Movement of Li during electrolysis of 0.1M-LiOD/D$_2$O solution.

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Abstract
Depth profile and concentration of Li, D, and H were measured for the Pd cathode after electrolysis of 0.1M-LiOD/D$_2$O solution. All of Pd cathodes had Li in the range of 1X10$^{-3}$ to 1X10$^{-1}$ in terms of Li/Pd ratio. D was found depleted and/or replaced by H after electrolysis when Pd cathode was left in the air.
Excess heat was also measured during the electrolysis, and no excess heat was observed within the uncertainty of 6.8%.

Introduction
Since M.Fleischmann & S.Pons(1) and S.Jones et al.(2) reported the cold fusion phenomena which they claimed to proceed through next reactions, many scientists tried to verify the phenomena.

\begin{align*}
d + d & \rightarrow ^3\text{He} (0.82\text{MeV}) + n (2.45\text{MeV}) \quad \quad \quad \quad \quad \quad \quad \quad \text{<1>}
d + d & \rightarrow ^3\text{H} (1.01\text{MeV}) + p (3.02\text{MeV}) \quad \quad \text{<2>}
d + d & \rightarrow \alpha \text{He} + \gamma + 23.4\text{MeV} \quad \quad \quad \quad \quad \quad \quad \text{<3>}
\end{align*}

But because of difficulty of reproducing the subtle experimental conditions, the truth of cold fusion has not been ascertained yet. In the previous work(3), we searched for protons that were expected from reaction <2>, but only the upper limit of 1.35X10$^{24}$ was obtained for the fusion rate of d-d pairs per second.

We also reported in reference (3) that Li in the electrolyte was deposited into the Pd cathode during the electrolysis of 0.1M-LiOD/D$_2$O solution.
This work investigates the depth profile and concentrations of Li, D, and H inside the Pd cathode by Elastic Recoil Detection Analysis (ERDA)(4), and effects of various electrolysis conditions on the Li deposition. Measurements of excess heat during electrolysis was also performed.
Experiments
1. The electrolysis cell.

A new cell was designed and built for the electrolysis. As shown in Figure 1, this is made of teflon, and open to the air only through a Si oil bubbler. It was placed inside a dewer vessel for thermal insulation from the environment and cooled by the forced flow of water through a copper pipe. The dewer vessel was placed inside a vinyl house for keeping it from the air flow in the room. The difference of the water temperature between the inlet and outlet was monitored by thermo-couples. The heat property of the cell and the cooling system was examined by placing a 2W heater at the position of electrodes and found that 90% of the input heat was taken away by the cooling system while the electrolyte (40ml) temperature reached to a constant of 30°C which was in excess of 24°C above the ambient temperature.

The 0.5%-Pd alumina pellets (NE Chemcat Co. Lot No.: 256-18130) were fixed above the electrolyte solution inside the cell as a recombination catalyst of D₂ and O₂ gas into D₂O. The 10X10X3mm Pd plate used for cathode and the 1mm φ Pt wire used for anode were supplied by Tanaka Kikinzoku Co. and Ichimura Metals Co., respectively. The enrichment (0.1M-LiOD/D₂O solution) was 99.96 atom% D (ISOTEC INC., A Matheson, USA Company).

Table I The conditions of electrolysis.

<table>
<thead>
<tr>
<th>MRUN</th>
<th>Time (h)</th>
<th>Electrolyte</th>
<th>Mode *</th>
<th>Cathode voltage(V)</th>
<th>Currents(A)</th>
<th>Charge(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>140.3</td>
<td>LiOD</td>
<td>P</td>
<td>-0.8 - -1.31</td>
<td>0.037 - 0.625</td>
<td>2.47X10⁵</td>
</tr>
<tr>
<td>03</td>
<td>214.4</td>
<td>LiOD</td>
<td>P</td>
<td>-0.8 - -1.25</td>
<td>0.030 - 0.002</td>
<td>1.64X10⁴</td>
</tr>
<tr>
<td>04</td>
<td>182.8</td>
<td>LiOD</td>
<td>P</td>
<td>&lt; -2.15</td>
<td>1.100 - 0.400</td>
<td>4.03X10⁵</td>
</tr>
<tr>
<td>05</td>
<td>261.9</td>
<td>LiOD</td>
<td>P</td>
<td>-2.65 - -3.32</td>
<td>1.130 - 0.146</td>
<td>1.87X10⁵</td>
</tr>
<tr>
<td>07</td>
<td>287.2</td>
<td>LiOD</td>
<td>G</td>
<td>-2.62 - -3.37</td>
<td>0.40</td>
<td>4.14X10⁵</td>
</tr>
<tr>
<td>08</td>
<td>549.2</td>
<td>LiOD</td>
<td>G</td>
<td>n.m. **</td>
<td>0.40</td>
<td>7.91X10⁵</td>
</tr>
<tr>
<td>09</td>
<td>957.7</td>
<td>LiOD</td>
<td>G</td>
<td>-3.03 - -4.37</td>
<td>0.40</td>
<td>1.38X10⁶</td>
</tr>
</tbody>
</table>

* P and G mean potentiostat and galvanostat, respectively.
** n.m. ; not measured.
2. Conditions of electrolysis and measurements.

