Anomalous Excess Heat by D$_2$O/Pd Cell under L-H Mode Electrolysis

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ABSTRACT

Using a plane symmetric configuration of centered Pd sheet cathode and Pt-wired anode in D$_2$O/LiOD electrolysis with the L-H mode pulse operation, anomalously large excess heat (32 watts in average for 2 months, 100-130 watts at peaks and averaged output/input power ratio 1.7) was once observed associating very few (-1 n/s) neutron emission. To investigate the reproducibility of this experiment, the second experiment with minor changes for cell was done for 4 months. We could reproduce excess heat, however with much smaller amounts (8 watts in average and 15 watts at peak), and twice larger neutron emission rates. Discussions are given by speculating possible condition changes in two experiments, i.e., cell voltages and over-potentials, formation of thin MOS film on Pd cathode surface and mechanism enhancing D/Pd ratio. Excess power density per cm$^2$ of cathode surface showed systematic change as a function of surface current density. This trend is consistent with results by many other authors.

1. Introduction

The so called Fleischmann-Pons effect$^{1)}$, i.e., unknown excess heat generation in Pd-cathode of D$_2$O/LiOD electrolysis has been confirmed by several groups$^{2)}$.$^{3)}$. Some of critical conditions to meet excess heat, e.g., unusual enhancement of D/Pd ratio (more than 0.85 in volume average) and critical current density (0.200 mA/cm$^2$) are being clarified$^{2)}$.$^{4)}$. 

FRONTIERS OF COLD FUSION
Results of many researches are converging onto an issue that the phenomenon occurs near surface of Pd cathode. To establish the reproducible excess heat effect, some key conditions are still missing. Those are conceived to be related to surface conditions of Pd cathode.

The dynamical electrolysis method used by present authors which once showed anomalously large excess heat\(^3\) may realize the above mentioned critical conditions. The method is based on the adoption of Pd-sheet cathode (instead of thin rod adopted by other groups\(^1\),\(^3\)) centered in wired Pt anode and L-H mode pulse current operation with several hours repetition period. This "Takahashi method" is now being tried by many groups\(^5\),\(^6\),\(^7\),\(^8\),\(^9\), many of which have been observing significant levels of excess heat, though what is going on is not well resolved.

The most important issue to be clarified is what is the source of excess heat, i.e., nuclear origin or something else. Observation of close relations between excess heat and nuclear products (\(^4\)He,\(^3\)He, n, t, changed particles and photons) is the key to find underlying physics.

In this paper, we report the protocol of Takahashi method, major results of the first experiment (Experiment-D\(^3\)) and our replication experiment (Experiment-D2). Simultaneous measurements of excess heat and neutron emission have been done in this work. In addition, off-line monitoring of tritium level is shown. Discussions are given on critical conditions to reproduce the Fleischmann-Pons effect.

2. Experimental Method: Protocol

A detailed description is given in Ref.3. The protocol is outlined as follows:

1) Setting-up: For cathode, 99.99% pure cold-worked Pd sheet with 1mm thick and 25mm square wide size is used. As shown in Fig.1, an electrodes-unit of centered Pd sheet cathode and plane-symmetrically wound Pt wire (0.5mm diameter, 7 turns with 5mm pitch) is made using polyethylene or acrylite supporter. Minimum cathode-anode distance is 10mm. This configuration of electrodes is expected to give uniform electrolytic current density on Pd cathode surfaces, hence to realize uniform deuteron loading into Pd sheet. A box-type or cylindrical cell container made of 5mm thick acrylite is used. The electrodes-unit is immersed into electrolyte of 700cc D\(_2\)O+0.3 mol/litter LiOD. An external cooling coil made of pyrex glass tube, through which temperature-regulated (20 °C±0.05 °C) light water is fed with 5-10 l/min flow rate (very
stable for long period), is also immersed in electrolyte. To stabilize the coolant temperature, a computerized chiller/heater equipment is used.

2) Procedure of electrolysis: For the beginning several days (typically one week), the sawtooth-current mode (repeated ramps from 0.25amp to 5.0amp with about 20min period) is tried to find generation of excess neutron counts above background level. Then we switch to the L-H current mode (typically, 0.2-0.4amp L-mode with 6 hours and 4.0-5.0 amp for H-mode with 6 hours) which is continued for 2-4 months to observe excess

![Diagram of electrolysis cell](image)

**Fig.1 : Schematic view of electrolysis cell for L-H mode operation and cooling system.**

heat, neutrons and tritium. We operate the electrolysis by current-controlled mode (constant current mode for L or H period). We monitor current and cell voltage. To compensate consumed D$_2$O by dissociation, we add fresh D$_2$O every several days (2-7 days depending on procedure) to the cell. Observation by oscilloscope found no AC power components during the L and H periods, except the beginning 10 min of switching.

