced by a mass flow controller (MCF, Brooks 5850 E series), and the feed side pressure was regulated by a pressure controller (Alicat PC series). The temperature was increased to 623 K at a rate of 3 K/min while introducing helium on both the feed and permeate sides of the membrane in order to prevent the membrane film from being damaged by the phase change [9,10] Once the temperature reached 623 K, hydrogen, instead of He, was introduced on the feed side. The hydrogen permeation flux was measured with a sob-bubble flow meter.

RESULTS AND DISCUSSION

1. Membrane Characterization

The largest pore size is very important, because it can determine the minimum thickness required to achieve a pinhole-free Pd-based layer. The fresh PNS has some large pores (Fig. 2(a)). Its largest pore size is greater than 5 μm. Uemiya reported that the thickness of a palladium layer strongly depended on the quality of the support, such as its pore size distribution and the number of defects on the surface [11]. He suggested a reasonable relation between the thickness of the Pd layer and pore size, which was a thickness of 13 μm vs. a pore size of 0.3 μm, 4.5 μm vs. 0.2 μm, 2.2 μm vs. 0.1 μm and 0.8 μm vs. 5 nm. Mardilovich et al. showed that the minimum thickness of palladium required to achieve a dense layer by electroless plating was approximately three-times the diameter of the largest pores in the support [12]. From their results, it can be inferred that membrane thickness larger than 15-200 μm would be

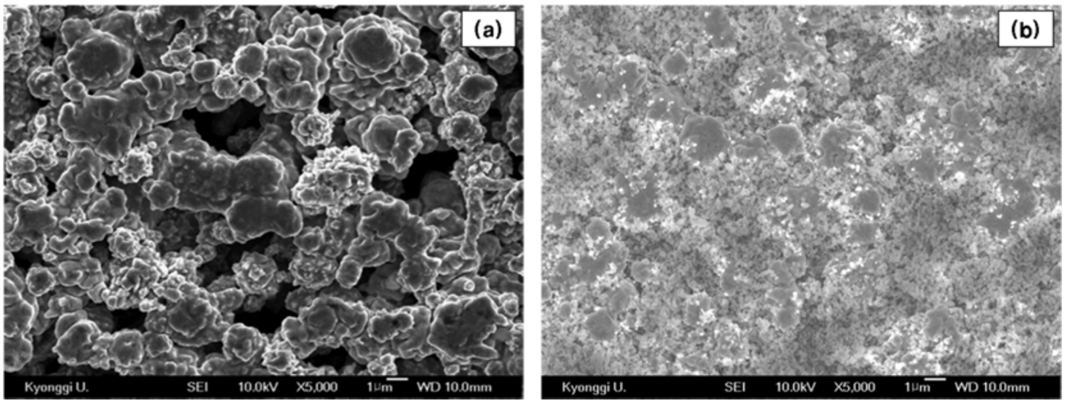

Fig. 2. Surface SEM images of (a) fresh PNS and (b) alumina-modified one.

required to have a pinhole-free Pd-based layer on the fresh PNS. Our several trials to deposit Pd-based layer less than 10 μm turned out to be impossible. So we applied the polishing process to achieve a thin Pd-based layer on the PNS in previous study [4]. However, the Pd-Cu-Ni ternary alloyed membrane deposited on the polished PNS could not withstand higher temperatures (>450 °C) because of the interdiffusion between the Pd-based layer and PNS.

Ryi et al. [2,13] and Li et al. [14] modified porous Hastelloy and stainless steel substrates with two different sized aluminum oxide sols (2.5 μm, 0.3 μm). They could not form a continuous aluminum oxide layer on the surface of the fresh disc when using the 0.3 μm sized aluminum oxide sol, because of the large sized pores of the disc. They achieved pinhole-free substrates after applying an aluminum oxide coating with the 2.5 μm aluminum oxide sol.

Filling the large pores with ceramic particles of the proper size is the easiest way to reduce the pore size of the support. Aluminum oxide sol was prepared with particles, 0.3 μm. To ensure that the pores of the PNS were filled with the aluminum oxide particles, a vacuum was applied to the other side of the disc. The alumina-modified PNS is depicted in Fig. 2(b). The surface pores and roughness of the alumina-modified PNS were drastically reduced, making it possible to deposit a thinner Pd-based layer. Also, the surface of the disc was entirely covered by the aluminum oxide layer, thereby preventing the interdiffusion between the PNS and Pd-based layer.

