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A Palladium/Porous-Glass Composite Membrane for Hydrogen Separation

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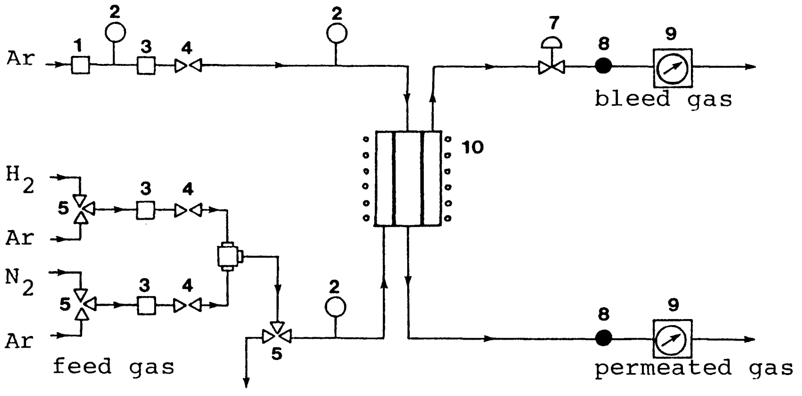
Palladium was deposited on a porous-glass tube using a technique of electroless-plating. This composite membrane exhibited a remarkable permeability to hydrogen. Moreover, hydrogen was selectively separated from H_2-N_2 and H_2-CO gas mixtures through the composite membrane.

Considerable efforts have been exerted to develop a new type of membrane for hydrogen separation. Membranes so far applied are classified into three groups; ceramic, polymer, and metal membranes. Ceramic membranes have high thermal stability and mechanical strength, but hydrogen selectivity is not very high.[1,2] In contrast, polymer membranes exhibit opposite properties; high selectivity and inferior thermal stability. Palladium membrane is extremely selective for hydrogen separation, while it is very expensive and of small mechanical strength compared with ceramic membranes.[3,4] In order to overcome these disadvantages, we have developed a composite membrane consisting of palladium and a porous-glass tube. This report deals with the characteristics of the composite membrane for hydrogen separation.

Porous-glass tubes (o.d. 10 mm, thickness ca. 0.8 mm) with an average pore size of 310 nm were supplied by Ise Chemical Industries Co. The porous-glass tube was exoleated and cleaned by use of trichloroethylene and ethanol prior to surface-activation. Sensitization and activation treatments leading to the formation of palladium nuclei were alternately performed using aqueous solutions of stannous chloride and palladium chloride, respectively. The outer surface of the tube was electroless-plated with palladium using a solution in Table 1.[5] The solution was renewed every one hour to keep the plating rate constant. The tube thus plated was washed with decationized water and ethanol, and then dried in vacuum at room temperature.

Table 1. Electroless-plating solution

$[Pd(NH_3)_4]Cl_2$	5.4 g dm^{-3}
2Na EDTA	67.2 g dm^{-3}
NH_4OH	350.0 g dm^{-3}
H_2NNH_2	4.6 mm^3 dm^{-3}



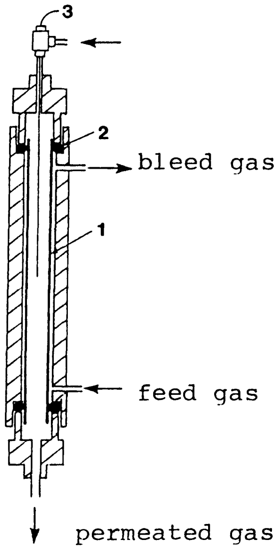


Fig. 1. Schematic diagram of the experimental apparatus.
1, pressure regulator; 2, pressure gauge; 3, mass-flow controller; 4, stop valve; 5, 3-way valve; 6, gas mixer; 7, back pressure regulator; 8, sample port; 9, wet gas meter; 10, separator.

Fig. 2. Detailed structure of hydrogen separator.
1, membrane; 2, O-ring seal; 3, thermocouple.

After plating for 17 h, the surface was thoroughly covered by palladium, the thickness of which was determined to be 13μm from the plated amount and density of palladium. Figures 1 and 2 show the schematic diagram of the experimental apparatus and the detailed structure of hydrogen separator, respectively. The membrane was sealed with O-rings at the top and bottom, and the effective length of the region for hydrogen separation was 24.0 cm. The temperature was measured at the center of the membrane. The membrane was heated to a desired temperature in a stream of argon. Rates of hydrogen permeation were measured by introducing a pure gas into the outer tube at a temperature in the range 673 - 773 K. In the measurements, argon was not introduced into the inner tube. The volumetric flow rate of permeated hydrogen was measured using a wet gas meter. The hydrogen permeability was also estimated from the experiments of separation of a H_2-N_2 or a H_2-CO gas mixture (the mixing molar ratio of 1) at 673 K. The mixtures were fed in a rate of 400 cm^3 min^{-1}. Permeated and bleed gases were analyzed by means of a TCD gas chromatograph.

