TRITIUM PRODUCTION IN PALLADIUM DEUTERIDE/HYDRIDE IN EVACUATED CHAMBER

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ABSTRACT

The controlled out-diffusion method was employed to induce a nuclear reaction in a palladium (Pd) plate with a MnOx film. The time-resolved mass spectra for Pd deuteride revealed tritium (T) production during the out-diffusion experiment. Similar time behaviors of mass number 1-4 and 6 in the spectra was also observed for Pd hydride. Film blackening was observed for most Pd deuteride as well as Pd hydrides using a normal monochromatic negative photographic film. The radiation from the Pd plate consists of two kinds of components for a Pd hydride. Secondary ion mass spectroscopy has shown considerable increase in counts of Li for Pd hydride after the out-diffusion experiment.

1 INTRODUCTION

Among several experimental methods for nuclear reaction in solid, the controlled out-diffusion one invented by Yamaguchi et al [1] has the advantage of involving smaller contamination in the reaction vessel with respect to other methods. In addition, the method is expected to yield higher reproducibility in the analysis of the electrode surface, near which is thought to be the center of the reaction.

Since most of the systems used to investigate the reaction include a preamplifier which would be affected by electromagnetic interference, it is better to employ another supporting detection method free from such interference. One available for the supporting method is autoradiography with use of X-ray film as a photon detection passive device. This method has shown the production of tritium [2], β emission [2] from Pd deuteride after discharge and β-emission [3] from Pd deuteride/hydride during discharge. Some anomalous emission from Pd deuteride/hydride has been detected without discharge by this method [4]. Autoradiography has also been applied to detect radiation from protons impinged Pd hydride [5]. In this study, the authors used a high sensitive monochromatic negative film instead of X-ray film.

2 EXPERIMENTAL

2.1 MATERIALS

The rectangular Pd (99.99% pure) plate sample of $0.3 \times 12.5 \times 25$mm was prepared according to the following procedure. After washing with acetone and aqua regia, it was vacuum annealed at 800°C for 3h under $\sim 10^{-3}$Torr then cooled down to room temperature in a furnace for 8-10h. Next, one side of the Pd plate was coated with a MnOx film of 20-40nm thickness by sputtering in an argon working gas at 80mTorr, followed by loading of deuterium or hydrogen gas (99.6% pure) under 6atm pressure for ~24h. The D or H to Pd loading ratio was measured to be 0.3~0.7. The impurities in the Pd were typically Pt (0.1ppm), Rh (1.8ppm), Ag (1.5ppm), Si (2.1ppm), Mg (1.1ppm), and numerous other metals with lesser concentrations. The deuterium gas with no detectable tritium (<0.25nCi/cm^3) was used for the study. The hydrogen used was research grade.

2.2 APPARATUS

A stainless-steel vacuum chamber of cylindrical shape with volume capacity of $880cm^3$ was used. The Pd plate set in the center of the chamber was connected to a constant current DC power supply through a $0.78\ \Omega$ current limiting series resistor to flow a current through the Pd. Temperature of the surface of Pd sample was measured by a thermocouple ($\pm 0.5°C$ precision) and a computerized recorder with digital multimeter to take date once every 9sec. A quadrupole mass spectrometer (QMAS) (AQA-100R, ANELVA) was employed for mass spectrometry of the gas in the chamber.

2.3 PROCEDURE

A current 0.5~4A was flowed through the Pd for 3h in DC mode under pressure of about $10^{-4}Pa$. Temperature measurement of the Pd started ~1h before the current flowing. Monitoring gas of mass numbers less than 22 started several min before the current flowing. These measurements continued simultaneously for the 3h and lasted up to 1h after stopping the current. The total number of runs for Pd deuteride and Pd hydride were 59 and 42, respectively. After the measurements, the Pd plate was autoradiographed to detect γ and X-ray photons and charged particles, using monochromatic negative film (FUJI PHOTO FILM CO. LTD, NEOPAN 400 PRESTO). For autoradiography, the Pd plate was directly sandwiched using two sheets of negative film. The film with Pd plate had been kept in a dark box carefully to avoid unexpected photons from the outside during exposure. The film exposure time was 3-8 days. The film development was enhanced ~8 times more than usual by increasing development time to 8 min and development temperature to 27°C (using FUJI PHOTO FILM CO. LTD, SUPER PRODOL). Secondary ion mass spectroscopy (SMS) for randomly selected areas of particular interest Pd hydride was sometimes performed after the experiments. The primary ion in SIMS was ^{69}Ga, the counting time was 5min and the measured area was 80×80 μm size for all the spectroscopy.

