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Some Experimental Results Relating to Cold Nuclear Fusion

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The extraordinary evolution of heat or γ -ray during the electrolysis by the following procedure are introduced: After the constant-current electrolysis with an applied current of 500 mA at a palladium rod cathode (10 mm ϕ \times 15 mm) for 3 days in D₂O solution containing 0.1 M DCl and 0.01 M PdCl₂, the electrolyte solution was replaced by 0.1 M LiOH (H₂O) solution, and then the electrolysis with 500 mA was continued. Whole through this experiment a constant current of 5 A which was indifferent to the electrolysis was passed through the palladium rod electrode. The extraordinary phenomena were observed immediately or 30 min after from the replacement of electrolyte solution. The phenomena were difficult to reproduce even by the repeating experiments of the entirely same procedure. Current-potential relations in the electrolysis of D₂O or H₂O at palladium electrodes and permeation behaviors of deuterium or hydrogen atom through palladium are discussed connecting with the extraordinary phenomena.

KEY WORDS: Electrolysis/ Palladiumized palladium/ Applied current indifferent to electrolysis/ Deuterium/ Proton/ Heat evolution/ γ -ray evolution

1. INTRODUCTION

Since the reports by Fleischmann et al.¹⁾ and Jones et al.²⁾ on the electrochemically induced nuclear fusion of deuterium using a palladium or a titanium electrode, many experimental³⁾ and theoretical⁴⁾ works have been done at various laboratories in connection with the "cold nuclear fusion". Firm evidence, however, has not been presented to conclude if the "fusion" is possible or not.

In the present paper, extraordinary evolution of heat or γ -ray observed during the electrolysis at a palladium electrode under the newly devised condition is introduced, though the reproducibility of the extraordinary phenomena has been poor. The electrochemical consideration on the "fusion" is also given.

2. EXPERIMENTAL

The cell used for the electrochemically induced nuclear fusion is shown in Fig. 1. A palladium rod of 5 or 10 mm in diameter and 10 or 15 mm in length served as the working electrode (cathode), and a platinum net surrounding the Pd electrode was employed as the counter electrode (anode). A silver-silver chloride electrode (SSE) with D₂O containing

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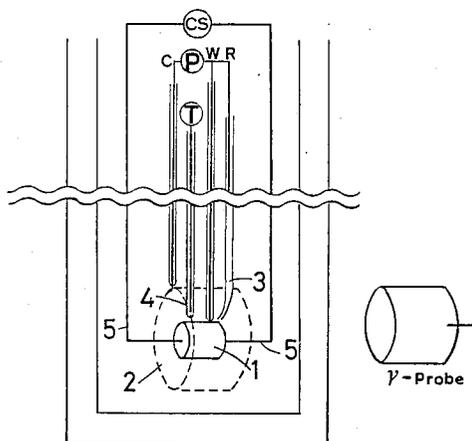


Fig. 1. Electrolysis cell. (1) palladium rod (cathode), (2) platinum net (anode), (3) silver-silver chloride electrode with 1 M LiCl in D_2O (reference electrode), (4) alumel-chromel thermocouple, (5) platinum lead wires covered with glass tubes by which the "indifferent current" is flowed. P; potentiostat/galvanostat, CS; current supplier for "indifferent current", T; thermometer.

1M LiCl was used as the reference electrode and set close to the working electrode with a Luggin capillary. The electrolyte solution was 50 ml of D_2O containing 0.1 M DCl and 0.01 M $PdCl_2$. The electrolysis was carried out applying a constant current (e.g. 500 mA) by a potentiostat/galvanostat (Model HA-502, a product of Hokuto Denko Co.).

