HYDROGEN PLASMA DRIVEN PERMEATION THROUGH SELECTED METALS

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Hydrogen permeation through membranes of selected metals was studied with low temperature plasma generation apparatus. The permeation was found to increase by applying plus voltages to the membrane. Under the plus bias conditions, permeation of hydrogen isotopes was measured with the membranes of SS-304, Ni, Cu, Ti, Pd and Fe. The permeation enhanced by the plus bias is due to the dissociation of neutral hydrogen molecules into atoms on the membrane by incident electrons.

1. Introduction

Hydrogen permeation through metal membranes has been studied on various materials and by various methods and it has been known that the permeation is enhanced by (1) gas pressure difference between both surfaces (gas driven permeation, GDP), (2) atomization of hydrogen molecules (atom driven permeation), (3) exposure to hydrogen plasma (plasma driven permeation, PDP) and (4) hydrogen ion beam injection (ion driven permeation). Intensive studies on quantitative evaluation and analysis have been made on beam injection permeation experiments, which can simulate the effects of high energy particles of hydrogen isotopes radiated into the first wall of a fusion reactor. While PDP process can simulate the effects of the low temperature hydrogen plasma in the edge plasma, which directly contact with the first wall, PDP has been regarded as being very complicated and too difficult to be quantitatively analyzed or evaluated. This is due to the fact that a low temperature hydrogen plasma contains various kinds of particles such as H_3^+, H_2^+, H^+, H^-, H, H_2, e^-

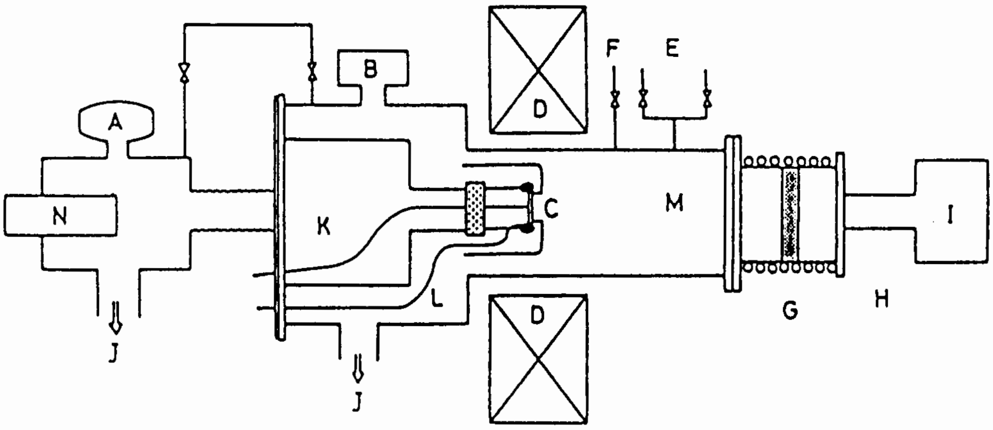
The authors of the present paper have conducted experimental work on the low temperature plasma driven permeation of hydrogen isotopes by using an ECR plasma generator and an RF plasma generator [1-3]. Characteristic measurements were made on low temperature deuterium plasmas with a mass spectrometer and a Langmuir probe[1]. Isotope effect in the PDP process has been observed and found to depend on the hydrogen gas pressure and the bias voltages applied [2]. The PDP through iron membrane was found to be enhanced by the positive bias applied to the membrane [3]. The present paper summarizes the typical findings on the hydrogen permeation made by authors for the past few years along with the recently obtained experimental results on the PDP. Analysis is made on the experimental data and discussion is extended to the effect of electrons of which rolls have been overlooked in the studies of low temperature PDP of hydrogen isotopes by many researchers.

2 . Experimental

Hydrogen (deuterium) plasma driven permeation through SS 304 membrane with thickness of 10 μm was studied by using an ECR low temperature plasma generator and compared with the pure gas driven permeation observed by using the same experimental apparatus without ignition of plasma. The experimental apparatus is shown in Fig. 1. The plasma was discharged by 2.45 GHz microwave under the magnetic field of around 1k Gauss (0.1 T) at the maximum point. The upstream discharge chamber was separated from the downstream chamber by the tested metal membrane. The plasma parameters of the generated plasma in the chamber were measured by a Langmuir probe.