3 RESULT AND DISCUSSION

3.1 MASS SPECTROSCOPY BY QMAS

Fig. 1 shows time behaviors of ion currents for mass number 1-6, 12 and 16 in the test chamber without Pd sample after several forward runs. The bar chart shown on the right side of the figure gives values of each ion current at 1h 59min after the beginning of measurement. Considerable ion current corresponding mass number 1 was detected, which indicates H^+ existed as dissolved ion from H_2. Though high current was seen for mass number 4 as residual D_2 gas, almost no current for mass number 6 was observed. This means almost no D_3 gas existed in the test chamber.

Fig. 2 shows time behaviors of ion currents with Pd deuteride for DC flow, where the dashed line indicate the time when current flow was started. The sudden increase in ion current for mass number 2, 3, 4, 5 and 6 is due to gas release from the Pd sample induced by current flow. To the contrary, the currents for mass number 1, 12 and 18 are seen to decrease gradually, which means that these gases with mass number 1, 12 and 18 existed in the test chamber before the forward run. Since H^+ was decreasing, Pd did not release H_2, HD and HT, which are thought to be the origin molecules of H^+. Thus, mass number 2, 3, 4, 5 and 6 should correspond D, T and/or ^3He, D_2 and/or ^4He, DT and T_2, respectively. The possibility of the existence of ^6Li as gas is thought to be small, given the temperature of the experiment. Consequently, T is thought to be released from Pd sample, because almost no mass number 6 was seen in background as shown in Fig. 1.
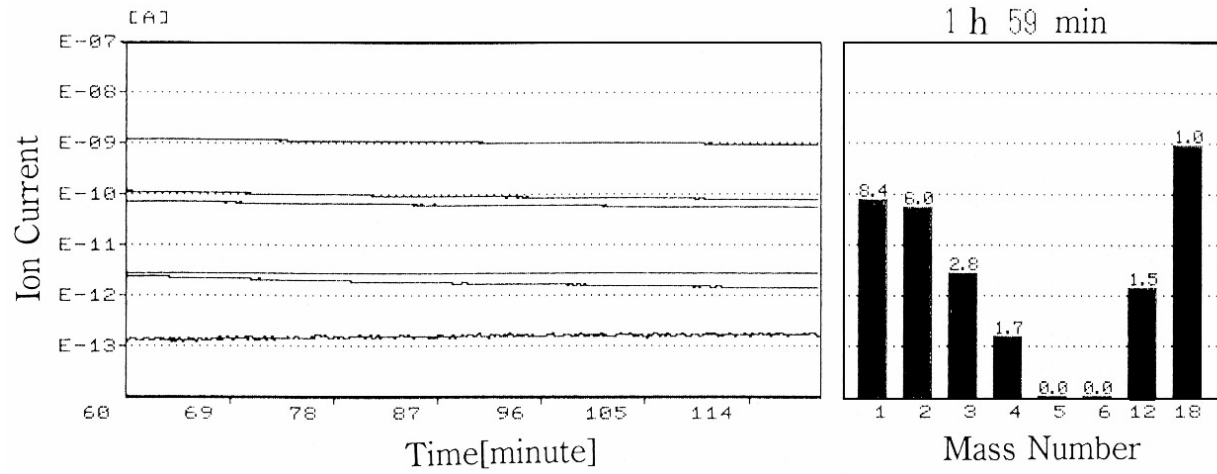
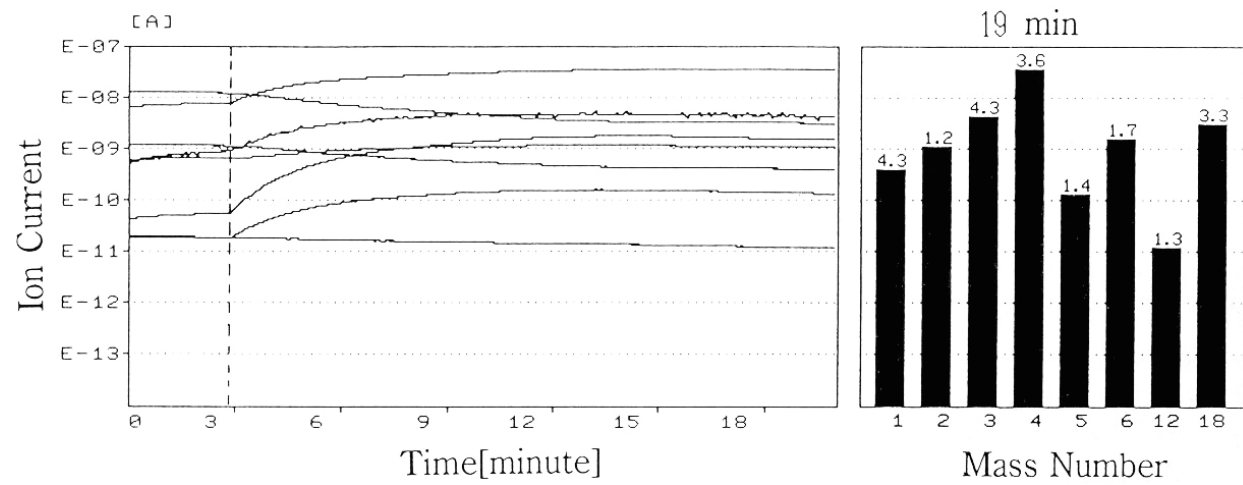Fig. 1. Time behavior of ion currents for mass number 1-6, 12 and 18 without Pd deuteride