In a typical experiment, another constant current (e.g. 5 A) which was indifferent to the electrolysis was passed through the working electrode using platinum lead wires (indicated as 5 in Fig. 1) and a DC current supplier (Model PAD 10-70, Kikusui Electronic Co.). This current will be denoted as "indifferent current" hereafter. Simultaneously with the electrolysis, γ -ray was monitored using a GM counter (Model TGS-113, Aloka), and temperature of the electrolyte solution was measured with the aid of an alumel-chromel thermocouple.

The reduction-oxidation behavior of hydrogen or deuterium ion was studied by the voltammetry at a palladium disk electrode (5.0 mm in diameter) of smooth surface or surface palladiumized with palladium black. The smooth palladium electrode was prepared according to the procedure described in the previous work,⁵⁾ and the palladiumized electrode was obtained by the constant current (30 to 50 $mA \cdot cm^{-2}$) electrolysis for 1 h in D_2O containing 0.01 M $PdCl_2$ with a platinum wire anode. Voltammograms were recorded using a potentiostat (Model HA-502, Hokuto Denko Co.), a function generator (Model HB-104, Hokuto Denko Co.) and an X-Y recorder (Model 3086, Yokogawa Electric Co.).

The permeation of hydrogen or deuterium atom through palladium was investigated using the cell illustrated in Fig. 2. The inner solution was separated from the outer solution by a palladium plate of 0.2 mm in thick and 154 mm^2 in surface area. Two SSEs composed of 1 M LiCl solution of D_2O , RE1 and RE2, were set in the inner and outer solutions.

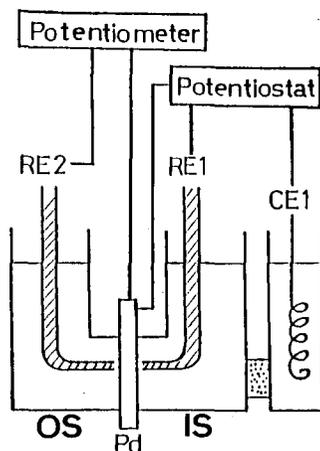


Fig. 2. The cell used for permeation of hydrogen or deuterium through a palladium plate. RE1, RE2; Ag/AgCl reference electrodes with 1 M LiCl (D_2O), CE1; platinum wire counter electrode. IS; inner electrolyte solution, OS; outer electrolyte solution.

The palladiumized surface of the palladium plate was prepared according to the procedures similar to that for palladium disk electrode. To implant hydrogen or deuterium atom into the palladium plate, a controlled potential referred to RE1 was applied to the plate by the aid of a counter electrode, CE1, of a platinum wire. The permeation was traced by measuring the potential difference between RE2 and palladium plate with a potentiometer (Model HA-151, Hokuto Denko Co.).

Electrochemical measurements were carried out at $25 \pm 0.5^\circ C$ unless otherwise mentioned.

Chemicals

The purity of palladium (Nilako Co.) used as the electrodes was more than 99.95%. Deuterium contents in D_2O , DCl and D_2SO_4 (Aldrich) used in this work were 99.9, 100.0 and 99.5 in atom % D, respectively. Lithium deuterioxide solution was prepared by dissolving lithium metal (99.9%) in D_2O . Lithium chloride (anhydrous) and $PdCl_2$ (anhydrous) of reagent grade were dried in vacuo at $150^\circ C$ for 24 h before the preparation of their D_2O solutions.

All other chemicals used were of reagent grade.

3. RESULTS AND DISCUSSION

The evolution of heat or γ -ray during the electrolysis at the palladium electrode

More than 50 runs of electrolysis experiments have been carried out using the cell as in Fig. 1 under various conditions as follows: working electrodes of palladium rods of $10\text{ mm}\phi \times 15\text{ mm}$ or $5\text{ mm}\phi \times 10\text{ mm}$ with smooth or palladiumized surface; electrolyte solutions