3) Calorimetry: As shown in Fig.1, we monitor cell temperatures by teflon coated thermocouples at 1 or 2 points (later we used 3-4 points$^{10}$), and inlet (TCin) and outlet (TCout) temperatures of coolant. The calorimetry system is designed to cover a wide range of heat-power variation (1-200 watts) keeping linearity between heat-power level and temperature rises. We checked temperature variation in the electrolyte zone, and found it very uniform except the regions inside the
electrodes-unit and close to the cooling coil. Strong stirring effect by gas bubbling and convection current flow is attributed to uniforming cell temperature distribution. Due to high flow rate (5 l/min for Experiment-D2) of coolant, the cell reaches thermal equilibrium in 30 min when we switch the mode from L to H (or reverse), so that thermal energy balance of cell becomes simply $Q'=kS(T-T_c)$, where $Q'$ is the heat source by joule-heating of electrolysis (+"nuclear" heating), $T_c$ the equilibrium cell temperature, $T_c$ the coolant temperature ($T_c=(T_{in}+T_{out})/2$), $S$ the effective surface of cooling coil and $k$ the heat conductivity of coil. We can ignore heat leak to (or from) ambient. Heat removal by coolant is $Q^- = 4.2V_c(T_{out}-T_{in})$, where $V_c$ is the coolant flow rate. Of course, it holds $Q^+ = Q^-$. Correction for electrolyte level height is done using the former equation (7% at most for D$_2$O addition cycle of 7 days).

![Fig. 2: Calibration for calorimetry for Exp.D2.](image)

For calorimetry calibration, we used a "dead" Pd plate (Exp.D) or a fresh Pd plate (Exp.D2, regarding no excess heat at beginning). Calibration run was done by step-wise changing of current for every one hour. Calibration curves for Exp.D2 is shown in Fig.2, which proves that the linear relation holds between heat-power level and temperature rise. We tried a gold plate cathode, instead of Pd, for calibration, but we found a slightly different slope, probably due to the change of bubbling on Au surface (electrochemical situation would be changed). Delta-T of coolant is a best monitor of calorimetry in principle, but the accuracy in the present system is not good due to a
small temperature rise (less than 1°C). Sensitivity of cell temperature is much higher. Difference of temperatures at inside and outside points is apparent due to the systematic shift of ambient-temperature compensation circuit of used data logger. We averaged temperatures of two points to make a calibration line. We obtained 7.0 watts per degree C as calorimetry constant for Exp.D2. Estimated error for excess heat is ±1.0 watt, mostly due to the effect of turbulence flow of electrolyte.

4) Measurements of nuclear products: To monitor neutrons, we have been using a cross-checking system between an NE213 recoil proton spectrometer and a $^{3}$He thermal neutron detector. The detailed circuit diagram and adjusting procedure are shown in Ref.11. We record time history of neutron counts every 4 minutes, energy spectra of recoil protons (equivalently neutron spectra) in L and H periods and integrated sum peak area of $^{3}$He(n,p)reaction. All the time, we monitor continuously rise-time distribution of neutron signals to check any drift and contamination of gamma and noise signals; no contamination was found in the series of this work. To monitor tritium level of electrolyte, we sample 1cc fresh D$_2$O before addition and 1cc electrolyte every week to be counted by a LSC (liquid scintillation counting) system.

3. Highlight of Exp.D

The detail of results is shown in Ref.3. Here we pick up few results which are used for comparing with Exp.D2 later. Observed excess heat (average in 6 hours L or H period) and neutrons as a function of sweep number of L-H mode are shown in Fig.3-a&b, respectively for the first and the second month of runs. It looks that there are a bias-level of excess heat of 10-30 watts continuously and superposed heat bursts of 30-100 watts. This feature resembles with the results of Pons-Fleischmann$^{12)}$. For the two months run, total input energy was 250 MJ, total output energy 410 MJ and excess heat 160 MJ. The results destroy the 2nd law of thermodynamics unless we find a hidden free energy source which is 1000 times greater than any conceivable chemical heat sources in the cell$^{3)}$. Neutron emission is positive, but its rate is only about 1 n/s/source. However, we see correlations with the evolution of excess heat; H-modes gave larger excess heats and larger neutron counts, compared with L-modes. In H-modes, when excess heat level increased, neutron count rates mostly decreased. If excess heats were generated by usual d-d fusions, we should
Fig. 3: Evolution of excess heat and neutron yield as a function of sweep cycle number of L-H mode electrolysis for Exp.D\textsuperscript{3}).