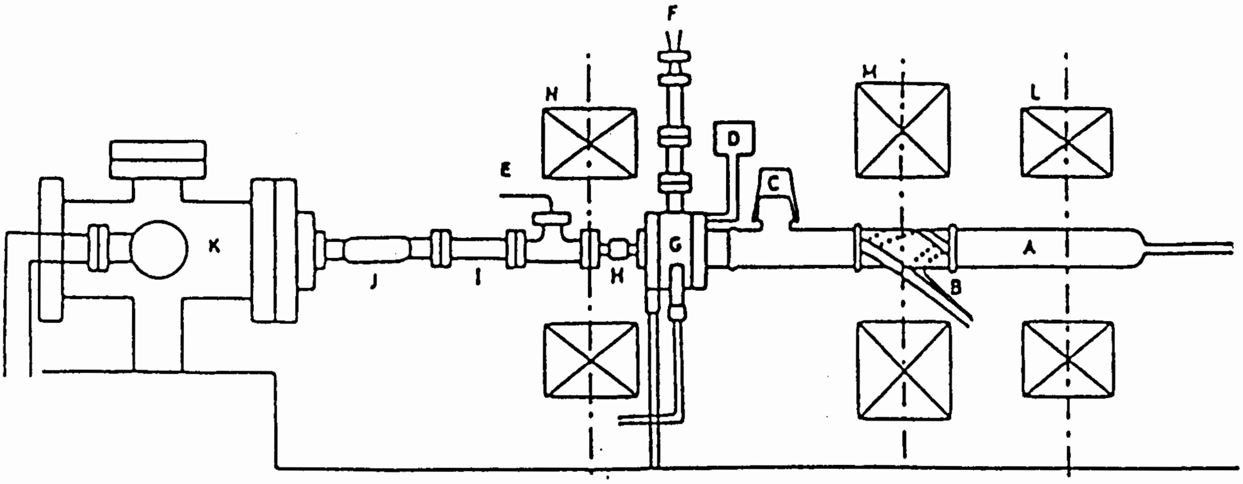
Temperature of the tested membrane was controlled in the range 100 - 400 °C (373 - 673 K) by the heater set in the sample holder in the plasma device and the temperature was measured by a thermocouple contacting on the back side of the tested membrane. The permeation rates were measured by a quadrupole mass analyzer installed in the downstream evacuation line. The pressure of the upstream plasma chamber was controlled from 0.02 Torr (2.6 Pa) to 1 Torr (1. 3 x10^2 Pa).

The RF discharge apparatus is illustrated in Fig.



A : Ionization Vacuum Gauge
B : Capacitance Manometer
C : SUS 304 Membrane
D : Magnet (1000 gauss)
E : H_2 or D_2 Gas Feed Inlet
F : T_2 Gas Feed Inlet
G : Ceramic Window
H : Micro-wave Guide
I : Micro-wave Genorator
J : Turbo Molecular Pump
K : Thermo Couple
L : Lead wire for Bias
M : Plasma Chamber
N : Quadrupole Mass Spectrometer

Fig. 1. ECR discharge PDP experimental apparatus.



A: Discharge Tube(Pyrex)
B: Helical Antenna
C: Probe Port
D: Capacitance Manometer
E: Thermocouple
F: Double Probe
G: Connecting Flange
H: Glass Tube
I: Flexible Tube
J: Ceramic Tube
K: Vacuum Chamber
L: Magnet(300gauss/25A)
M: Magnet(600gauss/25A)
N: Magnet(300gauss/25A)

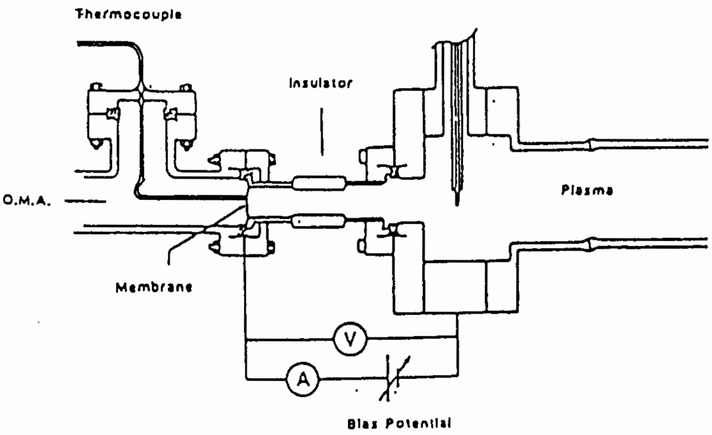


Fig. 2. RF discharge PDP experimental apparatus and a close view of the test section.
Test section