Fig. 2. Time behavior of ion currents for mass number 1-6, 12 and 18 with Pd deuteride

Fig 3 and 4 show similar time behaviors for Pd deuteride. The ion current for mass number 22 is seen to increase while that of 19 decreases gradually in Fig. 3. Thus, the ions corresponding to mass number 19 and 22 could be HDO and T_2O. respectively, though small amount of ^{19}F and ^{22}Ne might be released from the Pd. The T_2O could consist of T released from the Pd and residual O in the chamber.

A difference in time behaviors of ion currents is seen between mass number 4 and 6 in Fig. 4. The current for mass number 4 keeps almost constant after reaching the highest value while that for mass number 6 decreases gradually after 10 min from the beginning of measurement. This difference also indicates that gas components of mass number 6 are different from those of mass number 4. Consequently, the molecule with mass number 6 could not be D_3 but be T_2. Since the diffusion constant of D ($7.3 \times 10^{-7} m^2/s$) is slightly larger than that of T ($6.1 \times 10^{-7} m^2/s$) in Pd, the gradually decrease in ion current for mass number 6 would indicate that most of the T existed in near surface of the Pd. Furthermore, considerable current level for mass number 6 is seen in Fig. 4 before the start of current flow. This means that a small amount of T_2 gas had been released from the Pd before the current flow. Several kinds of elements [6,7] and ^4He [7] have reportedly been observed in Pd deuteride/hydride without discharge.
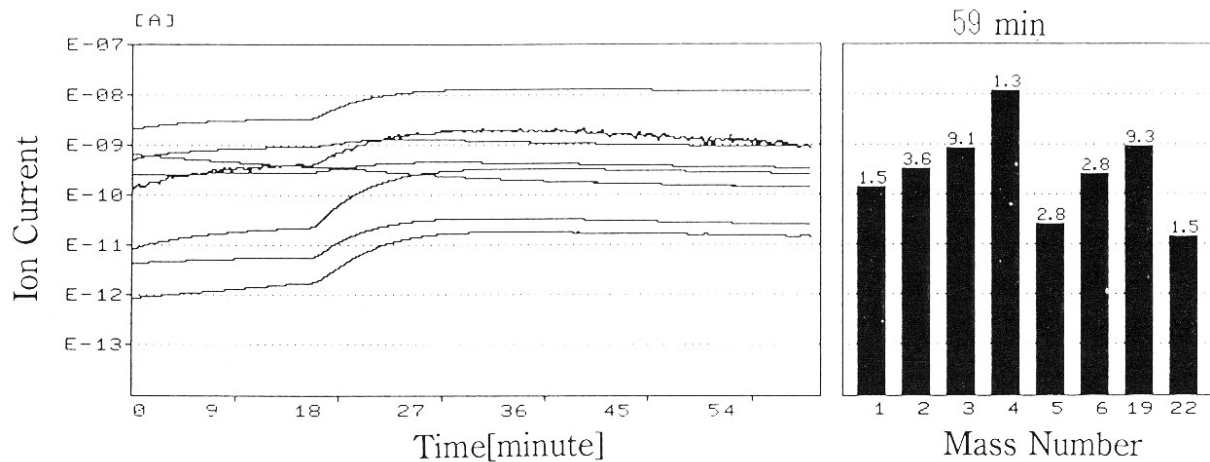