The conditions of electrolysis are shown in Table I. Two kinds of electrolysis modes were employed; constant cathode potential with respect to a reference electrode of a Pt wire (Potentiostat) and constant currents (Galvanostat). In the constant potential mode, electrolysis of D$_2$O initially began at the cathode voltage of -0.85V but it was observed to become less negative at the end of electrolysis, probably due to the change in the electrochemical property of the surface of the reference electrode. In MRUN03 - 05, a reverse vial was applied before electrolysis for a few seconds for cleaning the Pd surface. In MRUN07, D$_2$ gas was charged to the Pd cathode before electrolysis.

All the handling of a cell was conducted in the glove box filled with N$_2$ gas. The current, input voltage, reference voltage, and the temperature of the electrolyte and the ambient or cooling water, and difference of the inlet and outlet of cooling water were monitored.

3. Depth profile of Li, D, and H

For studying the depth profile of Li, D and H in the Pd cathode, ERDA was performed in a scattering chamber installed at the Al beam course of the RIKEN's heavy ion Liner ACcelerator (RILAC). The experimental set-up is shown in Figure 2. 51 MeV or 60 MeV Ar$^{6+}$ beams from RILAC were used. The Pd plate was placed at the center of the chamber at the angle of 30° with respect to the beam and forward-recoiled Li, D, and H ions were detected by a solid-state detector at 37°. In order to stop the scattered Ar beam, a thin Al foil was inserted in front of the detector. The detection system was calibrated by use of pure LiH compound and by Rutherford Front Scattering (RFS) of Ar by Pd. In order to explore the effect on the amounts of D and H in Pd of preservation conditions during the time after electrolysis and before ERDA analysis, D$_2$ gas loaded Pd plates were left standing for two days under various conditions, in air, N$_2$ gas, Ar gas, D$_2$O and H$_2$O, and ERDA analysis were performed. For loading D$_2$ gas a Pd plate was placed in about twenty atm D$_2$ gas for one day.

Results and Discussion

1. Excess heat measurements

Excess heat measurements were performed in MRUN01, 05, 07 and 09 and the results of total input heat and output heat are given in Table II.

Table II Input heat and output heat.

<table>
<thead>
<tr>
<th>MRUN</th>
<th>Input (MJ)</th>
<th>Output (MJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>1.090</td>
<td>1.082±0.073</td>
</tr>
<tr>
<td>05</td>
<td>1.659</td>
<td>1.654±0.112</td>
</tr>
<tr>
<td>07</td>
<td>2.921</td>
<td>2.921±0.196</td>
</tr>
<tr>
<td>09</td>
<td>10.25</td>
<td>10.37±0.705</td>
</tr>
</tbody>
</table>
No significant difference is observed between the input and output beyond the fluctuation of the temperature measurement which was estimated to be 6.8% from the experiment with a heater. Therefore no excess heat was observed in the present work within this uncertainty.

2. ERDA

A typical example of the ERDA spectrum is shown in Figure 3. In this run, the Ar$^+$ beam energy was 51 MeV and the beam current was about 10 nA. A 15 µm Al foil was used to stop the scattered Ar beam. The energies of recoil Li and H atoms from the surface are 11.2 MeV and 2.6 MeV, respectively. The events at the lower energies are those recoiled from the deeper depth from the surface. Although the presence of D atoms can hardly be recognized in this spectrum, D atoms could also be detected when the recoiling Li atoms are stopped by increasing the thickness of the Al foil.

The depth profile of Li observed in MRUN05 is shown in Figure 4. The closed square denotes the number of observed Li atoms and the open square, the number of calculated Pd atoms per cm$^2$ per 0.03 µm thickness of the Pd cathode. The abscissa shows the depth in unit of µm. The figure clearly demonstrates that Li atoms penetrate deep inside the Pd plate during the electrolysis, and that the amount is constant even up to the depth of 0.5 µm which was the maximum observable under the present conditions for ERDA. The observed Li quantities in the first and second 0.03 µm layers from the surface are found, by a separate experiment, to decrease as the duration of Ar bombardment become longer than 30 min. This decrease may be due to sputtering of surface by Ar beam. The mechanism of deep penetration of Li inside the Pd plate could not be clarified in this work, but it is likely to be a simple diffusion process.

The average concentration in terms of atom ratio of Li/Pd excluding the two surface layers ranged from $1 \times 10^{-3}$ to $1 \times 10^{-1}$ as shown in Table III. (The number of Pd atoms per cm$^2$ in the thickness of 0.03 µm is $2.04 \times 10^{17}$.) No clear systematic variation of the ratio was observed as a function of the total charge or average current at least within the experiment given in the
table. As the Li concentration in the first layer of the surface could not be accurately
determined, the dependence on the average current or total charge, however, can not be
denied. The most surprising finding is that although the cathode voltage varied only from
-0.8 to -1.25 V in MRUN03, a large deposition of Li was observed. According to the standard
redox potential, Li$^+$ is electrodeposited from an aqueous solution at the cathode voltage of
-3 V. The observed low deposition potential for Li$^+$ can be the interplay of Li and hydrogen
on the surface of a Pd cathode.

