# Electrochemical Calorimetry of $D_2O$ Electrolysis Using a Palladium Cathode — An Undivided, Open Cell System —

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The electrochemical calorimetry of the electrolysis of $D_2O$ has been carried out using a Pd cathode in an undivided, open cell fashion, together with measuring the total volume of the evolved gases. The excess heat production, observed using a Pd cathode pretreated by a special procedure, can not be explained as a result of the $D_2$–$O_2$ recombination alone. However, the present data certainly do not confirm "cold fusion", because no evidence has yet been obtained for neutron, gamma-ray, tritium or helium production during our electrolysis of $D_2O$ with Pd cathodes.

The recent reports on "electrochemically induced nuclear fusion" by Fleischmann, Pons, and Hawkins,[1] and Jones et al.[2] have caused great interest and activity as well as intense controversy within the scientific community. For example, based on "excess heat" originally observed by Fleischmann et al.,[1] and later by other groups,[3,4] electrochemically charged palladium cells might be expected to be prospective energy sources; however, a number of other groups[5–9] that have conducted calorimetric experiments in similar cells under a wide variety of experimental conditions have found no excess heat. As stated by the above-mentioned two groups in the first reports,[1,2] and recently realized in general,[3–12] such inconsistent results so far reported can be considered to originate from irreproducibility. The clear lack of reproducibility, suggesting that cold fusion in electrolytic cells depends on many factors, e.g., (i) electrode materials (size, pretreatment, ability of absorbing deuterium), (ii) electrolysis conditions (supporting electrolyte, current density, electrolysis time), and (iii) detection methods, should necessitate significant replication.

In the present study an electrochemical calorimetry of the electrolysis of $D_2O$ using a palladium cathode was carried out in an undivided, open cell fashion, together with measuring the total volume of the evolved gases. The contribution of $D_2$–$O_2$ recombination to the observed excess heat is being reported here. Though $D_2$–$O_2$ recombination has often been suggested as being the origin of excess heat production, this needs further clarification.[3,7–9,13]

## Experimental

**Materials.** The Pd samples investigated here included rods (6 mm in diameter×5 mm in length and 2 mm×(20—30) mm) of >99.9% purity (Tanaka Kikinzoku Co., Ltd). Deuterium oxide (Isotec Inc., 99.9%) was used as received. LiOD (or LiOH) solutions (0.1 M, 1 M=1 mol dm$^{-3}$) were prepared by adding a weighed amount of 99.9% pure Li metal (Alfa) to $D_2O$ (or $H_2O$). The LiOD/$D_2O$ (or LiOH/$H_2O$) solutions were electrolyzed in a two-electrode fasion in glass cells using a Pd cathode and a Pt anode of 99.99% purity (Tanaka Kikinzoku Co., Ltd.).

**Pretreatment of Pd Rods.** The Pd rods as cathodes were pretreated in this study mainly by the following two procedures. Treatment I: The rods were heated at 1540 °C in air for 1 h, and were then cooled to ambient temperature by quickly soaking them in $D_2O$ (or $H_2O$) and storing in $D_2O$ (or $H_2O$). Treatment II: The rods were annealed at 600 °C in vacuum (<10 mmHg, 1 mmHg≈133.322 Pa) for 6 h, and then cooled to room temperature under an atmosphere of deuterium gas.

**Apparatus and Procedures.** The calorimetric experiments were performed in a constant-temperature calorimetry mode. The calorimeter used is schematically shown in Fig. 1. The main body consisted of a water-jacketed glass vessel thermostated at constant temperature. The temperature inside the cell was measured with two thermistors which were positioned at different depths from the top of the cell (one upper-positioned relative to the heater and the other lower-positioned). During each experiment, the temperature of the vessel was constant within 0.01 °C, although the long-term stability was of the order of ±0.03 °C. The room temperature was kept at 25±2 °C. The temperature change in the cell (typically containing 0.1 M LiOD/$D_2O$ (60 cm$^3$)) caused by changes in the ambient temperature was found experimentally to be less than 0.016 °C/1 °C. The electrolyte solution was stirred with a stirrer: The stirring rate was maintained as constant as possible. The electrodes, heater, thermistors, and gas outlet (which was attached to a gas-collecting burette) were inserted through the top of the cell through a silicone elastomer lid.