2 with a magnified view on the membrane test section. RF (18 Mhz) was loaded into the plasma discharge tube at the power of 300 W in a pulsed manner, RF duty ratio = 10 sec. On : 20 sec. Off, through a helical antenna. The maximum magnetic field was 600 Gauss at the position of the RF antenna and the magnetic field at the membrane test section was 300 Gauss. The plasma parameters were measured by a double probe

Prior to the permeation experiments, the tested membrane was exposed to the hydrogen plasma for a few hours to remove the surface oxide layer and adsorbed water molecules on the tested membrane. The temperature of the tested membrane was measured with a thermocouple attached on the back surface of the membrane. The membrane holder was electrically isolated from the plasma chamber by insulators. Bias voltages, from -390 to + 200 V, were applied to the membrane to examine the permeability at different bias voltages.

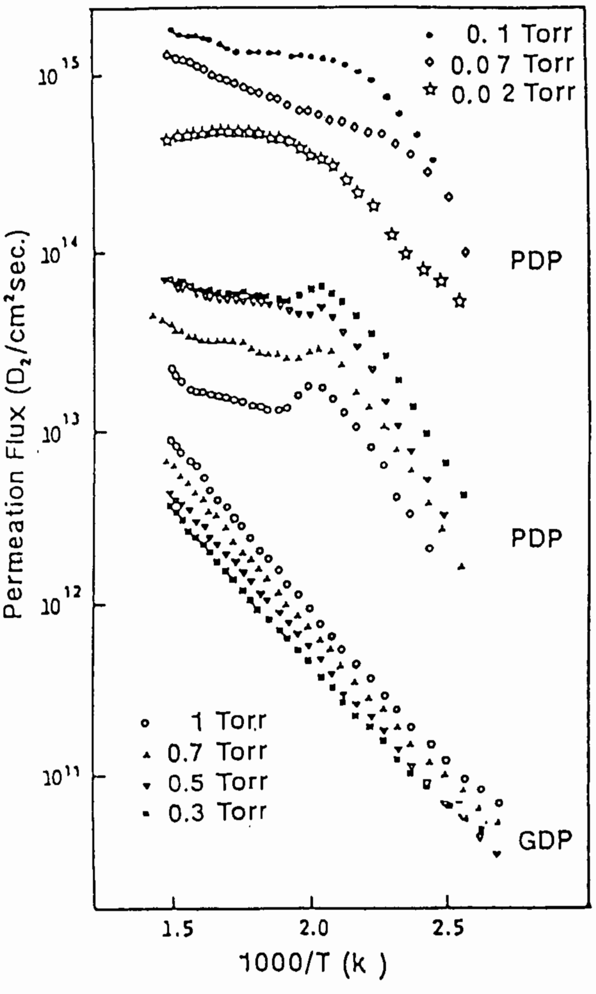


Fig. 3. Temperature and pressure dependence of PDP and GDP through SS304.

3, Results and Discussion.

The measured fluxes of PDP and GDP at the different temperatures are plotted in Fig. 3. The GDP is clearly shown to increase with increase in both deuterium gas pressure in the plasma chamber and the membrane temperature. Since the GDP flux is proportional to the root of the gas pressure, expressed by Sievert's low, the process is confirmed to be governed by the dissociation of deuterium molecules on the surface of the membrane.

The flux of PDP shows rather complex pressure dependence: the flux increases with increase in the gas pressure up to 13 Pa and decreases with increase in the gas pressure. This is due to the pressure dependence of plasma density or more specifically the pressure dependence of dissociated deuterium atom density, which is observed as the D_α emission intensity. The observed apparent activation energy of the PDP process shows temperature dependence; the observed activation energy in the temperature range above 200 °C is quite small, smaller than 8 kJ/mol, while one in the range below 200 °C is rather large, approximately 47 kJ/mol. It is estimated that the permeation mechanism is changed between these temperature regions. The detailed discussion on the mechanism will be made in a separate work.