Pd and Cu were deposited on porous nickel supports (PNS) by the magnetron sputtering method. Subsequently, Cu-reflow and Pd-Cu alloy formation was performed at 700 °C for two hours. The surface images of the Pd-Cu /PNS after Cu-reflow are shown in Fig. 3. To verify the effect of alumina modification, Pd-based membrane was fabricated on the fresh PNS with the same procedure. It is obvious that there are some large pinholes on the surface of the Pd-Cu membrane deposited on a fresh PNS. However, there are no indications of pinholes or cracks on the alumina-modified PNS. Cross-sectional SEM image in Fig. 4 indicates that Pd-Cu layer was ~7 μm. EDX analysis of fresh membrane showed that the compositions of Pd and Cu were 93 and 7 wt% respectively. EDX analysis was carried out after hydrogen permeation test at 816 K and showed that there was no intermetallic diffusion between Pd-Cu layer and PNS because alumina layer inhibited it effectively.

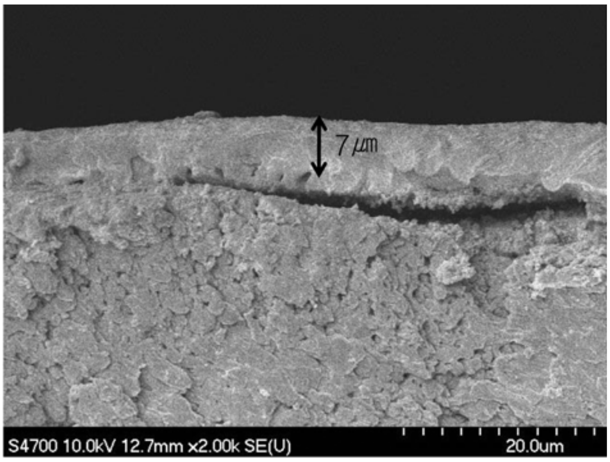

Fig. 4. Cross-sectional SEM images of Pd-Cu alloy membrane deposited on alumina-modified PNS.

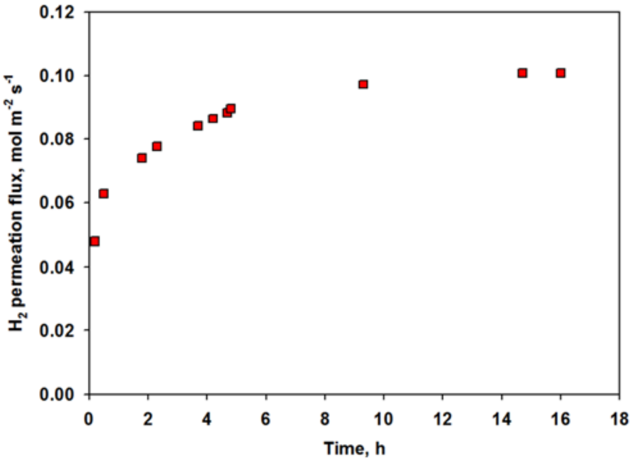

Fig. 5. Hydrogen permeation flux as a function of time at a temperature of 816 K and transmembrane pressure difference of 100 kPa.

2. Hydrogen Permeation Behavior

The hydrogen permeation fluxes were measured continuously over a period of 16 hours at a temperature of 816 K and at a pressure difference of 100 kPa. A helium leak test performed at room temperature and a pressure difference of 100 kPa confirmed that the

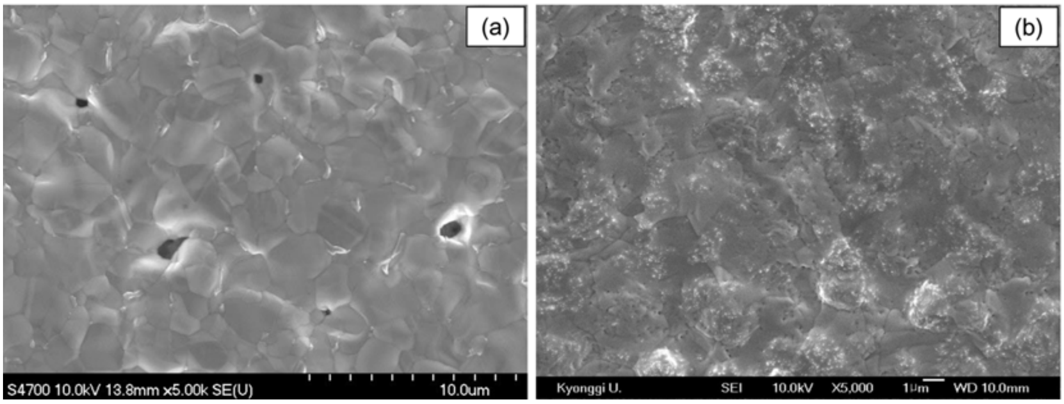

Fig. 3. Surface SEM images of Pd-Cu alloy membrane deposited on fresh PNS (a) and alumina-modified PNS (b).

membrane was free of defects. The hydrogen fluxes obtained for the composite membrane are displayed in Fig. 5. The hydrogen permeation flux increased with time and became constant after 16 hours. The helium leak test at 816 K conducted after the hydrogen permeation test confirmed that this enhancement of the hydrogen permeation with time was not because of the generation of defects. Tucho et al. absorbed the enhancement of hydrogen permeation for thin Pd-Ag membranes after heat treatment with inert gas [15]. They concluded that the enhancement of the permeation may be a result of the beneficial conditions for atomic diffusion, leading to other microstructural changes in addition to surface segregation. We can conclude that the increase in the hydrogen permeation flux is due to the structural changes which provide more beneficial conditions for atomic diffusion.

