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Hiroshi YOSHIDA, Satoshi KONISHI
Hiroji KATSUTA and Yuji NARUSE

日本原子力研究所
Japan Atomic Energy Research Institute

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Hiroji KATSUTA+and Yuji NARUSE

Division of Thermonuclear Fusion Research, Tokai Research Establishment, JAERI

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Palladium alloy membrane method is considered to be a useful technique for fusion reactor fuel purification process. To study the feasibility of this method, the effects of impurities on permeation characteristics of palladium alloy membrane were examined. Experiments were carried out at practical conditions: pressure; 120-1200kPa, temperature; about 700K.

No poisoning effect on hydrogen permeability of commercial Pd-Ag(Au.Ru) alloy was observed for impurities such as NH_3, CH_4, CO, CO_2, O_2 and N_2, which were mixed with hyper-pure H_2 at low concentration level (10-10000ppm).

Deterioration occured by contamination with oil vapor. However, regeneration of the membrane was easily performed by air baking followed by hydrogen reduction. Chemical reactions in the permeation cell were also examined.

Keywords; Fusion Reactor, Fuel Circulation System, Tritium, Hydrogen Isotopes, Impurities, Purification Process, Palladium Alloy Membrane, Permeability, Poisoning, Regeneration Treatments

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+ Division of Nuclear Fuel Research, Tokai Research Establishment, JAERI

比較的高い圧力，温度の下におけるパラジウム合金膜の水素透過特性に及ぼす不純物の影響

日本原子力研究所東海研究所核融合研究部
吉田　浩・小西　哲之・勝田　博司[+]・成瀬　雄二

（1982年1月30日受理）

本研究は，パラジウム合金膜法を核融合炉の燃料精製工程に適用する場合に問題となる不純物の影響について，種々の操作条件の下で実験を行ったものである。不純物としては，プラズマ排ガス中に含まれると予想されているNH_3，CH_4，CO，CO_2，O_2およびN_2に着目した。操作温度及び圧力は，実機の設計データを得る目的から，それぞれ700K，120～1200kPaとした。水素透過膜としては，Pd－Ag－Au－Ru系の合金膜を用いた。

この実験により，上記の不純物が多元系合金膜の透過特性に悪影響を及ぼさないことが実証された。また，油蒸気により汚染された合金膜の透過特性及び活性化処理による回復挙動が明らかにされた。パラジウムの触媒効果に着目して，透過器の内部で起こる化学反応及びその透過特性への影響についても考察した。

[+] 燃料工学部

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1. Introduction

Many species of impurities are assumed to be included in plasma exhuast gas of fusion reactor. The estimated species are $(H,D,T)_2O$, $N(H,D,T)_3$, $C(H,D,T)_4$, CO_2, CO, O_2, N_2 and inert gases such as He and Ar. These impurities must be removed from hydrogen stream to ensure safe operation of hydrogen isotope separation process with cryogenic distillation columns in the fuel circulation loop of fusion reactor.

Various methods such as multistage countercurrent freeze-out, catalytic oxidation, hot metal getter bed, cryogenic adsorption, falling liquid film separation, palladium alloy membrane method have been proposed for the purpose(1)-(4).

In the countercurrent freeze-out method,which system is composed of multistage adsorption beds with helium coolant, impurities except helium are removed in turn with the difference of their freezing points. The system will be complex because of the necessity of several regeneration and processing systems of regenerated gases to recover hydrogen $(H,D,T)_2$ from tritiated impurities.

In the catalytic oxidation method,catalytic oxidizer with cryogenic adsorption beds is used to convert O_2 to $(H,D,T)_2O$ and to remove it together with other impurities from hydrogen stream. Helium separator and regeneration system are reqiured for this purification system. Falling liquid film separator is expected to be a promising device for the separation of hydrogen and helium mixture.

In the hot metal getter bed, uranium metal is used as getter because its selective reactivity for impurities at high temperature. As seen in the table(Appendix), hydrogen can be obtained from tritiated impurities such as $(H,D,T)_2O$, $N(H,D,T)_3$ and $C(H,D,T)_4$.

Palladium alloy membrane method, which makes use of selective permeability for hydrogen, can remove every impurities from hydrogen. It has been established as a industrial technique of hyper-pure hydrogen production and has been adopted to off-gas treatment process in PWR(5),(6). Multi-component alloys and their thin membranes having high resistivity against thermal cycling and hydrogen embrittlement have been developed(5). In order to apply this method to fuel purification process in fusion reactor, effects of above impurities, thermal cycling and formation of metal hydride in hydrogen atmosphere on the membrane performance should be examined. Furthermore, separation characteristics of the diffuser should be studied to design compact system. Although many problems to be solved exist in this method, it has advantages in purity of hydrogen and in operation conditions(temperature, pressure, continuous treatment) of diffuser.

From these view ponits, authors have been studied the applicability of the palladium alloy membrane method to the fuel purification process in fusion reactor(4). This report describes the experimental results on the effects of impurities on hydrogen permeability and on regeneration characteristics of deteriorated membrane.