The heater used for calibrating the calorimeter was made of Nichrome wire placed within a thin-walled glass tube with a small amount of silicone oil to provide good thermal contact. The heater resistance was 100 Ω and the resistance

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of the copper connecting wire from the entrance glass sleeve to the heater was less than 0.1 $\Omega$, thus ensuring very little ohmic losses outside the calorimeter vessel.

The resistance of the thermistor during constant-current electrolysis and/or a calibration experiment was measured with a digital electrometer (Advantest TR8652) and the data were recorded with a survocorder (Graphtech, SR6342). In this case, the cell voltage was also recorded at the same time. The cell voltage changed, depending on the solution concentration at the time of measurement, since electrolysis increases the concentration of supporting electrolyte during the experiment and, thus, alters the cell resistance. To compensate for the consumption of $D_2O$ by the electrolysis, calculated amounts of $D_2O$ were added to the cell periodically. Unless otherwise noted, the electrodes were at all times covered by the electrolyte solution.

The resistance load calibration of the calorimeter was performed before and/or during the electrolysis. In the case of calibration before electrolysis, a series of fixed powers were applied to a resistance load (heater) that was included in the cell and the resistance of two thermistors placed at different positions was measured; consequently, resistance-change ($\Delta R$)-electrical energy input ($W_{in}$) calibration curves were obtained. On the other hand, in the case of the calibration during the electrolysis, a known power (at constant current density) was applied to the Pd/Pt circuit and a series of fixed powers were simultaneously applied to the heater.

Constant-current electrolysis (current densities: typically 60—300 mA cm$^{-2}$) was carried out in a two-electrode fashion with a constant current/voltage supply (PAB 70-1A, Kikusui Electronics Corp.) for periods ranging from typically 1 to 7 days. The Pd cathodes were generally placed in the center of the glass vessel and surrounded by a Pt wire counter electrode (0.2 mm in diameter and ca. 500 mm in length). The distance between the Pd and Pt electrodes was about 5 mm and, thus, the insulating membrane separator of polyolefin (thickness: 0.1 mm) with a number of holes hollowed out was placed between the two electrodes to avoid any short-circuiting.

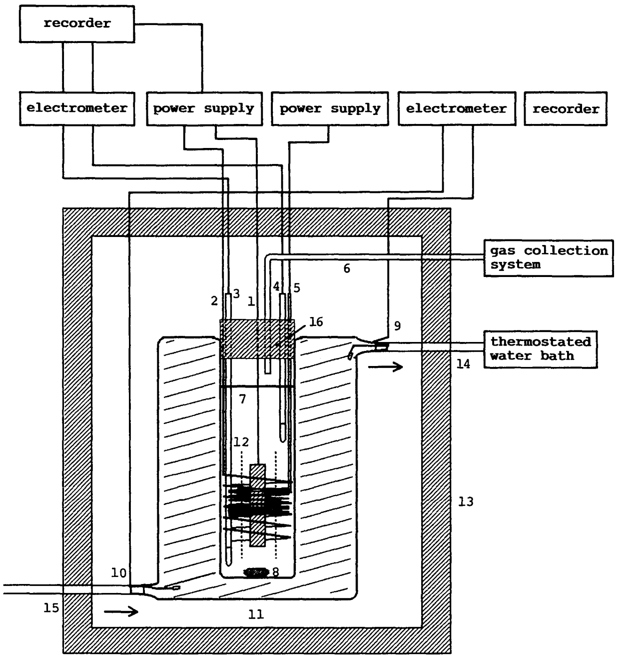

Fig. 1. Schematic diagram of the electrochemical cell used for calorimetric measurements. (1) Cathode, (2) Anode, (3,4,9,10) Thermistor, (5) Heater, (6) Gas outlet, (7) Electrolyte solution, (8) Stirrer bar, (11) Electrolysis cell with water jacket, (12) Membrane separator (13) Heat insulating box, (14) Thermostatted water outlet, (15) Thermostatted water inlet, (16) Cell lid of silicone elastomer.