Fig. 3. Time behavior of ion currents for mass number 1-6, 19 and 22 with Pd deuteride
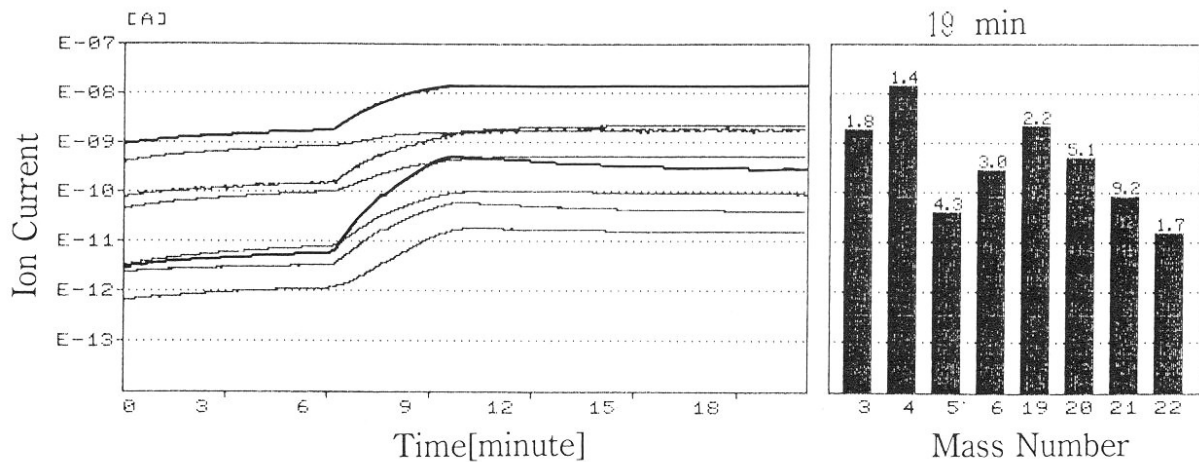
Fig. 4 Time behavior of ion currents for mass number 3-6 and 19-22 with Pd deuteride

Time behaviors of currents for Pd hydride are shown in Fig. 5, indicating that gases with mass number 1-4 and 6 were released from the Pd sample. In this case, mass number 3 might correspond to HD or T, and mass number 4 to D2 or HT. Thus, D and/or T are assumed to be produced in the Pd.