2. Experimentals

A conceptual flow sheet of the experimental apparatus and detail structure of permeation cell are shown in Figure 1 and Figure 2, respectively. Feed gas flowing into the permeation cell is preheated before it reaches the outer surface of the permeation tube. Feed pressure is regulated by control valve CV-1 and measured by pressure gauge PG-1(measuring range; 0-2000 kPa, precision; 0.1% of full scale). Feed flow rate is measured by mass flow meter FIR-1(measuring range; 0-300std.cm^3.H_2/min, precision; 1% of full scale). Permeated and unpermeated gas(bleed gas) leaving the cell are cooled to room temperature by cooling coil HX-1,2, and their pressures and flow rates are measured by pressure gauge PG-2(0-1000kPa, 0.1%F.S.), and mass flow meters FIR-2(0-100std.cm^3.H_2/min, 1%F.S.) and FIR-3(0-300std.cm^3.H_2/min, 1%F.S.), respectively. Control valves CV-2, 3 regulate the pressure of bleed gas. Operation temperature is measured with six thermocouples. Calibration of the mass flow meters was carried out with a standard wet-test meter.

Swage locks and brazing connections were used to joint all parts of the apparatus to keep the leak rate lower than 1 x 10^{-6}atm.cm^3.He/sec.

The permeation cell is composed of outer shell, inner shell, permeation tube and others. The end of the permeation tube is sealed, and the other end is brazed on nickel tube. Nominal content of silver in the palladium alloy is about 25%, whereas a certain amounts of gold and ruthenium are contained.

Experimental gases are hyper-pure hydrogen(purity $>$ 99.99999%), deuterium(N_2; 60ppm, O_2; 10ppm, water vapor $<$10ppm, HD; 2000ppm) and standard gas mixtures of hydrogen including such impurities as NH_3, CH_4, CO_2, CO, O_2 and N_2.

The composition of feed, bleed and permeated gas samples were determined by gas chromatographic analysis. Molecular sieve-5A column was used for measuring CH_4, O_2, N_2 and CO, and chromosorb-103 column was for NH_3.

3. Results and discussion

3.1 Basic hydrogen permeabilities

The effects of pressure and temperature on permeation flux, permeation coefficient, diffusion coefficient and isotope effect on the permeation characteristics of the membrane were measured under comparatively high pressure(120-1300kPa) and temperature(653-853K).

Figure 3 shows a typical experimental result. In the Figure, permeation fluxes for H_2 and D_2 obtained at various temperature were shown against square root pressure difference. Here, Ph and Pℓ are the driving and back pressures in the cell, respectively. Most of the data at each temperature lie on straight-lines, indicating that Sieverts' law holds in the experimental range. The slope, which is equivalent to the permeation coefficient, increases with the increase of the temperature. Arrhenius relation between the permeation coefficient and temperature was also observed. From these experimental results, following equations were obtained.

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$$Q_H = 7.31 \times 10^{-7}\exp[-\frac{1370}{RT}] \qquad (\mathrm{mol.cm/cm^2.min.kPa^{1/2}})$$

$$Q_D = 4.78 \times 10^{-7}\exp[-\frac{1470}{RT}] \qquad (\mathrm{mol.cm/cm^2.min.kPa^{1/2}})$$

where Q_H and Q_D are the permeation coefficients for H_2 and D_2, respectively. Dimension of gas constant R is cal/mol.K.

Figure 4 shows permeation coefficient ratio for H_2 and D_2. Solid line in the figure represents the following relation, which is determined by above experimental equations.

$$\frac{Q_H}{Q_D} = 1.53 \exp[\frac{100}{RT}]$$

The data by early workers are also shown to compare with the present results. The values by Tanaka$^{(13)}$ were obtained with a thin disk of palladium at very low pressure(about 2.7 kPa). The experimental conditions of the work by Ackerman$^{(14)}$ are: permeation membrane; Pd-25wt%Ag, driving pressure; 600-2200kPa, back pressure; 120-700kPa. It is noticed that whole data of Q_H/Q_D are much larger than the square root of isotopic mass ratio(= $\sqrt{2}$)$^{(15),(16)}$.

3.2 Regeneration characteristics

Deterioration by exposure to oil vapor or air and regeneration by air baking and hydrogen reduction of the membrane were examined.

Fig. 5 shows the effects of oil vapor exposure(run 1) and of air baking(run 2). The oil vapor exposure was performed for both sides of the membrane by evacuating for 10 hrs with oil pump. As the pretreatment of the surface of the membrane, the high pressure side of the cell was baked for 1 hr by dry air of 196kPa preceding run 1. In the case of run 2, the both sides were baked for 15 hrs by dry air of 195kPa. All treatments and permeation measurements were carried out at 713K. It is apparent that marked reduction of permeability occured by contamination with oil vapor, and that decontamination of it was easily performed by baking of air. Sievert's law was maintained for run 2 in spite of air baking for 15 hrs, this phenomena may be ascribed to reduction of oxide layer formed on the surface of metal during permeation measurement, or else no reaction of oxidation between metal and oxygen(8).

