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Anomalous Excess Heat by D_2O/Pd Cell under L-H Mode Electrolysis

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ABSTRACT

A Pd sheet cathode centered within a Pt-wired anode in D_2O/LiOD electrolyte was used 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, associated with very low neutron emission (~1 n/s). To investigate the reproducibility of this experiment, a second experiment with minor changes in cell design was undertaken for 4 months. We reproduced excess heat, however at much smaller levels (8 watts on average and 15 watts at peak), but with neutron emission rates that were twice as large as measured previously. Possible changes in the conditions of the two experiments are discussed; i.e., cell voltages and over-potentials, formation of thin MOS film on the Pd cathode surface and a mechanism enhancing the 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 from many other authors.

1. Introduction

The so-called Fleischmann-Pons effect, [1] i.e. anomalous excess heat generation using a Pd-cathode and a D_2O/LiOD electrolyte, has been confirmed by several groups. [2,3] Some of critical conditions needed to produce excess heat include unusual enhancement of the D/Pd ratio (more than 0.85 as the average for the entire cathode) and critical current density (>200 mA/cm2).

Results of many researches indicate that the phenomenon occurs in the near surface of the Pd cathode. To establish the reproducible excess heat effect, some key conditions are still missing. Those are proposed to be related to surface conditions of the Pd cathode.

The dynamic electrolysis method used by present authors, which once showed anomalously large excess heat, may have achieved the above mentioned critical conditions. The method is based on using a Pd-sheet cathode (instead of thin rod adopted by others) centered in a wire Pt anode and using 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, although the reason for success is not understood.

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

In this paper, we describe the Takahashi method, major results of the first experiment (Experiment-D3)), 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. The critical conditions required to reproduce the Fleischmann-Pons effect are discussed.

2. Experimental Method: Protocol

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

1) Setup: The cathode is a 99.99% pure cold-worked Pd sheet, l mm thick and 25 mm square. As shown in Fig. 1, the electrode-unit consists of a centered Pd sheet cathode and plane-symmetrically wound Pt wire anode (0.5mm diameter, 7 turns with 5 mm pitch). A polyethylene or acrylite rod supports the anode. Minimum cathode-anode distance is 10 mm. This configuration of electrodes is expected to give uniform electrolytic current density on Pd cathode surfaces, hence produce uniform deuteron loading into the Pd sheet. The electrodes-unit is immersed in electrolyte of 700 cc D_2O+0.3 mol/liter LiOD. The assembly is contained in a box-type or cylindrical cell container made of 5 mm thick acrylite. A cooling coil made of Pyrex glass tube, through which temperature-regulated (20ºC ±0.05ºC) light water is fed with 5 - 10 l/min flow rate (very stable for long periods), is also immersed in electrolyte. To stabilize the coolant temperature, computerized chiller/heater equipment is used.

2) Electrolysis procedure: Starting from the beginning of the run, several days (typically one week), the sawtooth-current mode (repeated ramps from 0.25 amp to 5.0 amp with a ~20 min cycle) is applied in order to determine the neutron counts above background . After that, we switch to the L-H current mode (typically, 0.2 - 0.4 amp L-mode for 6 hours, and 4.0 - 5.0 amp for H-mode with 6 hours). This is continued for 2 - 4 months to observe excess 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 for D_2O consumed by dissociation, we add fresh D_2O to the cell every 2 - 7 days. Observation by oscilloscope found no AC power components during the L and H periods, except during the first 10 min after switching.