## Results and Discussion

**Absorption of Deuterium into Pd Cathode during $D_2O$ Electrolysis.** The time-course of deuterium absorption into the Pd cathode during $D_2O$ electrolysis is shown in Fig. 2, where the D/Pd ratios were calculated as $[(m_{Pd,D}-m_{Pd})/M_D]/(m^\circ_{Pd}/M_{Pd})$; $m^\circ_{Pd}$ and $m_{Pd,D}$ represent the masses of the pure Pd cathode (before electrolysis) and the D-absorbed Pd cathode (after electrolysis for some period), respectively, measured directly using a chemical balance (with a precision of 0.1 mg); and $M_{Pd}$ and $M_D$ are the atomic weights of Pd and D, respectively. The D/Pd ratio increased with increasing electrolysis time in the beginning of the electrolysis and finally reached saturation. As expected, the time to reach saturation for electrolysis at 200 mA cm$^{-2}$ was much shorter than that for electrolysis at 50 mA cm$^{-2}$, i.e., about 6—10 and 20—25 h for electrolysis with 200 and 50 mA cm$^{-2}$, respectively,[14] though the saturation values were almost the same (0.60—0.65). These results are essentially similar to those obtained in electrochemical/quartz crystal micro-

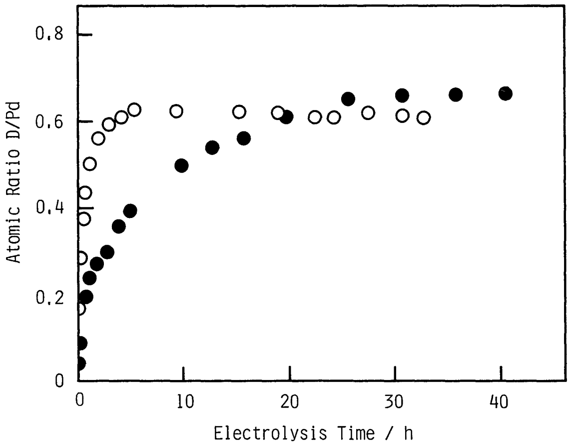

Fig. 2. The time-course of the deuterium absorption into the Pd cathode during the $D_2O$ electrolysis. Electrolyte solution: 0.1 M LiOD/$D_2O$. Cathode: Pd rod (2 mm in diameter, 20 mm in length). Anode: Pt wire (0.2 mm in diameter, 500 mm in length). Current density: (●) 50 mA cm$^{-2}$ (○) 200 mA cm$^{-2}$. Before its use, the Pd cathode was heated at 1540 °C in air for 1 h, cooled to ambient temperature by soaking quickly it into $D_2O$, and then annealed under reduced pressure at 600 °C for 6 h.

balance experiments[16] in which the absorption of deuterium into the Pd cathode was in situ observed as the decreasing resonant frequency of the Pd film-coated quartz crystal electrode used as the cathode with the electrolysis time.