In the present work permeation was measured on the species with mass 2, 3 and 4 , which correspond to H_2, HD and D_2, respectively. When tritium was introduced into the experimental apparatus, masses of 5 and 6, corresponding to DT and T_2, were also measured. Permeation experiments were tested under the closed mode, where the plasma chamber was initially evacuated and charged with hydrogen gas of H2, D2 or T2, thereafter the gas inlet and outlet valves of the plasma chamber were closed and the plasma was generated to measure the permeation fluxes. This operational mode was chosen rather than the flow mode of the hydrogen isotopic gases to reduce the amount of tritium required for the permeation experiments and this closed mode was applied to the permeation experiments of stable gases of H_2 and D_2 to compare the flow patterns among these three isotopic gases.

When the gas was changed from light hydrogen to deuterium in the closed mode operation, the permeation has shown a strange pattern; H_2 increased while D_2 was decreased as shown in Fig. 4. The observed D_α and H_α emission spectra are also presented in Fig. 4. From these experimental results, the decrease in the D_2 permeation is explained as decrease in D atom density in the upstream chamber; D_2 in the plasma chamber is mixed with H_2 gas released from the chamber wall. This precess is regarded as the recycling of adsorbed hydrogen in the plasma chamber wall. The results indicate that the isotopic equilibrium in the recycling process is attained in a few minutes under the present experimental conditions. In addition, the measurement of the permeation through a thin metal membrane may be used as a good technique to analyze the isotopic composition of the hydrogen plasma by mass analysis; the flux of the permeation is sufficiently low without use of a mechanical leak valve.

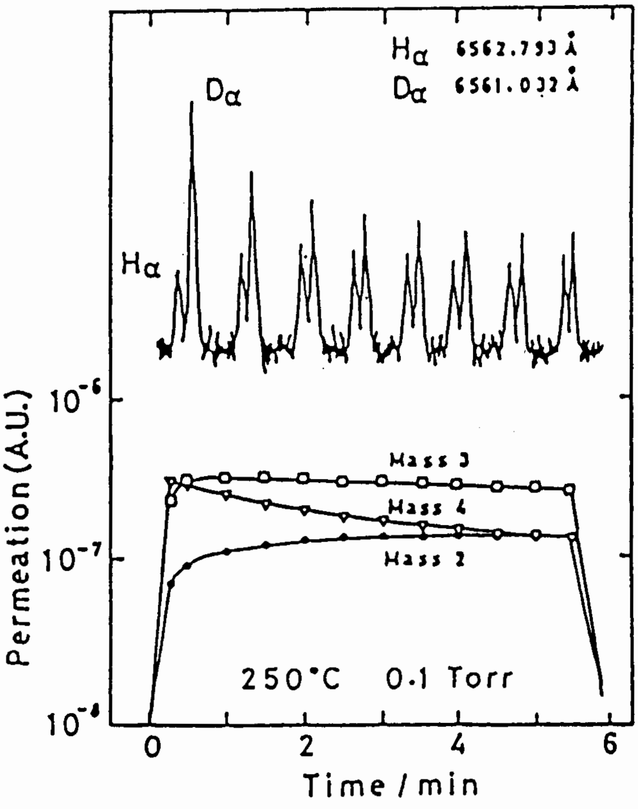


Fig. 4. Isotopic equilibrium in plasma chamber observed in the PDP process.

The permeation of tritium species is presented in Fig. 5. The isotopic equilibrium process in the plasma chamber is also seen in Fig 5. From the experimental observations on hydrogen isotopic gases, it is confirmed that H_2 or D_2 can be used to simulate the permeation of T_2, although the minor mass effects, or isotopic effects, are seen in the permeation rates. The details of the isotope effects have been discussed in a previous work [2].