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containing 0.1 M DCl, 0.05 M D₂SO₄ or 0.1 M LiOD in D₂O; electrolytic current between -15 and -1000 mA; electrolysis time for 10 to 300 h. In some runs, the electrolyte solution was replaced with H₂O solution after electrolysis for a definite time in D₂O electrolyte solution, and the electrolysis was continued. In addition, the effect of "indifferent current" ranging from 0.5 to 5 A was investigated. Here, the palladiumized electrode or the "indifferent current" were examined, since we assumed that the current density flowing through the palladium rod electrode and the activated surface of the electrode might be important factors for the electrochemically induced nuclear fusion. In this regard, Fleischmann et al.¹⁾ reported that the possibility of nuclear fusion was high when a large current was applied through an electrode of large volume, and Jones et al.²⁾ used an electrolyte solution containing PdCl₂ from which palladium should be deposited on the electrode surface during the electrolysis.

Among many experiments mentioned above, a rapid rise in temperature of electrolyte solution was observed in one run, and extraordinary evolution of γ -ray was found in other two runs. The procedure of these runs was as follows. After the constant-current electrolysis with the applied current of 500 mA at a smooth palladium rod electrode (10 mm ϕ \times 15 mm) for 3 days in D₂O containing 0.1 M DCl and 0.01 M PdCl₂ (the surface of the pal-

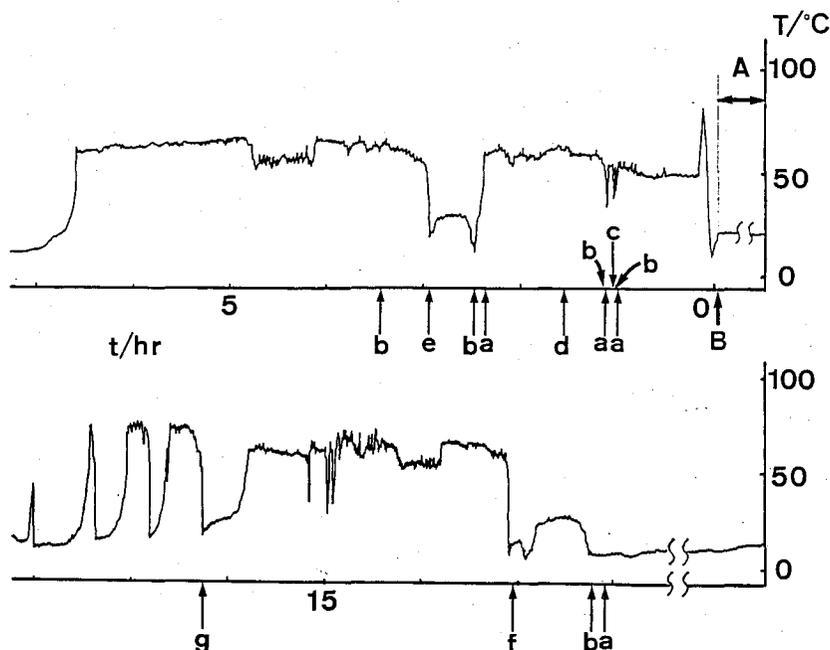


Fig. 3. The heat evolution during electrolysis under various conditions. A; constant current, 500 mA, electrolysis for 3 days in 0.1 M DCl (D₂O) with 5 A of "indifferent current (IC)". B; replacement of the electrolyte solution to 0.1 M LiOH (H₂O). a; IC off, b; IC on (5 A), c; diminish electrolytic current (EC) from 500 to 230 mA, d; EC 500 mA, e; EC 250 mA, f; EC 1 A, IC on, g; EC 1 A, IC off.

ladium electrode was completely covered with palladium black during the electrolysis), the electrolyte solution was replaced by H_2O containing 0.1 M LiOH under nitrogen atmosphere (to avoid the air-oxidation of the electrode), and then the electrolysis with 500 mA was continued. Whole through this experiment, the "indifferent current" of 5 A was applied. Here, it was confirmed gravimetrically that the atomic ratio of deuterium to palladium was almost quantitatively unity after the electrolysis with 500 mA for more than 1 day.