The tritium density reported by the supplier is less than 8.3×10^{-14} and that measured for residual stocked gas in the cylinder is less than $0.25nCi/cm^3$ Supposing that higher limit of $0.25nCi/cm^3$ was taken as the tritium density, the D_2 gas in loading cell contained 1.03×10^{-11} gram of tritium. On the other hand, the current level for mass number 6 was usually more than 10^{-2} of those of mass number 4 with Pd deuteride. Thus, the released T can be estimated to more than 3×10^{-5} gram from these values and the weight difference between before and after experiment. Therefore, even though supposing that whole the tritium in the loading cell with volume of $80cm^3$ under 5atm was absorbed in the Pd sample and was released during experiment, the amount of tritium monitored with the QMAS is at least 3×10^6 times larger than that contained in D_2 gas in the cell before loading. It should be concluded that T was produced in Pd deuteride. Similarly, the amount of T and D in Ha gas before experiment are too low to explain the large amount gas monitored for mass number 2 and 3 in the experiment, which supports that D and/or T was produced in Pd hydride.
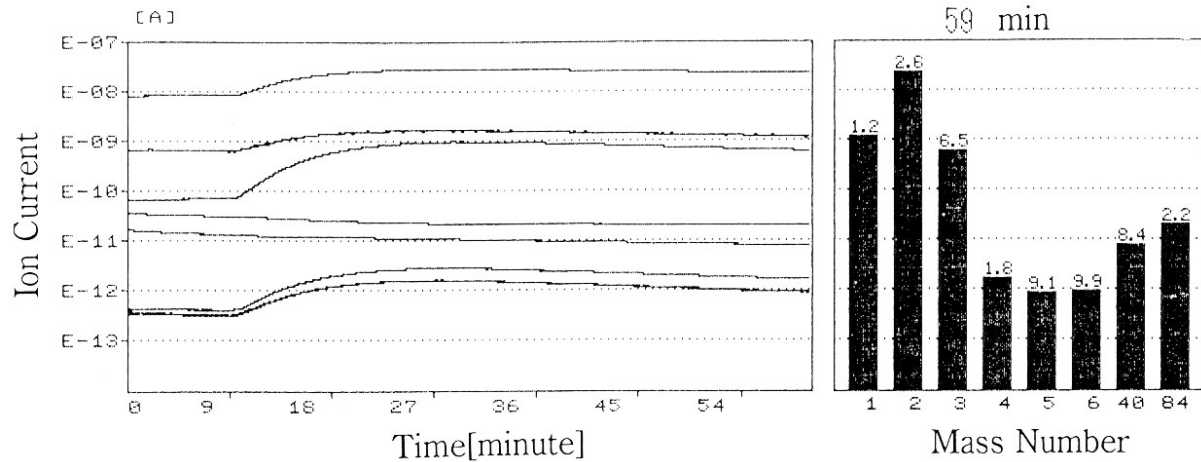

Fig. 5 Time behavior of ion currents for mass number 1-6, 40 and 84 with Pd hydride