After the membrane stabilization, gas permeation tests were conducted with pure hydrogen at temperatures in the range of 678 to 816 K and at pressure differences across the membrane of 100 to 2,000 kPa. The hydrogen fluxes for the composite membranes are plotted in Fig. 6. As expected, the hydrogen flux increased with increasing temperature and feed side pressure. The hydrogen flux increased to 1.06 mol m^{-2} s^{-1} at a temperature of 816 K and a pressure difference of 2,000 kPa.

First, the conventional method was done by Pd_{60}-Cu_{40} alloy by sputtering. There were so many defects because the sputtered metal layer increased with column shape. However, in this study, palladium and copper was continuously deposited. Cupper reflow was applied to filling of trench giga patterns in the copper metallization of semiconductors [16,17]. The procedure of copper deposition by sputtering is in a previous study [8]. As common behavior, copper has a lower melting temperature than palladium. As temperature increases, copper, deposited on top of the membrane, reflows into the small pores between the Pd columns, forming a thin Pd-Cu alloy membrane. The hydrogen permeability of our Pd_{93}-Cu_7 membrane was <1/3 that of the Pd membrane fabricated by electroless plating as shown in Table 1. The hydrogen permeability initially decreased with increasing Cu composition with a sharp maximum centered at 40 wt% Cu with a 40% increase in permeability over pure Pd [18]. Small deviations from the 40 wt% of Cu resulted in a large loss of permeability, indicating that the Cu-reflow is a good method to get highly selective membranes but at the expense of a huge loss of permeability. The effect of copper composition on Cu-reflow behavior and hydrogen permeability should be further studied.

Hydrogen diffuses through the palladium-based alloy membrane via a solution and diffusion mechanism. This phenomenon is frequently described by

$$J_F=\frac{Q_F}{l}(P_{up}^n-P_{down}^n) \tag{1}$$

where J_F and Q_F denote the hydrogen flux (mol m^{-2} s^{-1}) and permeability (mol m m^{-2} s^{-1} Pa^{-n}) for the palladium alloy membrane (film), respectively, and l is the thickness (m) of the palladium-based alloy layer. P_{up} and P_{down} are the pressures on the feed and permeate sides, respectively. If the diffusion of hydrogen atoms through the dense metal layer is rate-limiting, the hydrogen flux depends on n=0.5, as in the well-known Sieverts' law. In our work, Q_F and the *n*-value were calculated from the overall hydrogen flux, rather than the hydrogen flux through the palladium layer, because the membranes were composite, consisting of a dense film and a porous support, separated by aluminum oxide. Fig. 7 shows the dependency of the hydrogen flux on the feed side pressure for the prepared composite membrane at various temperatures. As shown, a pressure exponent of 0.56 gave good fits, indicating that some of the surface reaction is involved in the hydrogen permeation behavior.

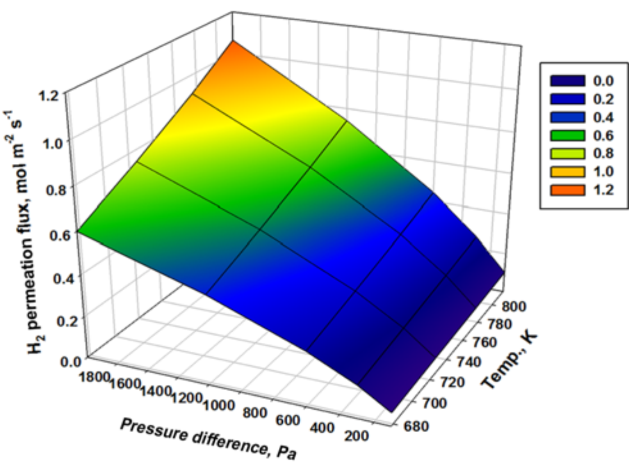

Fig. 6. Hydrogen permeation flux as functions of the temperature and pressure difference across the membrane.