Figure 3 realizes the time-course of temperature of the electrolyte solution in the experiment by which the extreme evolution of heat was observed. Immediately after the replacement of D_2O by H_2O solution, the temperature rapidly rised to 80°C , and a vigorous spurting of gas from the electrode surface was observed at the same time. The heat evolution and gas spurting continued for about 20 h accompanying with several times of rests. It was confirmed during this experiment that the magnitudes of the electrolytic current and the "indifferent current" were important factors for the heat and gas evolution. When the supply of "indifferent current" was turned off, the heat and gas evolution was stopped, and the temperature of the solution fell as indicated by a in Fig. 3. When the applied current was diminished from 500 mA to less than 230 mA, the temperature also fell as indicated by c in Fig. 3.

The time-course of counts of γ -ray in the experiment by which extraordinary γ -ray evolution was observed is given in Fig. 4. Thirty min after the replacement of D_2O by H_2O solution, the γ -ray of which counting rate was 9.5 times as high as the background was

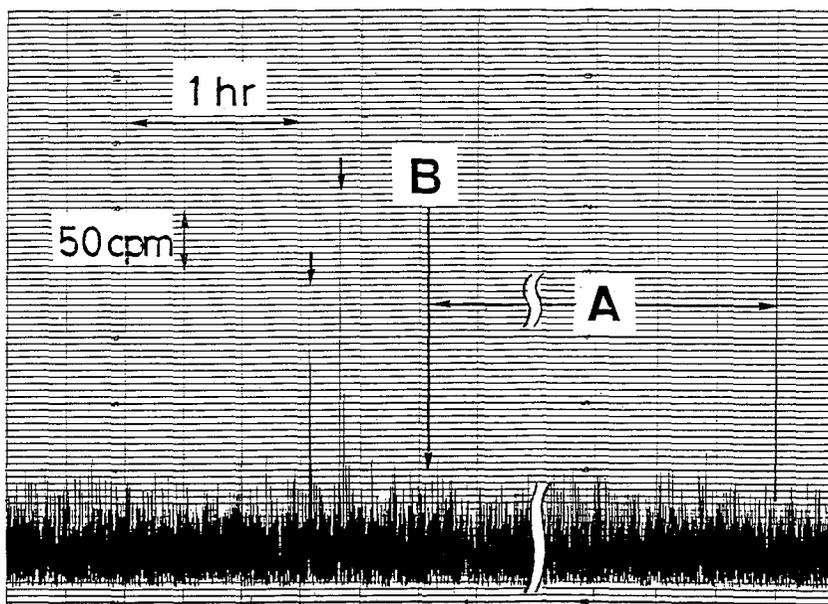


Fig. 4. The γ -ray evolution during the constant current (500 mA) electrolysis in 0.1 M LiOH (H_2O). A; constant current (500 mA) electrolysis for 3 days in D_2O solution containing 0.1 M DCl and 0.01 M PdCl_2 with 5 A of "indifferent current". B; replacement of the electrolyte solution to 0.1 M LiOH (H_2O).

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observed for more than 1 min. The second evolution of γ -ray whose count was 7 times greater than the background was also observed for 2 min at 15 min later than the first γ -ray evolution. We presume that the possible nuclear reaction for the γ -ray emission is the d-p reaction (1), taking into account the γ -ray emission occurred when proton (p) was loaded into the palladium electrode in which deuterium (d) had been accumulated.



The similar γ -ray evolution was observed in the other experiment of the same procedure.

These results suggest that large current flowing through the palladium electrode and the electrode surface activated with palladium black might be effective for the evolution of the heat or γ -ray. The large current may accelerate the movement of deuterium or hydrogen atom in the electrode.