**$D_2$-$O_2$ Recombination.** Figure 3 shows the relation between the $N_{obsd}/N_{calcd}$ value and the electrolysis time, where $N_{obsd}$ is the molar quantity per second of the gases (mainly expected as $D_2$ and $O_2$) actually evolved by electrolysis, estimated on the basis of measurements of their total volume; $N_{calcd}$ is the molar quantity per second of $D_2$ and $O_2$ gases to be produced by the electrolysis of $D_2O$ ($D_2O \rightarrow D_2 + 1/2\ O_2$), calculated in terms of the applied current and the electrolysis time. Data from the beginning of the electrolysis to 3 days of electrolysis were obtained under the condition that the lower half of the Pd cathode was soaked in a 0.1 M LiOD/$D_2O$ electrolyte solution, i.e., the upper half was above the surface of the electrolyte solution (effective electrode area: 0.94 $cm^2$, Experiment A) and those during 3—7 day electrolysis were obtained at a Pd cathode fully soaked in the electrolyte solution (effective electrode area: 1.88 $cm^2$, Experiment B). In both experiments the current density was kept at 60 mA $cm^{-2}$. From this figure we can see that during the period from the beginning of the electrolysis to about 10 h $N_{obsd}/N_{calcd}$ increases with increasing the electrolysis time, suggesting the significant absorption of deuterium into the Pd cathode for such a period. Thus, this should be compared with the fact that the D/Pd value gradually increases with increasing electrolysis time (Fig 2). In addition, the thing to be noted here is the fact that after 1 day electrolysis the $N_{obsd}/N_{calcd}$ value seems to be almost constant (about 0.95—0.98), though a slight scattering is seen, irrespective of the half and full soaking of the Pd cathode in the electrolyte solution. It is well known that palladium is an effective catalyst for the recombination of $O_2$ and $D_2$ (of course $H_2$) in a gas phase.[4] If the unsoaked portion of the half-soaked Pd cathode could catalyze a $D_2$–$O_2$ recombination reaction, the $N_{obsd}/N_{calcd}$ value for Experiment A would be expected to be smaller than that for Experiment B. Some researchers have claimed that the "excess heat" recently reported for $D_2O$ electrolysis may be due to the $D_2$–$O_2$ recombination catalyzed by the Pd cathode.[7–9] Strictly speaking, the steady state value of $N_{obsd}/N_{calcd}$ is not 100% in Experiments A and B. The small difference probably indicates a small amount of $D_2$–$O_2$ recombination (2—5% at most) and/or an experimental error. The data in Fig. 3, as a whole, however, demonstrate that the $D_2$–$O_2$ recombination does not substantially occur under the electrolysis conditions employed in this study.

**Electrochemical Calorimetry.** The calorimeter was calibrated by passing different amounts of direct current through the electric heater (resistance: 100 $\Omega$) in the electrolyte solution before and/or during the electrolysis and measuring the potential drop across it. For each value of the electrical input power ($W_{in}$), the steady-state resistance change ($\Delta R$) (which can be easily converted to temperature change ($\Delta T$)) was measured and plotted in order to yield a calibration curve, as typically shown in Fig. 4. The $\Delta R$ vs. $W_{in}$

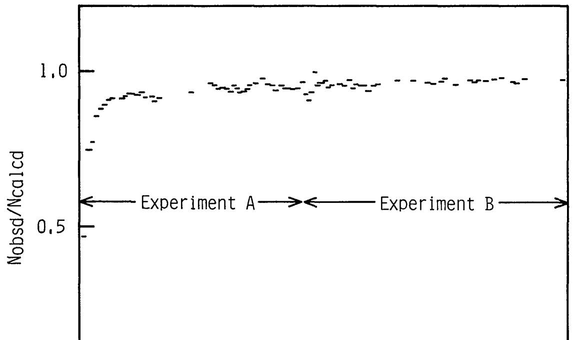

Fig. 3. Plots of $N_{obsd}/N_{calcd}$ as a function of electrolysis time. Electrolyte solution: 0.1 M LiOD/$D_2O$. Cathode: Pd (2 mm in diameter, 30 mm in length). Anode: Pt wire (0.2 mm in diameter, 500 mm in length). Current density: 60 mA $cm^{-2}$. The Pd cathode was pretreated by Treatment II (see Experimental section). See the text for Experiment A, Experiment B, $N_{calcd}$, and $N_{obsd}$.