Table IV Numbers of D and H in PdD when kept in the air, N$_2$ gas, Ar gas, D$_2$O, and H$_2$O.

<table>
<thead>
<tr>
<th></th>
<th>D</th>
<th>D/Pd ratios from weight*</th>
<th>D/Pd ratios from ERDA**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>2.01X10$^{15}$</td>
<td>1.74X10$^{15}$</td>
<td>0.700</td>
</tr>
<tr>
<td>N$_2$</td>
<td>8.62X10$^{15}$</td>
<td>1.81X10$^{17}$</td>
<td>0.695</td>
</tr>
<tr>
<td>Ar</td>
<td>5.88X10$^{15}$</td>
<td>2.33X10$^{17}$</td>
<td>0.681</td>
</tr>
<tr>
<td>D$_2$O</td>
<td>4.91X10$^{15}$</td>
<td>2.02X10$^{17}$</td>
<td>0.695</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>6.29X10$^{16}$</td>
<td>6.40X10$^{16}$</td>
<td>0.675</td>
</tr>
</tbody>
</table>

The number of Pd atoms in 0.03 mm X 1cm$^2$ is 2.04X10$^{17}$.

* These were calculated from the change of the weight of Pd between before and after
loading D$_2$ gas.

** These were average ratios in Pd calculated from the surface to 0.4 mm observed by
ERDA.

Results of tests on escape and isotopic exchange of hydrogen are summarized in Table IV.
The atom ratios of the total D to Pd were calculated from the weight difference of the Pd
plates between before and after the D$_2$ gas loading. The Pd plates stored in air lost a large
amount of hydrogen (D+H) especially near the surface and experienced a replacement of a
large fraction of D by H. A large loss of hydrogen may be caused by the reaction of D
(and/or H) with O$_2$ in the air on the surface of Pd. This conjecture is supported by the fact
that the surface of a Pd plate becomes wet when it is left in air. The decrease of hydrogen
is much smaller for the Pd plate stored in H$_2$O, but the degree of isotopic exchange of
D with H was the same with that in air.
The Pd plate stored in N$_2$ and Ar gas experienced a little loss of D, and the
existence of H may be due to impurities either in D$_2$ gas or in the ambient gas. In
D$_2$O, no appreciable loss of D and a little isotopic exchange was observed. These
results suggest that for prevention of escape or isotopic exchange of D adsorbed in Pd,
a Pd sample has to be kept either in N$_2$ or
Ar gas until just before the elemental

Figure 5 Depth profile of D&H in PdD
stored in N$_2$ gas, Ar gas and D$_2$O.
Depth profiles of hydrogen atoms observed in Pd plates stored in N₂ gas, Ar gas and D₂O are shown in Figure 5. The square symbol shows the number of D atoms and the triangle shows the number of H atoms, and the horizontal line shows the number of Pd atoms.

The depth profile of hydrogen atoms observed in MRUN08 is shown in Figure 6. In this run, the Pd cathode was quickly transferred to a bottle filled with N₂ gas after electrolysis and stored until the ERDA experiment. It is noteworthy that although the electrolysis was performed using 99.96% enriched D₂O and LiOD, and all the handling of setting-up the electrolysis cell was conducted in a glove box filled with N₂ gas, 19.5% of hydrogen atoms adsorbed in the Pd was light hydrogen. As the hydrogen adsorbed in the Pd cathode during the electrolysis escaped from the surface in bubbles as soon as the electrolysis was stopped, the real amount of D in Pd during the electrolysis could hardly be estimated. But from the weight change of the Pd plate, the D/Pd and (D + H)/Pd ratios were evaluated to be 0.67 and 0.84 using the D/H ratio observed by ERDA.

The present investigation of the adsorbed D and H in Pd by ERDA has revealed that D is quickly replaced by H if the Pd is left in air after electrolysis. Besides, even if highly enriched D₂O and LiOD were used in electrolysis, the isotopic composition of hydrogen adsorbed in Pd was found to be D : H = 4 : 1. Such results cast doubt on the high alleged D/Pd ratios reported for the electrolysis in an open cell system.

<table>
<thead>
<tr>
<th>Reference</th>
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<tbody>
<tr>
<td>(1) M. Fleischmann, S. Pones and M. Hawkins, 1989, <em>J. Electroanal. Chem</em>, 261, 301</td>
</tr>
<tr>
<td>(3) S. Miyamoto et al. 1993, <em>Frontiers of Cold Fusion (Proceedings of the Third International Conference of Cold Fusion)</em>, 523</td>
</tr>
</tbody>
</table>