Fig. 6 shows the recovery of permeability through the air-baked cell during hydrogen reduction. The baking treatment was carried out for the high pressure side of the cell, and the other experimental conditions are described in the Figure. It is noticed that substantial reduction of permeability is brought about by air baking and that recovery rate is very rapid at initial stage of hydrogen reduction. The required time of the reduction treatment to obtain constant permeation coefficient is as short as about 10 min at temperature of 713K.

From these experimental results, it was concluded that regeneration of deteriorated membrane with oil vapor from vacuum pump can be easily performed by air baking followed by hydrogen reduction treatment.

3.3 Impurity effects on hydrogen permeabilities

Permeation flow rate and its pressure dependence were measured for hydrogen, in which various impurities such as O_2, NH_3, CH_4, CO, etc. are included. These chemical species are assumed to poison palladium and palladium-silver alloy membrane.(7)-(11)

Fig. 7 shows the change of the permeability of cell during operation under constant pressure and temperature. In the series of measurements from run 6 to run 11, operating temperatures and pressures were maintained constant values, respectively. Besides, the flow ratios of feed to bleed were kept at constant value of about 70. The details of the pretreatments of the cell preceding runs were also described in the figure caption. No particular change of the permeability occured for various compositions of feed gas within this operating period up to about 25 hrs. If the partial pressure of hydrogen in the high pressure side of the cell is assumed to be equal to the total pressure of feed gas, permeation coefficient obtained for runs 7 to 11 agrees well with that (2.52×10^{-7} mol.cm.cm^{-2}. min^{-1}. kPa$^{-1/2}$) for pure hydrogen(run 6). This fact indicates that above impurities have no influence on the permeability of the present membrane. In order to confirm this fact, pressure dependence of the permeability for H_2-O_2 system (run 12 and 13) and H_2-NH_3 system (run 14 and 15) were examined.

Fig. 8 shows the relationship between permeabilty and square root pressure difference ($\sqrt{Ph} - \sqrt{P\ell}$). Here, the value of Ph was assumed to be equal to the total pressure of the feed. The data for run 1 (see Fig.5) and run 16 were obtained for pure hydrogen before and after present measurements shown in Figure 8. A good linear relation, namely, Sievert's law held for the systems of H_2-O_2 and H_2-NH_3 without depending on the flow ratio of feed to bleed. Permeability for run 15 disagreed with those of other runs whereas good agreement between run 12 to 14 and run 1 or 16 was observed. It is considered that the disagreement was caused by the difference in partial pressure of hydrogen in the high pressure side of the cell. Based on a few assumptions, we can calculate the concentration profile in the high pressure side of the cell. The estimated mean partial pressures from the calculation were 99.5 and 95% of their feed pressures for run 13 and run 15, respectively. Since this phenomena are very important in designs of practical devices for fuel purification process, the detailed discussion will be reported later.

Further, the concentrations of impurities in bleed gas calculated from material balance around the permeation cell were respectively 20 and 50% for run 13 and run 15. It was assumed that oxygen was converted completely to water vapor by the reaction of $2H_2 + O_2 \rightarrow 2H_2O$, and that the dissociation reaction $2NH_3 \rightarrow 3H_2 + N_2$ of ammonia was negligibe.

3.4 Chemical reactions in permeation cell

Impurities may be highly enriched in the high pressure side of the cell under some operating conditions. Besides, the cell was assembled with tubes of palladium alloy, nickel and stainless steel. Therefore, various chemical chemical reactions forming poisonous species for palladium alloy membrane may take place in the cell. In order to investigate the possibility of the reactions (7)-(11), gas chromatographic analysis of bleed gas were carried out for various operating conditions.

Table 1 summarizes the results of analysis and experimental conditions. In the series of experiments, H_2-NH_3 and H_2-O_2-CH_4 systems were used as feed gas, and flow ratio of feed to bleed was altered under constant temperature of 707K.

From run 17 to 19, it was confirmed that the concentration of ammonia increased roughly proportional to the flow ratio of 2 to 8. The main cause for the error between the enrichment degree and the flow ratio may be analytical errors due to high condensability of ammonia. In run 20 to 23, nitrogen due to the reaction $2NH_3 \rightarrow N_2 + 3H_2$ was measured quantitatively. An obvious increasing tendency of nitrogen with decreasing of mean gas velocity in the high pressure side of the cell was seen in the series of runs. Further, the nitrogen concentration for run 17 corresponds to about o.7% decomposition of ammonia fed to the cell. This reaction is considered to be a merit in the palladium alloy membrane method from the point of recovery of tritium from ammonia $N(H,D,T)_3$ in plasma exhaust gas.