Voltammetric study on the hydrogen or deuterium evolution at palladium electrodes in H_2O or D_2O solutions

Cyclic voltammograms realized in Fig. 5 were recorded at a scan rate of $0.0005 \text{ V}\cdot\text{s}^{-1}$ using the stationary palladium disk electrodes of palladiumized (a) and smooth (b) surfaces in D_2O solutions containing $0.05 \text{ M D}_2\text{SO}_4$ or H_2O solution containing $0.05 \text{ M H}_2\text{SO}_4$. When the palladiumized electrode was used in D_2O solution, three cathodic and two anodic

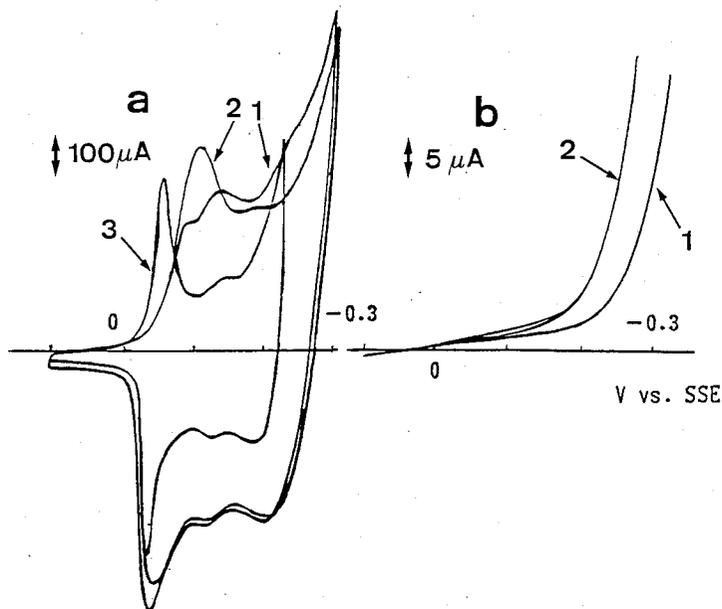


Fig. 5. Voltammograms at a palladiumized palladium electrode (a) and at a smooth palladium electrode (b). curves 1; the first scan in $0.05 \text{ M D}_2\text{SO}_4$ (D_2O), 2; after more than 10 times of scans in $0.05 \text{ M D}_2\text{SO}_4$ (D_2O), 3; as 2, but in $0.05 \text{ M H}_2\text{SO}_4$ (H_2O). scan rate; $0.0005 \text{ V}\cdot\text{s}^{-1}$.

peaks were appeared on the voltammogram at the first scan. Repeating the scan more than 10 times, the voltammogram finally obtained was as curve 2 in Fig. 5 (a), where two cathodic and one anodic peaks are observed. The cathodic and anodic peaks correspond to the adsorption and desorption, respectively, of the mono layer of deuterium atoms on the surface of the palladiumized palladium electrode.⁵⁾ Similarly, two cathodic and an anodic peaks were observed in the voltammogram in H₂O solution (curve 1 in Fig. 5) after more than 10 times of scans. Cathodic peaks for the adsorption of hydrogen atom were at -0.05 and -0.14 V, and were about 0.06 and 0.05 V less negative than those of deuterium atom. On the other hand, the anodic peak for the desorption of hydrogen atom is at only 0.018 V less negative than that of deuterium atom. Hence, the adsorption of deuterium atom is considered to be more irreversible than that of hydrogen atom. The hydrogen gas evolution which appeared as the final rise in voltammogram 1 in Fig. 5 were about 0.06 V less negative than the deuterium gas evolution (the final rise in curve 2).