3.2 AUTORADIOGRAPHY

Typical autoradiographs for Pd hydride after experiment are shown in Fig. 6. The lower photographic film was in direct contact with the Pd surface with MnOx film. As the part of photographic film contacted with MnOx film has not been exposed, T would not be produced in this area or radiation from nuclear products could not penetrate the MnOx film. Of particular interest is the fact that the stronger exposed part in the upper photographic film corresponds to the boundary area between the exposed area and the non-exposed one of the lower photographic film. This means that a nuclear product with stronger radiation was produced in a boundary area between bore and MnOx covering area and that the radiation penetrated the 0.3 mm thickness Pd plate. The radiation would be X-ray due to Bremsstrahlung caused by the deceleration of electron from β-ray decay of tritium in the Pd plate near its surface. The active nuclear· reaction is considered to occur when D is released from the Pd and then the D density becomes high in the boundary area. This is supported the fact that the Pd with large decrease in loading ratio after experiment has a tendency to give more film blackening. Pd plates with marked decrease in loading ratio during the exposure time also has a tendency to give higher blackening to negative film Moreover, the Pd which showed more deformation during loading or during experiment has a tendency to give more film blackening. McKubre et al. [8] have reported that excess heat production needs the presence of some flux of D passing through the interface.
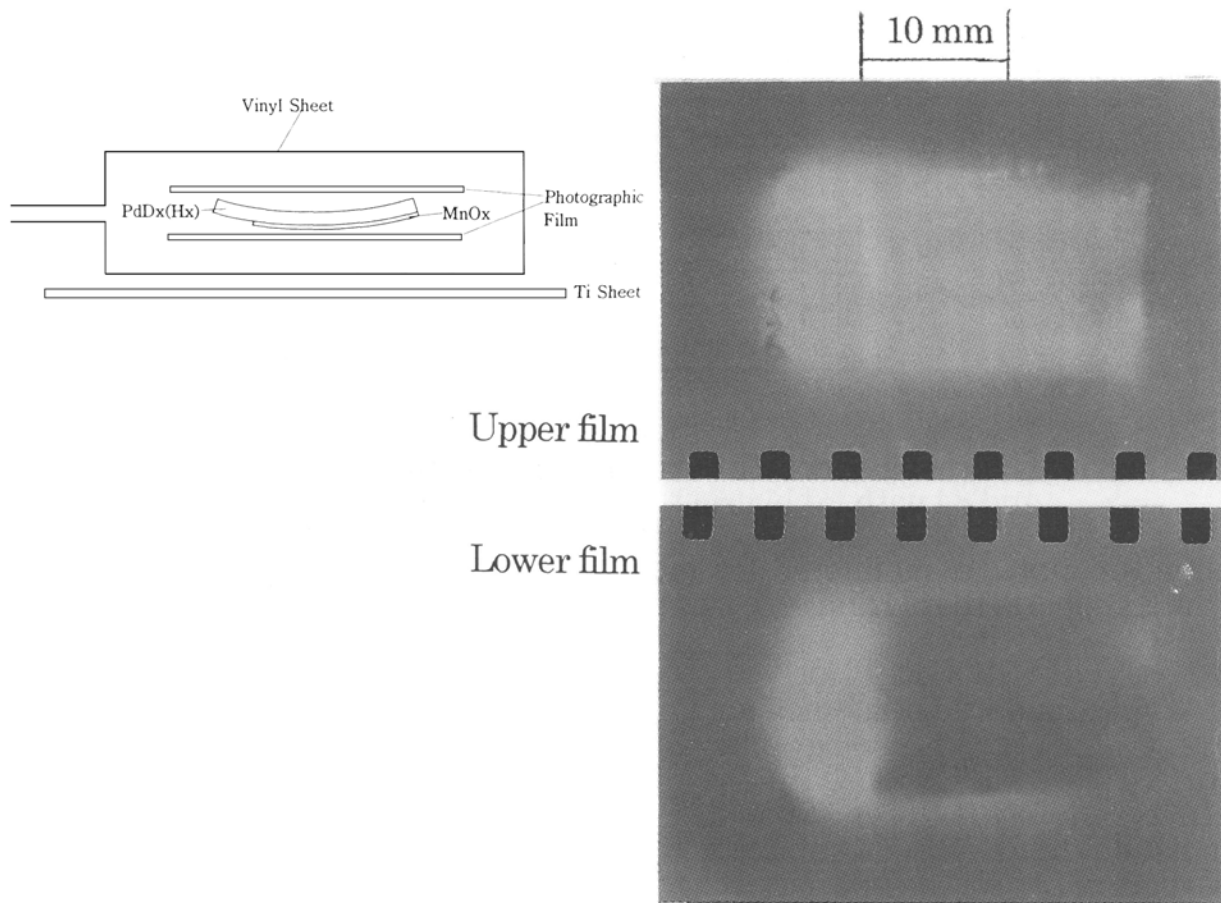

Fig. 6. A pair of autoradiographs after out-diffusion experiment for a Pd hydride

3.3 SECONDARY ION MASS SPECTROSCOPY

SIMS was performed for several Pd hydrides before and after experiment; three randomly selected areas of each Pd sample were analyzed. A marked increase in counts of Li after experiment was sometimes observed; a Pd hydride showed increase in the content of the Li by a factor of two hundred. Contamination due to atmospheric exposure seems to be too small to explain this.

The whole set of results gives the suggestion that possible nuclear reactions perhaps occurred in the narrow near surface layer, producing new impurity elements such as T and Li. The radioactivity of the sample after the experiment may be a result of a nuclear reaction different from that occurred in plasma in the high energy region. From the point of view that Pd hydride also yields similar result as Pd deuteride, proton and deuteron should have similar role in the reaction.

4 CONCLUSION

Sudden increase of partial pressure for gases with mass 3, 4, 5 and 6 were observed from Pd deuteride with an MnOx film just after the beginning of DC flow in an evacuated chamber. Time-resolved mass spectra revealed that the gas corresponding to mass number 6 is T_2. That is, tritium was produced in the Pd after loading of deuterium. Similar time behaviors of mass number 1-4 and 6 were also observed for Pd hydride, suggesting that a similar reaction with tritium production occurs in Pd hydride as well. The autoradiograph for almost all Pd samples gave blackening part on normal monochromatic negative film, indicating beta and/or X-rays radiated from the Pd. Such a film blackening was obtained without setting in the reaction chamber Pd deuteride as well as Pd hydride. It shows that the reaction would also take place by only loading deuterium or hydrogen.

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