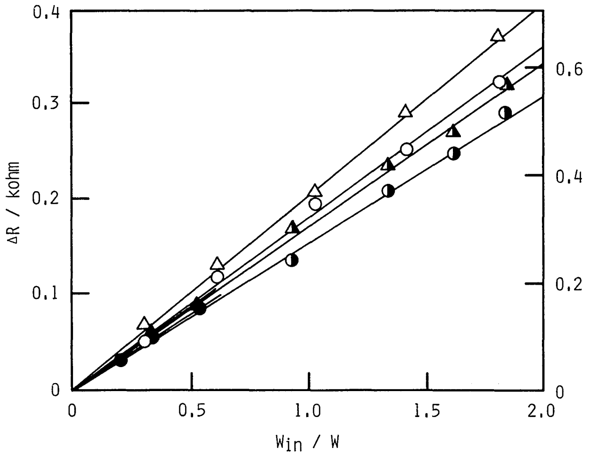

Fig. 4. Typical calibration plots of resistance change ($\Delta R$) (or temperature change ($\Delta T$)) vs. electrical input power ($W_{in}$) obtained before the electrolysis (△,○) and during the electrolysis (◭,▲,◑,●). Electrolyte solution: 0.1 M LiOD/$D_2O$. Cathode: Pd (6 mm in diameter, 5 mm in length). Anode: Pt wire (0.2 mm in diameter, 500 mm in length). Current density: (▲,●) 60 mA $cm^{-2}$, (◭,◑) 122 mA $cm^{-2}$. The Pd cathode was pretreated by Treatment I. The thermistors were placed at the lower position (○,◑,●) and the upper position (△,◭,▲) relative to the heater (or the Pd cathode).

calibration plots are almost linear in the examined range of $W_{in}$. However, it is also obvious that their slopes largely depend on the position of the thermistor relative to the heater in the cell and on whether the electrolysis is carried out or not during the calibration experiment (and also on the current density applied to the Pd cathode). This fact may suggest that temperature gradients exist in the cell and that both the thermal conductivity and the heat capacity are complicated by gas evolution. Thus, in the following experiments the calibration of the calorimeter was carried out occasionally using two thermistors placed at different positions relative to the heater during electrolysis.

Figure 5 shows typical results of a calorimetric experiment that was performed together with measuring the total volume of the evolved gases (shown in Fig. 3) where the Pd cathode was pretreated by Treatment II. In this figure the ordinate indicates the ratio of "excess heat ($W_{ex}$)" to input power ($W_{in}$) and the abscissa the electrolysis time (in day). $W_{in}$ and $W_{ex}$ were calculated according to the following equations:

$$W_{in} = I \cdot E \tag{1}$$

and

$$W_{ex} = W_{out} - (E - 1.54) \cdot I, \tag{2}$$

where $I$ is the cell current, $E$ the cell voltage, $W_{out}$ the observed output power. The second term on the right-hand side of Eq. 2 corresponds to Joule heating ($W_J$); 1.54(V) is the thermoneutral potential for heavy water[17,18] and $E-1.54$ is, therefore, the amount of voltage effective in heating the contents of the $D_2O$ electrolysis cell. Although Fig. 5 shows some scatter, it seems likely that a small amount of excess heat is produced irrespective of the half and full soaking of the Pd cathode in an electrolyte solution. For example, the excess specific rate of heating observed during the 2nd and 6th days after electrolysis are calculated to be approximately 1.8 and 1.2 W cm$^{-3}$ of the Pd cathode (in this case $W_{in}$=4.3 W cm$^{-3}$).