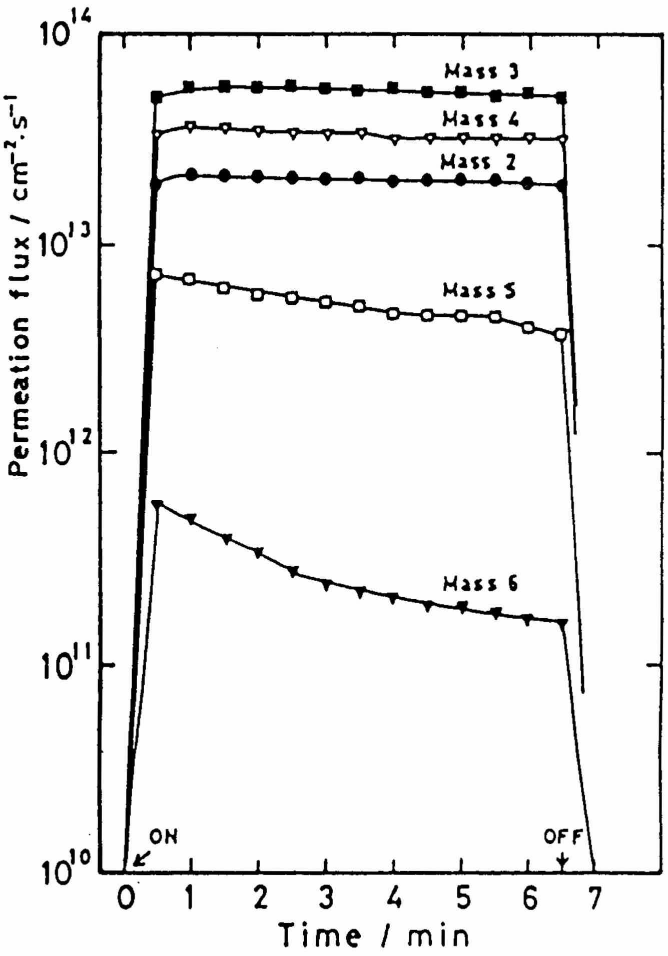


Fig. 5. ECR discharge PDP of hydrogen isotopes including tritium.

Further work on PDP has been made by using an RF plasma generator where the sample test section is detached from the major plasma tube as shown in Fig. 2 so that the sample changing becomes very easy and the practical plasma density at the membrane surface is lowered. Therefore it is considered that the direct effect of plasma is reduced at the location of the tested membrane.

Deuterium permeation experiments were conducted on the membrane samples of Fe, Ni, Cu, Ti and Pd. Except Pd membrane, the permeation was practically not observed when the bias voltage was applied to the membrane in the range from -390 V to 0 V (minus bias). On the other hand, when plus bias voltages were applied to the membrane, permeation was observed in every metal membrane. The permeation has shown the strong dependence on the applied plus bias, or the current passing through the membrane under the bias potential. This fact suggests that the permeation is enhanced by electrons supplied from the main plasma to the surface of the membrane.

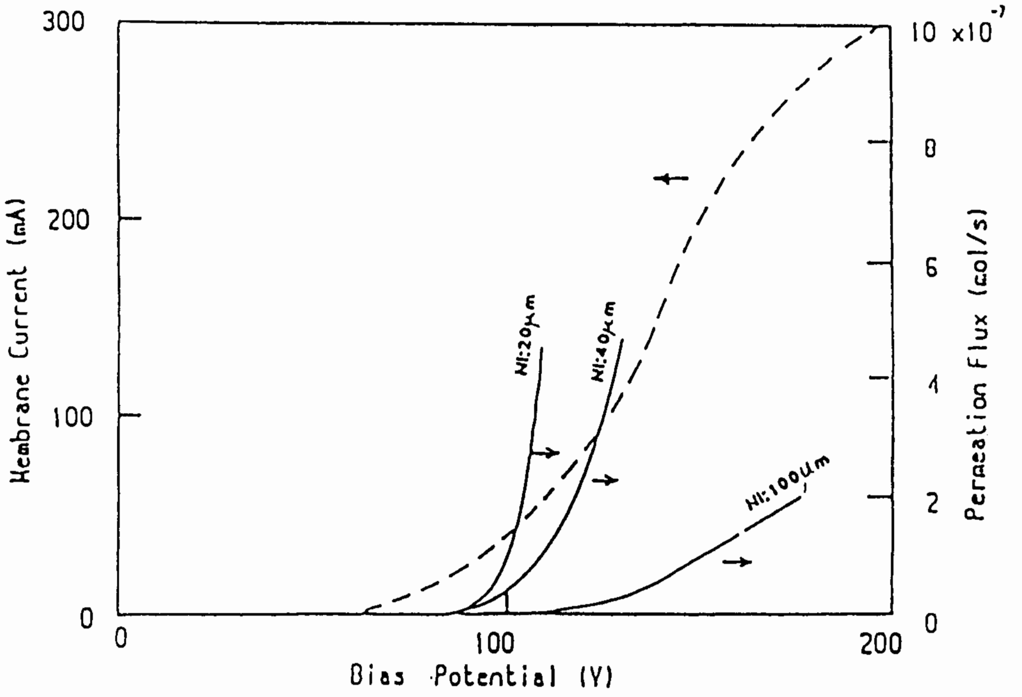


Fig. 6. Plus bias hydrogen permeation observed for Ni membranes by RF discharge apparatus.
Thickness: 20, 40 and 100 μm