For the H_2-O_2-CH_4 system, marked decrease of oxygen concentration, no formation of carbone mono-oxide and enrichment of methane were observed in run 24 and 25. In the present gas analysis using molecular sieve 5A, we could not measure the concentration of water vapor and carbon di-oxide because of the adsorption characteristics of the column for these species. Then, it was not easiy to know entire chemical reactions took place in the cell. Taking account for the catalytic activity of palladium(14) for the reaction $2H_2 + O_2 \rightarrow 2H_2O$ together with the facts above mentioned, we can draw following interesting reasoning. Oxygen in the feed gas might be preferentially converted to water vapor, which reaction is unfavorable for tritium recovery, and oxidation of methane such as $2CH_4 + O_2 \rightarrow 2CO + 4H_2$ or $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ might not be taken place. Then, it should be necessary to examine the effect of the mixture of water vapor, methane and hydrogen on the permeability, especially for the operating conditions of high enrichment of impurities. A typical run performed under such operating condition is shown in Figure 7(run 9), it indicates that no change of the permeability occured. This fact reveals that poisoning of the membrane neither by carbon deposition reactions e.g. $CH_4 + H_2O \rightarrow CO + 3H_2$ followed by formation of metal carbide such as $xPd + CH_4 \rightarrow Pd_xC + 2H_2$ has occured in the cell at least under present experimental conditions.

4. Conclusions

In order to research the applicability of palladium alloy membrane method to fuel purification process for fusion reactor, effects of impurities on permeabilities of multi-component alloy membrane, regeneration of the membrane deteriorated by contamination with oil vapor, chemical reactions in the palladium diffuser were studied. The experimental results are summarized as follows.

(1) Marked reduction of hydrogen permeability occured by oil vapor from vacuum pump. However, regeneration of the membrane could be easily performe by air baking followed by hydrogen reduction.

(2) Constant permeation coefficient for H_2 could be obtained for H_2 gas, which includes a littled amount of such impurities as NH_3, CH_4, CO_2, CO and O_2.

(3) Sieverts' law helds for H_2-O_2 and H_2-NH_3 systems of high pressure range from 100 to 900kPa.

(4) Ammonia decomposition reaction in the H_2-NH_3 system was occured at a certain operation conditions of palladium diffuser.

(5) Poisoning of the membrane due to carbon deposition or formation of metal carbides was not occured for H_2-O_2-CH_4 system. Selective conversion of oxygen to water vapor was presumed for the system.

Through the present study, it is concluded that multi-component palladium alloy membrane(Pd-Ag-Au-Ru) is available for removal of various impurities from fuel gas in fusion reactor.

Acknowledgement

The authors wish to thank Mr. Matsuda(Division of Thermonuclear Fusion Research), and Mr. Kinoshita(Division of Thermonuclear Fusion Research) for helpful comments and discussions on the study.

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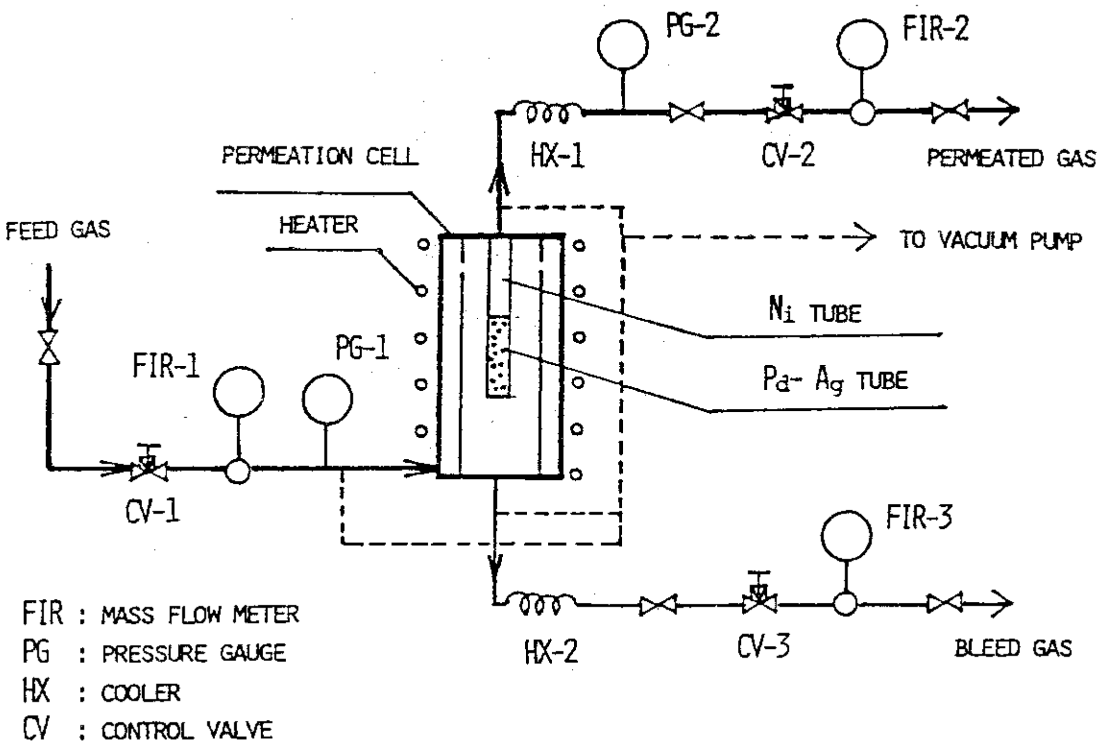


Fig.1 Conceptual flow sheet of experimental apparatus.