a) First one month  

b) Second one month

Fig. 4: Observed variation of tritium levels in electrolyte (solid points), compared with BG runs (white points).

observe $10^{14}$n/s/source so that observed excess heats could not be due to d-d fusions. A hypothetical interpretation\textsuperscript{3}) was given based on the multibody deuteron fusion reactions which emitted only high energy charged particles ($\alpha,d,t,^3\text{He}$) as direct products and would produce very low level neutrons as secondary products.

Fig. 4 shows the results of tritium observation. We observed meaningful tritium generation in Exp.C\textsuperscript{13})
No. 86 & 87 runs) to give \((n/t) \times 10^{-5} \). In Exp.D (No.115 run), we find increase of tritium level, but only one blank sample (fresh D₂O) also showed an increased level and we can not conclude tritium generation.

4. Replication Experiment: Exp.D2

Procedure of this replication experiment is shown in Table-1. To do this, we renewed electrolyte and Pd cathode sheet (same batch of Exp.D, batch No.1 from Tanaka Precious Metal Co.), added one thermocouple (see Fig.1) in electrolyte, put two thermocouples into inlet and outlet pipes of coolant and removed a thermocouple-support of soda glass. After about 10 hours of calibration run, we started the sawtooth run. After 2 days of the sawtooth run, we found clear increase of neutron count rates (see Fig.5), but we continued the sawtooth mode for 7 days. Time-dependent calorimetry within 20 min period of sawtooth is difficult since it takes 30 min for reaching thermal equilibrium, so that

![Image]

**Fig.5**: Neutron generation by sawtooth current mode electrolysis

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**Table-1: Procedure of Experiment D2**

1) **Calibration Run**: Exp. No. 118
   - Beginning of electrolysis, renewed Pd sheet. (regarding no excess heat)
   - Stepup of electrolysis current for 9 steps: 0, 1, 2, 3, 4, 5, 6, 7, 8 amperes; one hour per step.

2) **Sawtooth Run**: Pre-loading. Exp. No. 119
   - 0.17 (minimum) to 5.0 (maximum) amperes.
   - 20 minutes period. 7 days.

3) **L/H Mode Run**: Main Run. 6 hr / 6 hr
   - Exp.No.120; L/H = 0.17 A / 4.0 A (0.3 W / 44 W) 20 days
   - L/H = 0.4 A / 5.0 A 14 days
   - L/H = 0.4 A / 6.0 A 20 days
   - L/H = 1.0 A / 7.0 A 20 days
   - Exp.No. 121; Step up Mode (same with Calibration) 2 days
   - Exp.No. 122; L/H = 0.4 A / 3.0 A 20 days
   - Exp.No. 123; L/H = 0.4 A / 4.0 A 50 days

(Electricity in Campus was off for one day btw. Run-1 and Run-2 of Exp. 122.)
Fig. 6: Evolutions of excess heat and neutron yield by sawtooth current mode electrolysis; 3 cycles data are bunched and averaged.

we averaged over 3 cycles of sawtooth-periods to reduce averaged input and output. The results are shown in Fig. 6, compared with neutron emission rates. We saw excess heat in a day and excess heat increased gradually to reach 6 watts (29% of input) in 7 days.

From 8th day we started L-H mode run and continued for more than 3 months. For the first one month, excess heat level was rather constant (6-10 watts for H-mode and 2-4 watts for L-mode). We did not see rapid increase as in the case of Exp.D. Experiments were interrupted twice (in No.122 and No.123 runs), due to electric power shut down of Campus, for one day long each event. When we restarted electrolysis with L-mode, cell temperature increased slowly from 20.0 °C to higher value in 6 hours. Excess heats after restarts were about half of those before the power shut down,
and recovered in 2-3 weeks. For about 3 months run of Exp.D2, we changed currents for either L or H modes to take excess heat data for seeing if we found systematics between excess heat and current density. A typical data is shown in Fig. 7, which shows gradual increase of excess heat in a month. Corresponding excess neutron rates over background (B.G=1200 counts per 6 hr) show higher count rates for H-modes and smaller for L-modes, as in the case of Exp.D, however absolute yields increased about twice of those in Exp.D, although average-excess heat level decreased to about 1/4 of that in Exp.D(average). This result is predicted by the multibody fusion theory3). Exp.D2 is still running the 4th month, and we have not observed big heat bursts like those in Exp.D.