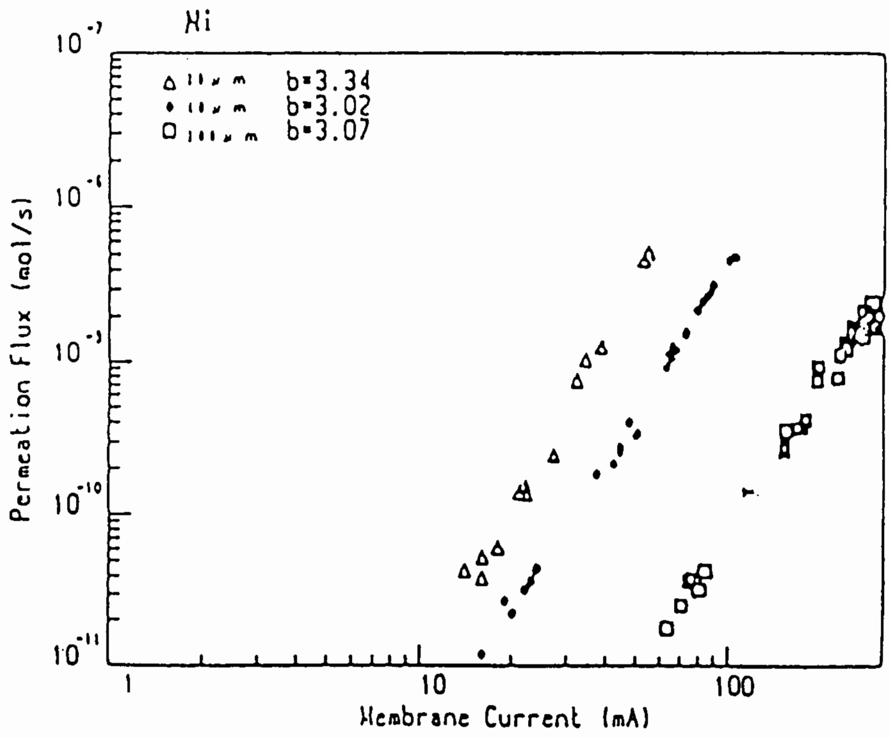


Fig. 7. Correlation between the hydrogen permeation and plus bias current.
Flux is expressed by, log (Flux) = a + b log (Current), where b is slope.

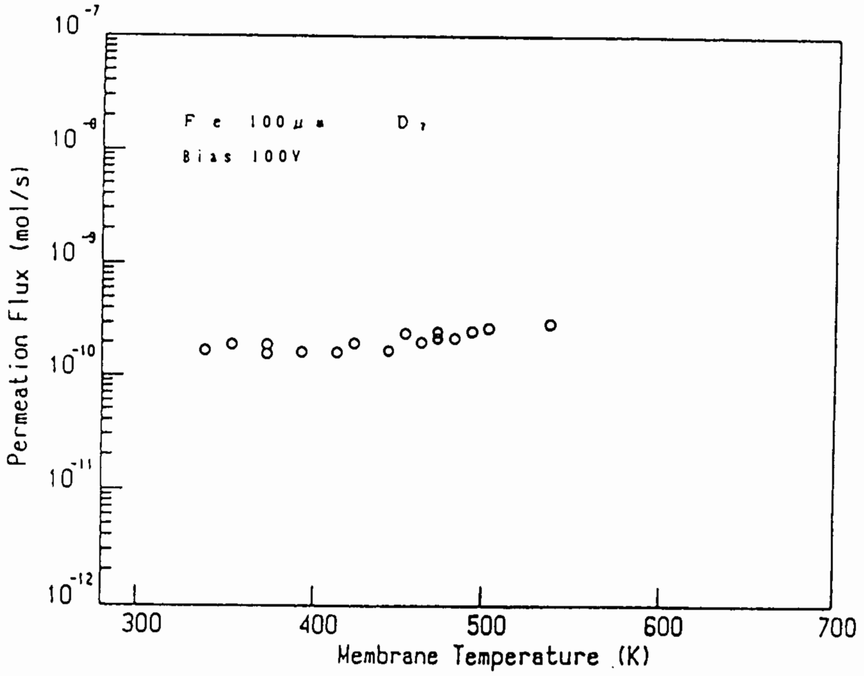


Fig. 8. Temperature dependence of deuterium plus bias permeation through Fe membrane.