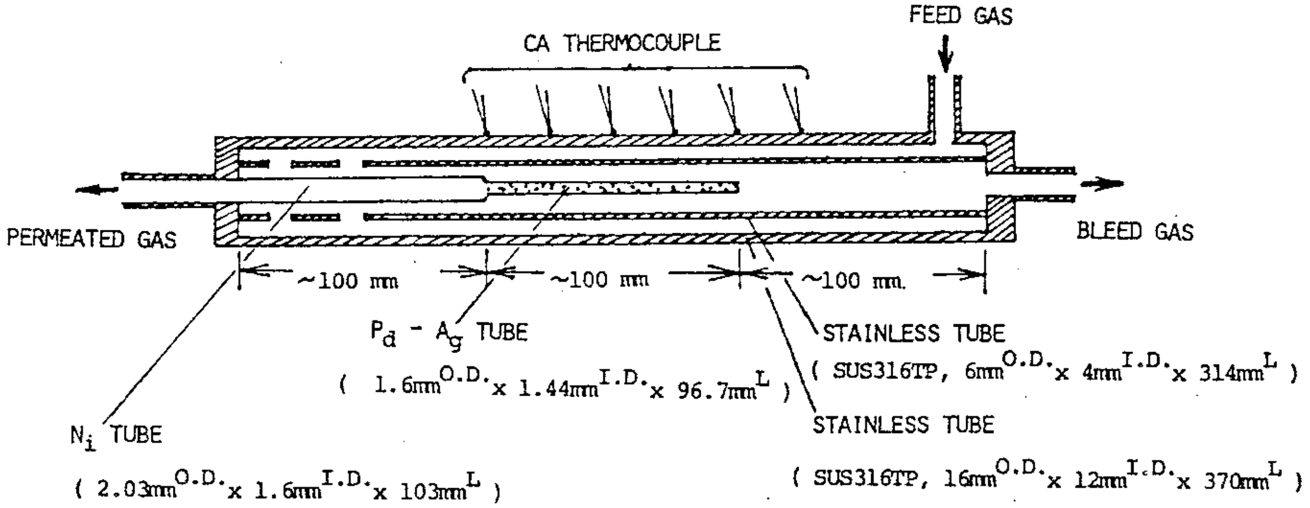


Fig.2 Details of permeation cell.

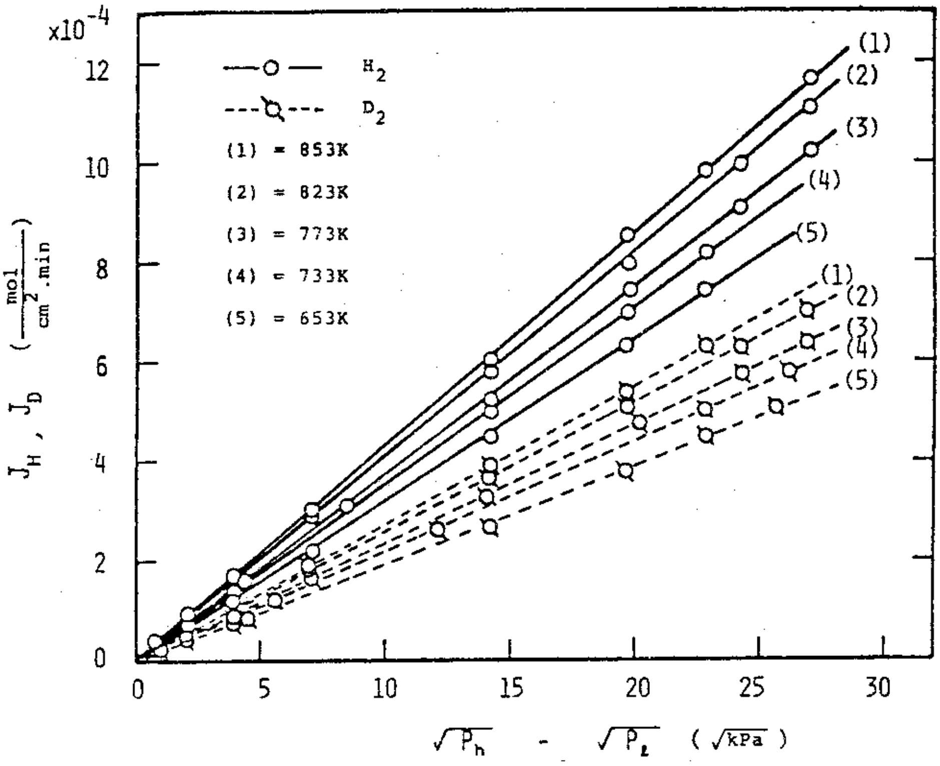


Fig.3 Pressure dependence of hydrogen permeability for activated palladium-silver alloy.

Pre-treatments of cell were made by air baking for 8hrs at 196kpa followed by hydrogen reduction for 18hrs at 196kpa. All treatments were performed at 853K. Pressure of permeated gas during runs was kept at 101. 3kpa.