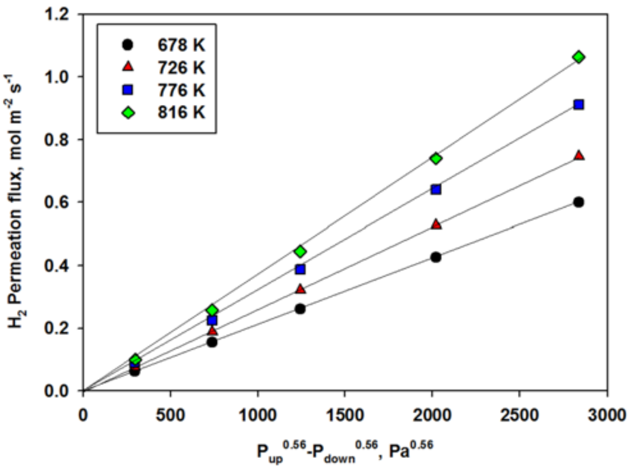

Fig. 7. Hydrogen permeation flux as a function of the difference between the pressure exponent of 0.56 at various temperatures.

Table 1. Comparison of hydrogen permeation performance for Pd-based composite membrane

Membrane	Thick. [μm]	Temp. [K]	ΔP [kPa]	H_2 flux [mol m^{-2} s^{-1}]	H_2 permeability [mol m^{-1} s^{-1} Pa$^{-0.5}$]	Ref.
Pd/Al_2O_3/PHA	7.5	773	100	2.8×10^{-1}	1.6×10^{-8}	[2]
Pd-Cu_7/PNS	7	773	100	9.0×10^{-2}	4.8×10^{-9}	This study

Hydrogen transport through a dense Pd-based alloy membrane is an activated process. The relationship between the hydrogen permeability and temperature can be described by the Arrhenius law:

$$Q = Q_0 \exp\left(\frac{-E_a}{RT}\right) \tag{2}$$

or

$$\frac{Q}{l} = \frac{Q_0}{l} \exp\left(\frac{-E_a}{RT}\right) \tag{3}$$

where Q is the hydrogen permeability (mol m m^{-2} s^{-1} pa^{-n}), l is the membrane thickness (m), E_a is the activation energy (kJ mol^{-1}), R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature in Kelvin. The activation energies for Pd-based membranes have been reported to be in the range from 5.4 to 38 kJ mol^{-1} [1,4]. There are few data showing the effects of different factors on the activation energy. The fabrication method appears to influence the degree of permeation in ultrathin Pd-based membranes, probably due to the differences in the microstructure or impurities on the surface, in the bulk, or at the grain boundaries [19]. The activation energy of the membranes evaluated from the Arrhenius plot of the overall hydrogen permeability against the reciprocal temperature in Fig. 8 was 19 kJ mol^{-1} for a pressure difference of 2,000 kPa, which is similar to the values reported for other Pd-based membranes at lower pressures [2,19-20].

CONCLUSIONS

The membrane analysis and hydrogen permeation tests at high pressure differences for the Pd-Cu composite membranes deposited on the aluminum-oxide-modified porous nickel support with sputtering followed by Cu-reflow revealed that:

- A defect-free Pd-Cu alloy membrane could be made by sputtering followed by Cu-reflow on the aluminum-oxide-modified porous nickel support.
- High pressure (~20 bars) operation could be achieved with a semi O-ring installed flange-type stainless steel module.
- The hydrogen flux increased up to 1.1 mol m^{-2} s^{-1} at a temperature of 816 K and a pressure difference of 2,000 kPa.
- The membrane has an n-value of 0.56, indicating that there is some surface reaction involved in the hydrogen permeation behavior.
- We hope that the membrane and its module can be used for processes requiring a high pressure, such as carbon capture and sequestration (CCS) and membrane reactors.

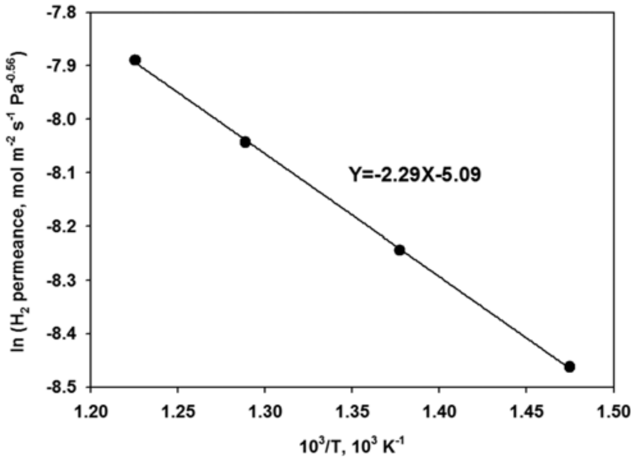

Fig. 8. Arrhenius plot of overall hydrogen permeability as a function of reciprocal temperature.

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