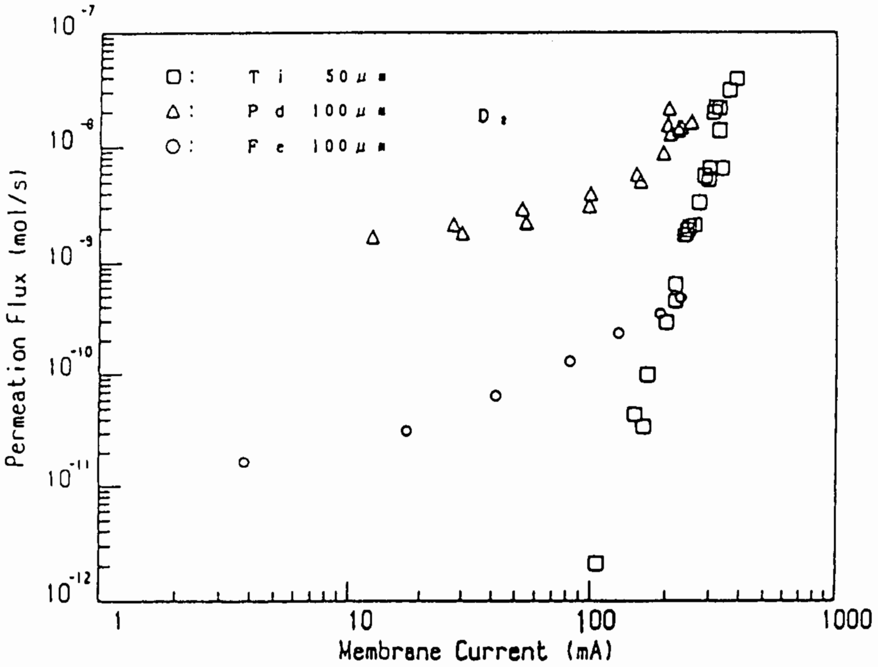


Fig. 9. Plus bias plasma driven permeation (Electron Driven Permeation) of deuterium through Fe, Pd and Ti membranes.

The permeation experiments on nickel membranes with different thickness of 20, 40 and 100 μm were conducted. The results are shown in Fig. 6. The permeation depends clearly on the membrane thickness, which suggests that the diffusion in the membrane is the controlling step in the permeation. It is noted that the current in the bias circuit increases with increase in the bias potential. The correlation between permeation flux and the membrane current is considered in Fig. 7 where the permeation through the nickel membranes are plotted against the membrane current. The results are interesting . The plots show the straight lines with the slopes of ca. 3. These results suggest that the permeation process is not linear against the current.

The temperature dependence of the deuterium permeation through iron membrane is plotted in Fig. 8. Practically, the permeation does not show the temperature dependence. This is due to the large diffusion constant of iron and suggests that the recombination is controlling the permeation.

The summary of the permeation experiments on these metals of Fe, Pd and Ti are plotted as a function of the measured bias circuit current in Fig. 9. It is noted hydrogen permeation occurs even in the case of Ti under the plus bias conditions. The mechanism of the permeation under plus bias is interpreted as the dissociation of hydrogen molecules on or near the surface of the membrane.

4. Summary

In the present work, plasma driven permeation (PDP) of hydrogen isotopes has been studied by using two types of low temperature plasma devices; an ECR discharge plasma device and an RF discharge plasma device. Using the ECR discharge device, the hydrogen permeation rates of normal PDP and GDP through SS 304 membrane with the thickness of 10 μm were measured at different pressures and at different temperatures. The observed apparent activation energy of the PDP process shows temperature dependence; the observed activation energy in the temperature range above 200 °C is quite small, 3 - 8 kJ/mol, while one in the range below 200 °C is rather large, approximately 47 kJ/mol. The permeation was reduced by the minus bias applied on the tested membrane but enhanced by addition of the plus bias.

This effect was studied in detail by using the RF discharge device on selected metals of Ti, Ni, Fe, Cu and Pd. It is concluded that the incident electrons dissociate the hydrogen molecules adhering on the membrane surface into atoms and the atoms can easily dissolved into the membrane, which leads to the increase in the permeation flow. The observed permeation is referred as electron driven permeation.

References

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