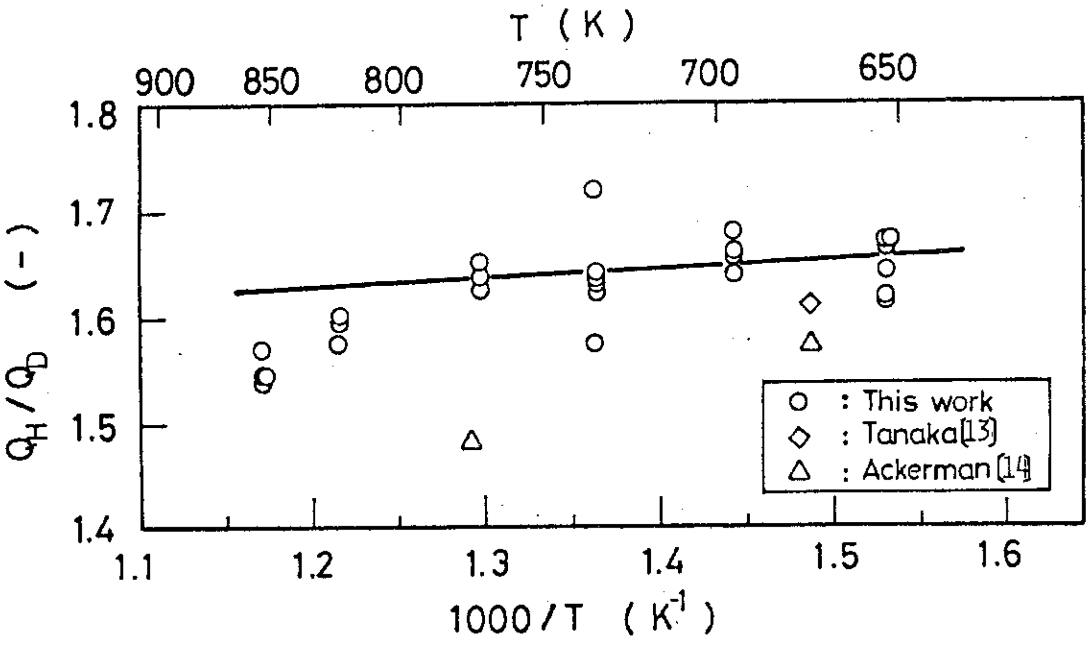


Fig.4 Temperature dependence of hydrogen permeation coefficient for activated palladium-silver alloy menbrane.