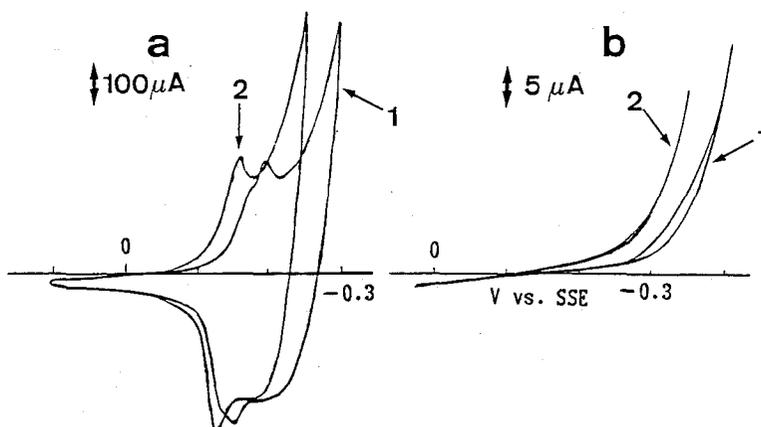


Fig. 6. Voltammograms at a palladiumized palladium electrode (a) and at a smooth palladium electrode (b). curves 1; after more than 10 times of scans in 0.1 M DCl (D₂O), 2; as 1, but in 0.1 M HCl (H₂O). scan rate; $0.0005 \text{ V}\cdot\text{s}^{-1}$.

Adopting HCl and DCl instead of H₂SO₄ and D₂SO₄, respectively, as electrolytes, one cathodic adsorption peak appeared in the voltammograms (Fig. 6). The differences between potentials for adsorption peak, desorption peak or final rises for gas evolution in H₂O solution and those in D₂O solution were almost identical to those with H₂SO₄ and D₂SO₄. The specific adsorption of Cl⁻ on the electrode surface may be responsible for the one cathodic peak instead of two peaks.

The cyclic voltammograms at the palladiumized palladium (a) and the smooth palladium electrodes (b) recorded in 0.1 M LiOH (H₂O) or LiOD (D₂O) are realized in Fig. 7. The adsorption peak at the palladiumized palladium electrode appeared at about -0.69 and -0.80 V in H₂O and D₂O solutions, respectively, and the final rise is at -0.81 V in H₂O solution which is about 0.12 V less negative than that in D₂O solution. The slope of the final rise in D₂O solution is smaller than that in H₂O solution. At the smooth palladium

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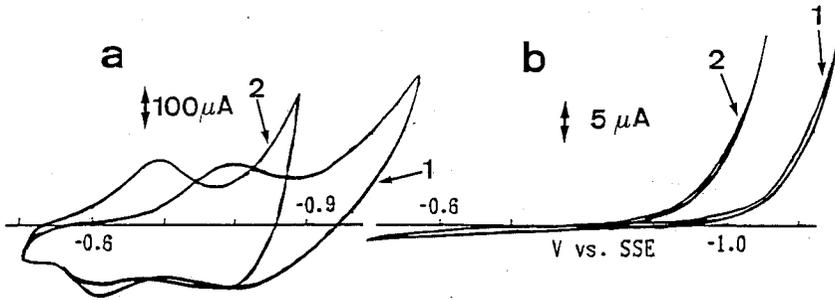


Fig. 7. Voltammograms at a palladiumized palladium electrode (a) and at a smooth palladium electrode (b). curves 1; after more than 10 times of scans in 0.1 M LiOD (D₂O), 2; as 1, but in 0.1 M LiOH (H₂O). scan rate; 0.0005 V·s⁻¹.

electrode, the final rises in both LiOH and LiOD solutions are 0.11 V more negative than those at the palladiumized electrode.