Doubly increased neutron yields in Exp.D2 improved statistics of neutron spectroscopy, so that we could obtain neutron spectra having two components at 2.45 MeV and 3-7 MeV region as we observed in Exp.B and Exp.C3), which were explained as the consequence of competing process of d-d and d-d-d fusions13).
Fig. 8: Net gain (Output / Input - 1.0) of excess heat as a function of electrolytic current density.

5. Discussions

For summarizing observed excess heats in Exp. D and Exp. D2, we plotted net gain (output / input - 1.0) as a function of electrolytic current density on Pd sheet surface (~11.5 cm²), as shown in Fig. 8. Net gain of excess heat decreases as we increase current density, though absolute magnitude of excess heat increases, for both cases of Exp. D and Exp. D2. We observed very high gain more than 10 for L-modes; this feature is very different from results by other authors using continuous (DC) current mode operation. To compare our results with those by other groups, we deduced excess power per cm² of Pd surface to be plotted on the Storms' graph, as shown in Fig. 9. Results from Exp. D2 follow the "limit" curve of Storms (solid curve) and look consistent with other results. This graph suggests us that excess heat phenomenon occurs near surface, not volumetric effect of Pd cathode. Much larger excess heats by Exp. D look consistent with Liaw's molten salt experiment and burst data of Pons-Fleischmann. It seems that the solid curve by Storms is not the limit. However, high power density (more than 10 watts/cm²) were observed as bursts and not controllable yet.

We could reproduce excess heat in Exp. D2, but magnitudes were so different. It seems that we were not
Fig. 9: Trends between excess power per surface area \( (\text{W/cm}^2) \) and electrolytic current density. (see Ref. 14)

Aware of essential changes in two experiments. In Fig. 10, we compare histories of cell voltage for Exp.D and Exp.D2. We notice that cell voltages in Exp.D are anomalously high (-25 volts in the beginning and increased to -30 volts at the end), compared with those in Exp.D2 (-14 volts in the beginning and very slowly increased to reach 20 volts after 3 months). This fact shows that "effective" surface area of Exp.D Pd cathode was much smaller than that of Exp.D2. What is the reason of this change? We only renewed Pd sheet and electrolyte and took out a soda glass pipe. We made a surface analysis (-1 μm depth) by SIMS for the used Pd sheet of Exp.D, and found deposits of Al-27 and Ca-40 as comparable amounts as Li-7. Ca-40 might come from pyrex glass. We do not know exactly from where Al-27 came. Anyway, we can conceive that thin MOS (metal oxide semiconductor)-like or MH (metal hydride) layers on both surfaces of Pd sheet were formed. It is interesting that McKubre pointed out the drastic effect of Al impurity in electrolyte to meet reproducible excess heat\(^{16}\). As shown in Fig.11, we can speculate that the thin MOS film formation on Pd surface as "blocking layer" may play a role enhancing cathode over potential (hence cell voltage) and
suppressing deuteron diffusion-out from Pd to meet locally high D/Pd ratio near surface, because of depletion of free electrons in the MOS layer where atomic potential barrier is much higher than that in Pd zone. It seems a critical issue that reproducible MOS surface condition can reproduce excess heat phenomenon. In this respect, interests are on our recent experiment of deuteron-beam implantation into Pd or Ti foil with thin Al layer on surface which showed a drastic effect to emitted 8 MeV α-particles (by d-d-fusion), and other charged particles at 3, 3.5 and about 4.5 MeV; which, from the logic of experiment, should be regarded as "cold" nuclear reactions of deuterons\(^{17}\). We have to further resolve the role of "Takahashi method", namely whether or not it satisfies the discussed critical condition, i.e., locally high D/Pd region with the help of MOS surface film formation on Pd surface.

**Fig. 10**: Evolution of cell voltages; for Exp. D (uppermost graph), Exp. D2 (middle and lower graphs).

**Fig. 11**: Role of MOS (metal oxide semiconductor)-like film on surface of Pd cathode.

[References]
5) E.Storms: "Measurements of Excess Heat from a Pons-Fleischmann Type Electrolytic Cell Using Palladium Sheet", to be publ. in Fusion Technology, see also E.Storms, this Conf. (ICCF3, Nagoya, 1992).