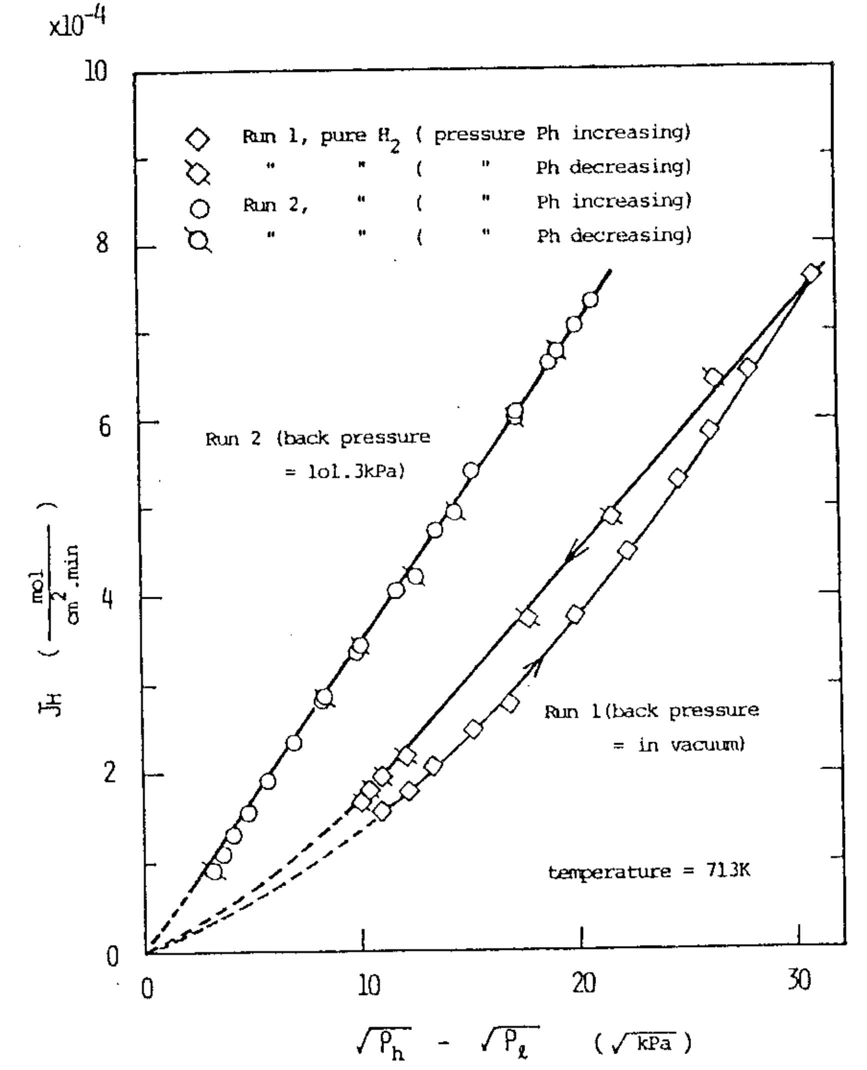
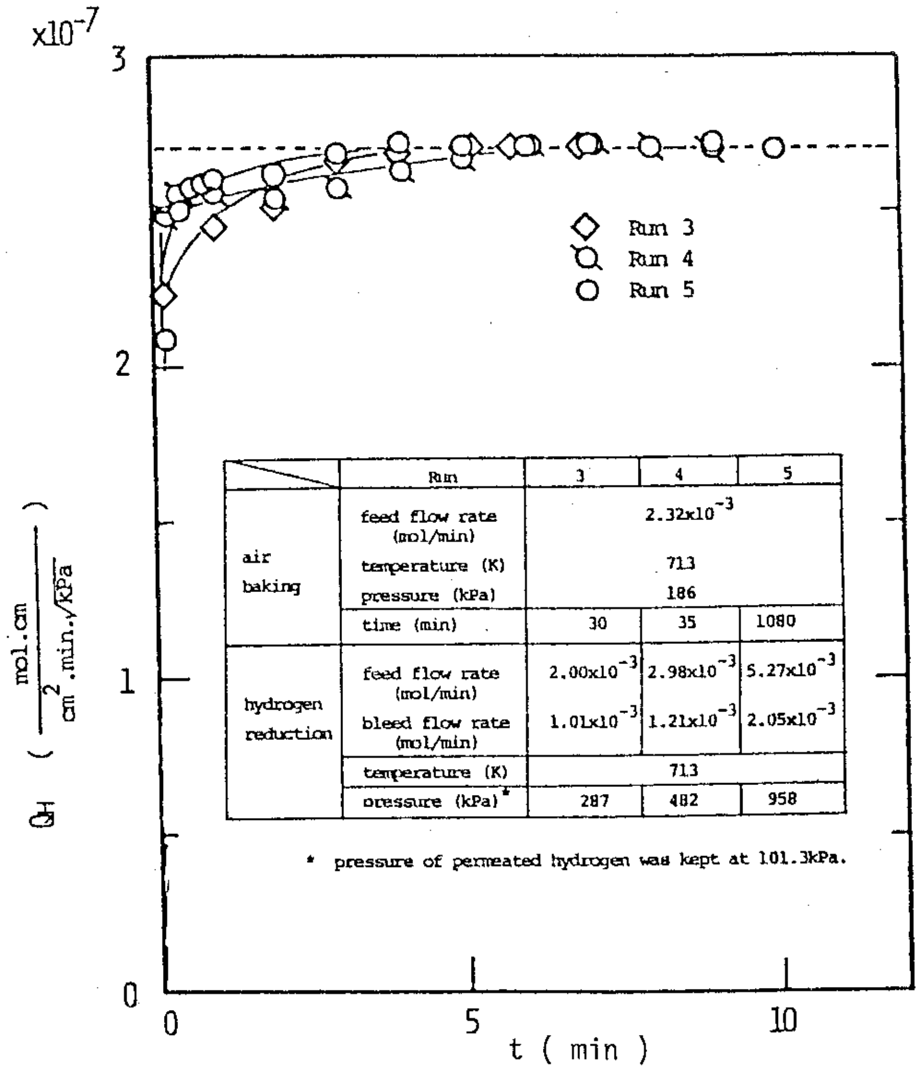


Fig. 5 Temperature dependence of hydrogen permeation coefficient ratio.



	Run	3	4	5
air baking	feed flow rate (mol/min)	2.32x10^{-3}		
	temperature (K)	713		
	pressure (kPa)	186		
	time (min)	30	35	1080
hydrogen reduction	feed flow rate (mol/min)	2.00x10^{-3}	2.98x10^{-3}	5.27x10^{-3}
	bleed flow rate (mol/min)	1.01x10^{-3}	1.21x10^{-3}	2.05x10^{-3}
	temperature (K)	713		
	pressure (kPa)*	287	482	958

* pressure of permeated hydrogen was kept at 101.3kPa.

Fig.6 Pressure dependence of hydrogen permeability for contaminated palladium-silver alloy membrane.

Pre-treatments of cell were as follows. Run 1; both sides of cell were evacuated 10 hrs by oil pump, thereafter high pressure side of cell was baked for 1 hr at 196 kPa by dry air, Run 2; both sides of cell were baked 15 hrs at 196 kPa by dry air after Run 1 was completed. All treatments were performed at 713 K.