The calorimetric experiments preliminarily conducted using Pd cathodes which were pretreated by various physical and chemical procedures (including Treatment I and Treatment II), though the reproducibility was not so good (a principal feature in all studies concerning "cold fusion" is the irreproducibility of the results reported to date[1–13]), suggested that the pretreatment of Pd cathodes may be one of the key factors to produce "excess heat", as is relatively well recognized in cold fusion experiments.[4,5,9,11,19–21] Among the pretreatment procedures examined so far, an effective procedure is Treatment I (shown in Experimental section). The typical calorimetric results obtained using a Pd cathode pretreated by Treatment I are represented in Table 1. From this table we can draw some interesting conclusions concerning excess heat production.[22] First, excess heat production is observed irrespective of the position of the thermistor relative to the heater (or Pd cathode), i.e., $W_{ex}$>O and $W_{ex}/W_{in}$ (the ratio of excess heat to input power)=13—42%. Second, it is observed that $W_{out}$ is, though slightly, larger than $W_{in}$ at several measuring points. Third, $W_r/W_{ex}$ (the ratio of $D_2$–$O_2$ recombination heat to excess heat) is about 80% after 1 h electrolysis, about 20% after 42 h and after that less than 10% (except for the value estimated on the upper-positioned thermistor after 125 h). This decrease in $W_r/W_{ex}$ with increasing the electrolysis time is thought to partly reflect the absorption of deuterium into the Pd cathode, because the deuterium absorption and the $D_2$–$O_2$ recombination result in the same contribution

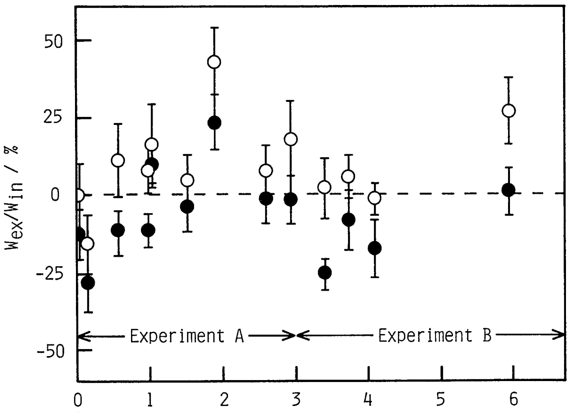

Fig. 5. Typical data of the calorimetric experiment conducted, together with that shown in Fig. 3. $W_{ex}/W_{in}$ indicates the ratio of excess that ($W_{ex}$) to input power ($W_{in}$). Experimental conditions are the same as in Fig.3. Thermistors were placed at the upper position (○) and the lower position (●) relative to the heater (or the Pd cathode).

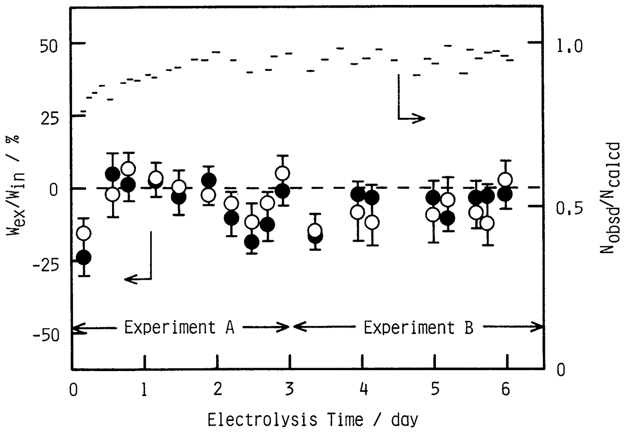

Fig. 6. Plots of $N_{obsd}/N_{calcd}$ and $W_{ex}/W_{in}$ as a function of electrolysis time for the $H_2O$ electrolysis. Electrolysis solution: 0.1 M LiOH/$H_2O$. Other experimental conditions are the same as those in Fig. 3. Thermistors were placed at the upper position (○) and the lower position (●) relative to the heater (or the Pd cathode).