Permeation of hydrogen or deuterium in palladium electrodes

Employing 0.1 M HCl as the inner and the outer solutions in the cell in Fig. 2, the con-

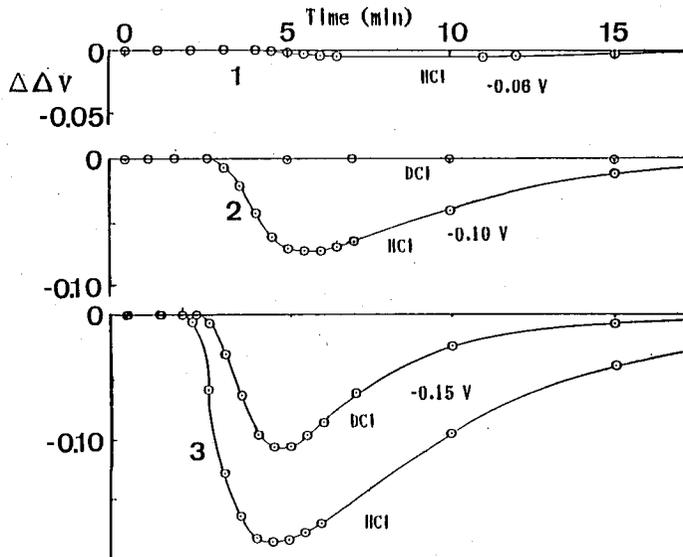


Fig. 8. Effect of the implantation potential of hydrogen or deuterium from acidic solution on their permeation through a palladiumized palladium plate. $\Delta\Delta V$; the variation of the potential difference at the interface between the palladium plate and the outer solution (ΔV , V vs. RE2). Implantation of hydrogen or deuterium from 0.1 M HCl (H₂O) or 0.1 M DCI (D₂O) inner solutions, respectively, at 1; -0.06, 2; -0.10, 3; -0.15 (ΔV , V vs. RE1).

trolled potential electrolysis at the inner solution/palladiumized palladium interface was carried out for 3 min at various potentials and hydrogen or deuterium atom was implanted to the palladium plate.⁶⁾

The time-course of the variation, $\Delta\Delta V$, of the potential differences, ΔV , between RE2 and palladium are shown in Fig. 8. When the implantation potential was -0.06 V vs. SSE (RE1) and the electrolyte solution was 0.1 M HCl (H_2O), ΔV started to shift toward negative at about 4 min after the beginning of the electrolysis. The shift of $\Delta\Delta V$ indicates that hydrogen implanted from the inner solution/palladium interface diffuses in the palladium toward the outer solution. The permeation of hydrogen atom was facilitated with the increase of the negative electrolysis potential as seen in Fig. 8-b and -c. When the electrolyte solution was 0.1 M DCl (D_2O) instead of 0.1 M HCl (H_2O), the permeation of deuterium atom was not observed with the electrolysis at more positive than -0.10 V. Time-courses obtained in the permeation experiments using 0.1 M LiOH (H_2O) or 0.1 M LiOD