Figure 3 shows an Arrhenius relation between the rate of hydrogen permeation and temperature. The activation energy of the composite membrane for hydrogen permeation was determined to be 10.7 kJ mol^{-1}. This value is in agreement with that for Pd-metal membrane reported by Hurlbert and Konecny.$^{6)}$

The rate of hydrogen permeation linearly increased with increasing temperature. Under these conditions nitrogen was not permeated at all. The observed rates of hydrogen permeation at 673 and 773 K were 19.8 and 25.4 cm^3

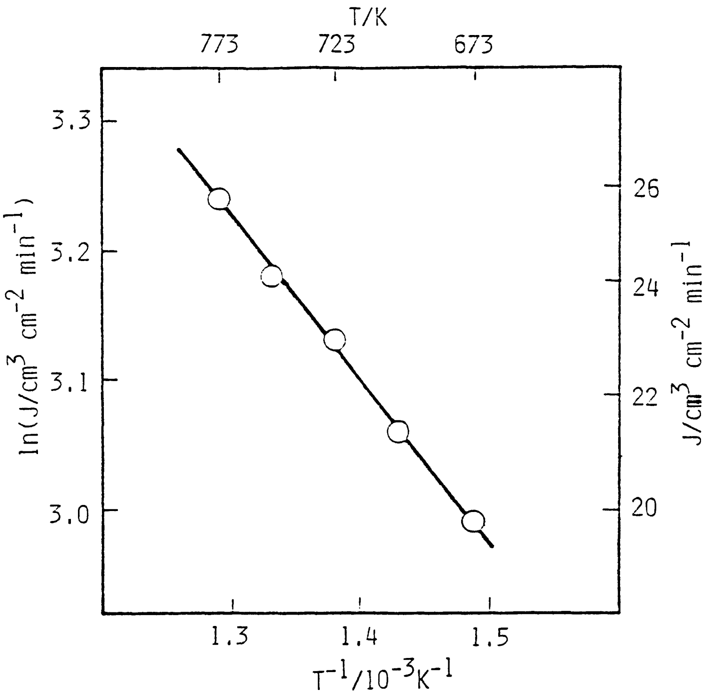


Fig. 3. Arrhenius relation between the rate of hydrogen permeation (J) and temperature under the pressure difference of 2 kg cm^{-2}.

cm^{-2} min^{-1} under the pressure difference of 2 kg cm^{-2}, respectively. The reported rate[2)] of hydrogen permeation with Pd-metal membrane was 2.3 cm^3 cm^{-2} min^{-1} at 773 K and under the pressure difference of 3 kg cm^{-2}. Thus, the composite membrane is at least 10 times more efficient for hydrogen permeation than the Pd-metal membrane. When compared the coefficient of hydrogen permeation, there was no difference between the composite and the Pd-metal membranes. Such a high rate should be a result of the decrease in the thickness of membrane, since the rate of hydrogen permeation is in inverse proportion to the thickness of membrane. As the reduction of the thickness of Pd-metal membrane is inevitably accompanied by the drawback of the mechanical strength, Pd-metal membrane having a thickness of about 150 µm is generally used. In the case of the composite membrane, the thickness of palladium film could be reduced to 13 µm with the mechanical strength being maintained. It is obvious that the composite membrane has a distinct advantage over Pd-metal membrane.

Figure 4 shows the results on hydrogen separation from a H_2-N_2 gas mixture at 673 K. The variation in % recovery of hydrogen is expressed as a function of pressure difference between the outside and the inside of testing tube. No detectable amount of N_2 was observed in the permeated gas, irrespectively of the pressure difference. A simple calculation shows that hydrogen was permeated under these conditions to give an equal partial pressure of hydrogen inside and outside of the membranes. The same results were obtained with a H_2-CO gas mixture.

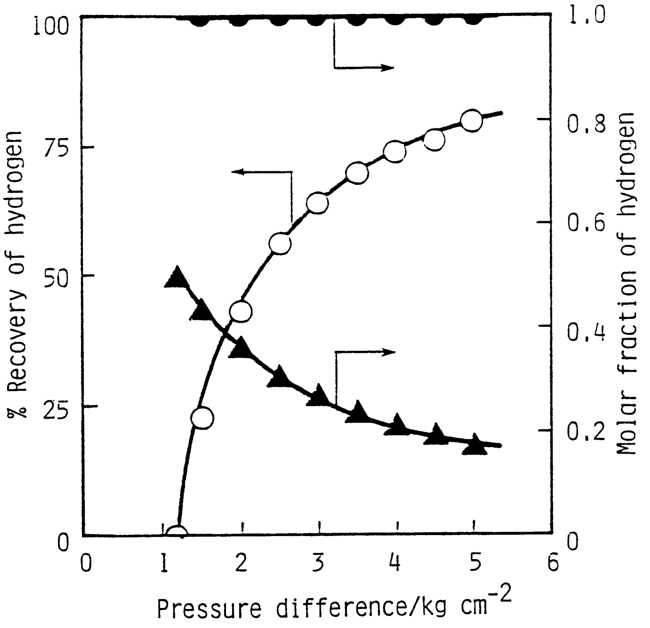


Fig. 4. % Recovery of hydrogen as a function of pressure difference at 673 K. Feeding rate, 400 cm^3 (STP) min^{-1}. H_2/N_2 molar ratio, 1. ●, permeated; ▲, bleed gas.

When the membrane was exposed to hydrogen below 573 K, however, the high selectivity of hydrogen separation was destroyed as a result of the formation of pinholes. It is known that palladium hydride is transformed from α-phase to β-phase with the expanded lattice by cooling below 573 K under hydrogen atmosphere.$^{7)}$ The formation of pinholes is attributed to the hydrogen embrittlement which accompanies the α- → β- phase transformation.

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