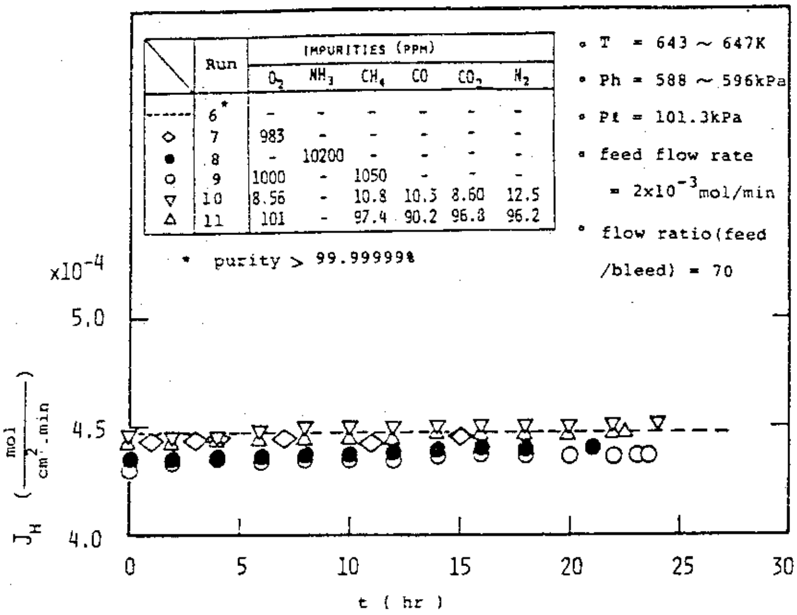


Fig.7 Recovery in permeability of air baked palladium-silver alloy membrane under hydrogen reduction treatment.

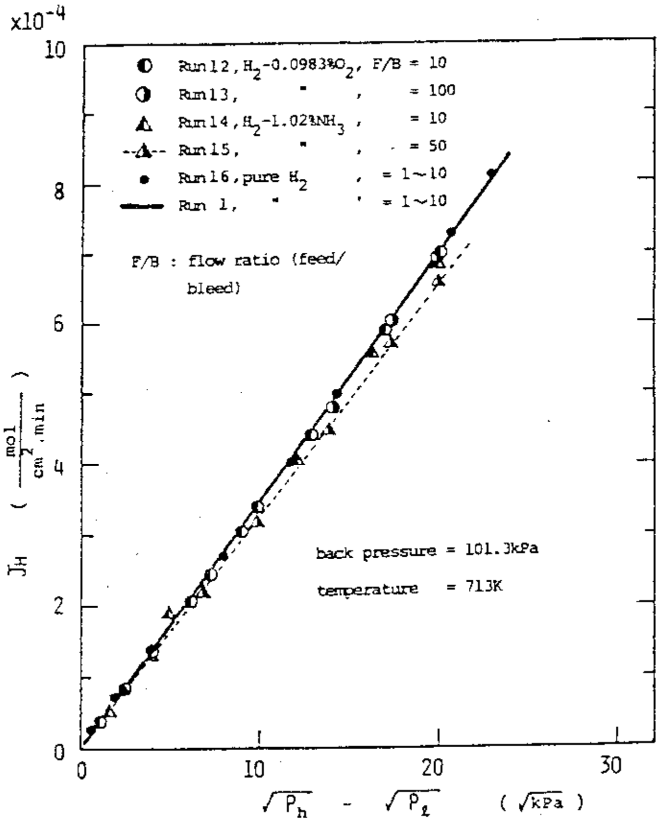


Fig.8 Effect of impurities on pressure depencence of hydrogen permeability for activated palladium-silver alloy membrane.

Pre-treatments of cell for Run 12 was made by air baking for 30 min at 713 K, and Run 13 to 16 were successively performed without pre-treatments.

Table 1 Impurity composition in bleed gas under various flow conditions of permeation cell.

Run	flow rate (mol/min)		temperature (K)	pressure** (kPa)	gas velocity (cm/sec)	impurities in feed gas (ppm)						impurities in bleed gas (ppm)					
	feed	bleed				NH_3	N_2	CH_4	O_2	CO_2	CO	NH_3	N_2	CH_4	O_2	CO_2	CO
17	2.8 $\times10^{-3}$	3.7 $\times10^{-4}$	707	356	3.8	10200	+	+	+	+	+	58100	*	*	*	*	*
18	2.2 "	9.2 "	"	309	4.4			"				23500	*	*	*	*	*
19	2.7 "	15.4 "	"	205	8.8			"				16300	*	*	*	*	*
20	3.0 "	1.0 "	"	870	1.5			"				-	1100	+	+	-	+
21	4.0 "	2.0 "	"	640	2.8			"				-	640	+	+	-	+
22	2.1 "	1.1 "	"	320	3.0			"				-	120	+	+	-	+
23	1.2 "	0.5 "	"	120	4.3			"				-	30	+	+	-	+
24	0.7$\times10^{-3}$	2.2$\times10^{-4}$	"	174	2.4	*	+	1050	1000	-	+	-	+	4940	+	-	+
25	1.5 "	9.6 "	"	178	5.9			"				-	+	2670	20	-	+

\+ lower than detection limit of TCD type gas chromatograph using hydrogen carrier gas

\- unmeasurable by TCD type gas chromatograph using molecular sieve-5A

* not detected by TCD type gas chromatograph using chromosorb-103 column

** pressure of permeated hydrogen was kept at 101.3kPa.

APPENDIX. REACTIVITY OF URANIUM METAL

Reactant	Reaction Temperature (°C)	Products
H_2	250	α-and β-UH_3
N_2	700	UN ; UN_2
O_2	150-350	UO_2 ; U_3O_8
H_2O	100	UO_2
NH_3	700	UN
CH_4	635-900	UC
CO	750	UO_2+UC
CO_2	750	UO_2+UC