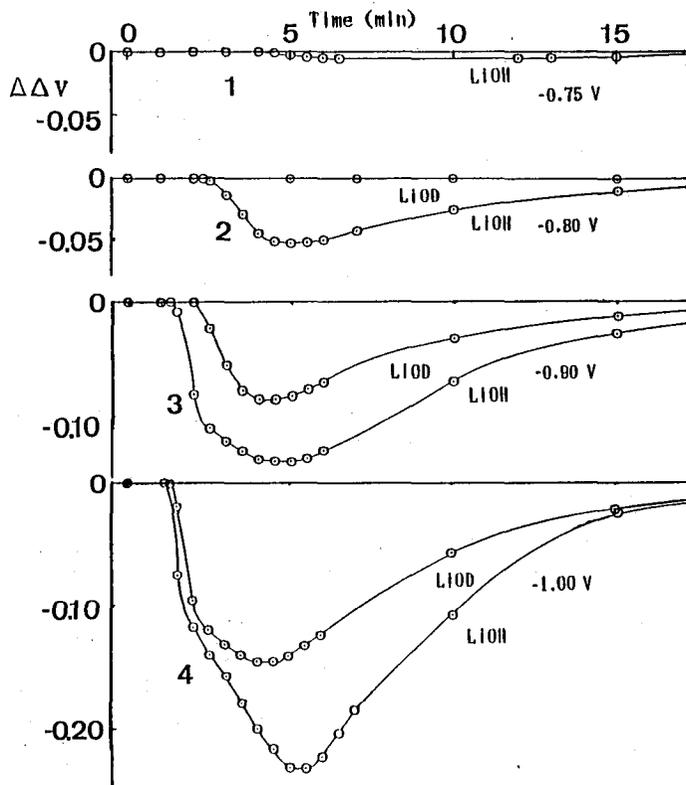


Fig. 9. As Fig. 8, but implantation from alkaline solution. $\Delta\Delta V$; the variation of the potential difference, ΔV , at the interface between the palladium plate and the outer solution. Implantation of hydrogen or deuterium from 0.1 M LiOH (H_2O) or 0.1 M LiOD (D_2O) inner solutions, respectively, at 1; -0.75 , 2; -0.80 , 3; -0.90 , 4; -1.00 (ΔV , V vs. RE1).

(D₂O) as electrolyte solutions are shown in Fig. 9. Even with the electrolysis in alkaline solution, the implantation potential effective for the permeation of hydrogen atom started at more positive than that for deuterium atom. The difference in the permeation behavior between hydrogen and deuterium atoms is attributable to the difference in the adsorption potentials between these atoms observed in voltammograms.

The adsorption and permeation of hydrogen on and in palladium preferential to those of deuterium have been demonstrated by the voltammetric and permeation experiments. The results suggest that deuterium accumulated in a palladium electrode by the electrolysis in D₂O solution may be exchanged for hydrogen when the solution is replaced to H₂O solution, and the possibility of collision between deuterium and hydrogen atoms may be enhanced during the exchange. The collision might be one of the factors of the evolution of the extraordinary heat and γ -ray.

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REFERENCES

- (1) M. Fleischmann, S. Pons and M. Hawkins, *J. Electroanal. Chem.*, **261**, 301, (1989).
- (2) S.E. Jones, E.P. Palmer, J.B. Critt, D.L. Decker, G.L. Jensen, J.M. Thorne, S.F. Taylor and J. Rafelski, *Nature*, **338**, 737, (1989).
- (3) e.g. M. Fleischmann, S. Pons, M.W. Anderson, L.J. Li and M. Hawkins, *J. Electroanal. Chem.*, **287**, 293, (1990). M.J.C. Packham, K.L. Wolf, J.C. Wass, R.C. Kainthla and J.O'M. Bockris, *J. Electroanal. Chem.*, **270**, 451, (1989). D. Lewis and K. Sköld, *J. Electroanal. Chem.*, **294**, 275, (1990). M. Fleischmann, S. Pons and R.J. Hoffman, *Nature*, **339**, 667, (1989). R.D. Petrasso, X. Chen, K.W. Wenzel, R.R. Parker, C.K. Li, C. Fiore, *Nature*, **339**, 667, (1989). S. Srinivasan, Y.J. Kim, O.J. Murphy, C.R. Martin and A.J. Appleby, Proceedings of the Workshop on Cold Fusion Phenomena, p 10, Santa Fe, New Mexico, 23-25 May 1989.
- (4) e.g. J. Maddox, *Nature*, **340**, 15, (1989). J.S. Cohen and J.D. Davies, *Nature*, **338**, 705, (1989). Z. Sun and D. Tomanek, *Phys. Rev. Lett.*, **63**, 59, (1989). A.J. Leggett and G. Baym, *Phys. Rev. Lett.*, **63**, 191, (1989). G.L. Shaw, R.W. Bland, L. Fonda, H.S. Matis, H.G. Pugh, M. Shin and R. Slansky, *Nuovo Chimento Soc. Ital. Fis.*, **102A**(5), 1441, (1989).
- (5) Z. Yoshida and S. Kihara, *Anal. Chim. Acta*, **172**, 39, (1985).
- (6) T. Maoka and M. Enyo, *Surface Technology*, **8**, 441, (1979).