Table 1. Calorimetric Data of the Electrolysis of $D_2O$ in an Undivided, Open Cell[a)]

| Electrolysis time | $I$ | $E$ | $W_{in}$ | $W_J$ | $W_{out}$[b)] | $W_{ex}$[b)] | $W_{ex}/W_{in}$[b)] |
|---|---|---|---|---|---|---|---|
| h | A | V | W | W | W | W | % |
| 1 | 0.074 | 5.40 | 0.40 | 0.29 | 0.39 | 0.10 | 25 |
| | | | | | 0.37 | 0.08 | 20 |
| 42 | 0.074 | 6.44 | 0.48 | 0.36 | 0.56 | 0.20 | 42 |
| | | | | | 0.48 | 0.12 | 25 |
| 71[f)] | 0.150 | 8.97 | 1.35 | 1.11 | 1.54 | 0.43 | 31 |
| | | | | | 1.22 | 0.11 | 8 |
| 125 | 0.074 | 5.79 | 0.43 | 0.32 | 0.39 | 0.07 | 16 |
| | | | | | 0.44 | 0.12 | 37 |
| 143 | 0.074 | 5.73 | 0.42 | 0.31 | 0.48 | 0.17 | 40 |
| | | | | | 0.47 | 0.16 | 38 |
| 150 | 0.074 | 5.74 | 0.42 | 0.31 | 0.44 | 0.13 | 31 |
| | | | | | 0.44 | 0.13 | 31 |
| 172 | 0.222 | 10.95 | 2.43 | 2.09 | 2.61 | 0.52 | 21 |
| | | | | | 2.40 | 0.31 | 13 |

| Electrolysis time | $N_{calcd}$[c)] | $N_{obsd}$[d)] | $N_{calcd}-N_{obsd}$ | $W_r$[e)] | $W_r/W_{ex}$[b)] | $W_r/W_{in}$ |
|---|---|---|---|---|---|---|
| h | mol $s^{-1}$ | mol $s^{-1}$ | mol $s^{-1}$ | W | % | % |
| 1 | $5.75\times10^{-7}$ | $3.33\times10^{-7}$ | $2.42\times10^{-7}$ | 0.071 | 71 | 18 |
| | | | | | 89 | |
| 42 | $5.75\times10^{-7}$ | $4.69\times10^{-7}$ | $1.06\times10^{-7}$ | 0.031 | 15 | 6.4 |
| | | | | | 26 | |
| 71[f)] | $1.17\times10^{-6}$ | $1.13\times10^{-6}$ | $4.0\times10^{-8}$ | 0.012 | 2.8 | 0.89 |
| | | | | | 11 | |
| 125 | $5.75\times10^{-7}$ | $5.30\times10^{-7}$ | $4.5\times10^{-8}$ | 0.013 | 18 | 3.0 |
| | | | | | 11 | |
| 143 | $5.75\times10^{-7}$ | $5.26\times10^{-7}$ | $4.9\times10^{-8}$ | 0.014 | 8.2 | 3.2 |
| | | | | | 8.8 | |
| 150 | $5.75\times10^{-7}$ | $5.63\times10^{-7}$ | $1.2\times10^{-8}$ | 0.004 | 3.1 | 0.95 |
| | | | | | 3.1 | |
| 172 | $1.73\times10^{-6}$ | $1.80\times10^{-6}$ | g) | g) | g) | g) |

a) Electrolysis conditions; Cathode: Pd (6 mm in diameter, 5 mm in length, electrode area: 1.22 $cm^2$), Anode: Pt wire (0.2 mm in diameter, 500 mm in length), Electrolyte: 0.1 M $LiOD/D_2O$ (60 ml), Current density: 60 or 122 mA $cm^{-2}$. Before its use, the Pd cathode was pretreated by Treatment I (See Experimental section). b) Upper and lower values were measured (or calculated) on the basis of the upper- and lower-positioned thermistors relative to the heater, respectively. c) Rate of gas evolution by $D_2O$ electrolysis ($D_2O \rightarrow D_2+1/2\ O_2$) (Calculated). d) Rate of gas evolution by $D_2O$ electrolysis (Measured). e) Rate of heating due to $D_2$–$O_2$ recombination calculated assuming that $O_2$ and $D_2$ corresponding to $N_{calcd}-N_{obsd}$ are all used in their recombination. $W_r=(N_{calcd}-N_{obsd})\cdot\Delta H_{D_2O}$, $\Delta H_{D_2O}$ is the standard enthalpy change for the reaction $D_2O \rightarrow D_2+1/2\ O_2$. f) After the calorimetric experiment, the neutron measurement with respect to the same electrolysis system was continued for 50 h[27)] and then the calorimetry was performed again. g) Negative values were obtained because $N_{calcd}<N_{obsd}$.

to the estimation of the total volume of evolution gas. The $D_2$–$O_2$ recombination has been often regarded as being the origin of excess heat production.[7–9)] However, even if we assume that no deuterium absorption occurs at all, it can not be concluded that $W_{ex}$ originates from $D_2$–$O_2$ recombination alone. $W_r/W_{ex}$ is 89%, at most, and is less than 10% after 71 h of electrolysis. In other words, even if $D_2$–$O_2$ recombination contributes to excess heat production, the degree of its contribution is of the order of several percent. Fourth, $N_{calcd}$ was less than $N_{obsd}$ after 172 h of electrolysis. At present we have no reasonable explanation for this, other than experimental error.[28)]

For a comparison with the above-mentioned experiments (Figs. 3 and 5), a control experiment was carried out using a Pd cathode (2 mm in diameter, 30 mm in length) in 0.1 M $LiOH/H_2O$ solution (Fig. 6). In this case, $W_{ex}/W_{in}$ was less than about 8% irrespective of the half and full soaking of the Pd cathode. In addition, the plot of $N_{obsd}/N_{calcd}$ vs. electrolysis time is essentially the same as that obtained for $D_2O$ electrolysis, suggesting that also $H_2$–$O_2$ recombination does not occur substantially in the case of the $H_2O$ electrolysis studied here.

## Conclusions

The excess heat production that has been observed for the electrolysis of $D_2O$ using Pd cathode pretreated by a special procedure (Treatment I and Treatment II) in an undivided, open cell, can not be attributed to $D_2$–$O_2$ recombination alone. Even if the recombination contributes to excess heat production, the degree of its contribution (i.e., $W_r/W_{ex}$) is of the order of several percent after long-term electrolysis. It should be emphasized, however, that the present data certainly do not confirm "cold fusion", because we have not yet obtained any consistent correlations with other experimental data (such as neutron, $\gamma$-ray, tritium or helium measurements). In order to confirm the obtained results in this study from a different point of view, differential calorimetric studies (based on the calorimetry of the twin heat-flow type) of both Pd/H and Pd/D systems in a closed-cell fashion are now in progress. A closed system with complete $D_2$–$O_2$ recombination allows a much simpler energy balance compared with an open system.[4,10]

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28) We have also observed the excess heat in the other experiments: The electrolysis of $D_2O$ (containing 0.1 M LiOD) was conducted at a current density of 60 mA $cm^{-2}$ using the Pd cathode (6 mm in diameter × 5 mm in length), which before use was heated at 1540 °C for 90 min in an air, quickly cooled to the ambient temperature by soaking it into $D_2O$ and then annealed at 600 °C for 6 h under the reduced pressure, and the Pt anode (0.5 mm in diameter × 500 mm in length). In this case, $W_{ex}/W_{in}$ was in the range of 10—40%. After the 214 h electrolysis, the electrolyte solution was replaced by 0.1 M NaOH/$D_2O$ (the other electrolysis conditions were held constant) and then the electrolysis was continued for 1 day. After that, the electrolyte solution was again replaced by 0.1 M LiOH/$H_2O$ and the electrolysis was carried out continuously. For these electrolysises, $W_{ex}/W_{in}$ of about 10% was observed.