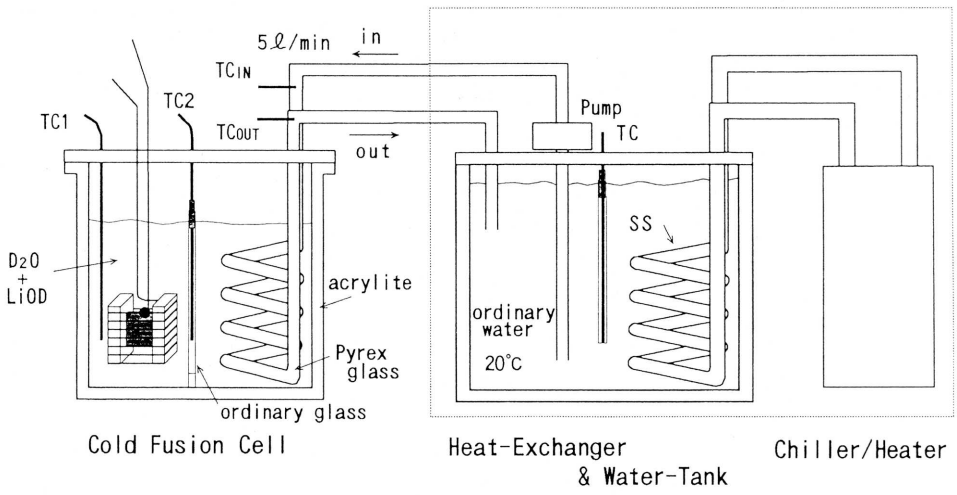

Fig. 1. Schematic view of electrolysis cell for L-H mode operation, and cooling system.

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 the temperature rise. We checked temperature variation in the electrolyte zone, and found it to be very uniform except for regions inside the electrode-unit and close to the cooling coil. Strong stirring by gas bubbles and convection causes uniform cell temperature distribution. Due to the high coolant flow rate (5 l/min for Experiment-D2), 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 $Q^+ = kS(T_e - T_c)$, where Q^+ is the total power being generated by joule-heating of electrolysis plus "nuclear" heating, T_e the equilibrium cell temperature, T_c the coolant temperature where $T_c=(T_{in}+T_{out})/2$, S the effective surface of cooling coil and k the thermal conductivity of the coil. We have ignored heat leaking 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 that $Q^+ = Q^-$. Correction for electrolyte level height is done using the former equation (7% at most for D_2O addition cycle of 7 days).

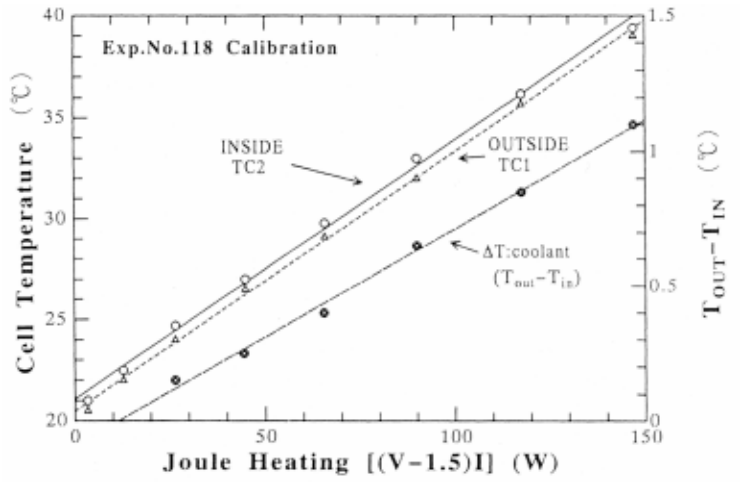

Fig. 2. Calibration for calorimetry for Exp. D2.

For calibration, we used a "dead" Pd plate (Exp. D) or a fresh Pd plate (Exp. D2), assuming no excess heat is produced at the beginning of the run. The calibration run was done by step-wise changing of the current in one-hour cycles. Calibration curves for Exp. D2 are shown in Fig. 2, which proves that the linear relation holds between applied power and temperature rise. We tried a gold plate cathode, instead of Pd, for calibration, but we found a slightly different slope, probably caused by a different bubbling behavior at the Au surface because the electrochemical properties are different. The Delta-T of the coolant is the best monitor of calorimetry in principle, but the accuracy in the present system is not good because only a small temperature rise (less than 1°C) occurs. Sensitivity of the cell temperature is much higher. The temperature difference between the inside and outside is noted as a systematic shift in the ambient temperature compensation circuit used in the data logger. We averaged the 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 in the 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 3He 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 3He(n,p)reaction. We monitor continuously rise-time distribution of neutron signals to check any drift and introduction of gamma and noise signals. No gamma contribution was found in this work. To monitor tritium level of electrolyte, we take a l cc sample of fresh D_2O before addition and a l cc sample of electrolyte every week, which are counted by a LSC (liquid scintillation counting) system.

3. Highlight of Exp. D

The results are shown in Ref. 3. We picked out a few results, which are compared with Exp. D2, as described below. 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. 3a and 3b, respectively for the first and the second month of runs. A steady excess heat of 10 ~ 30 watts is observed on which is superposed heat bursts of 30 ~ 100 watts. This feature resembles the results reported by Pons and Fleischmann. [12] For the two months run, total input energy was 250 MJ, total output energy 410 MJ, which gives an excess energy of 160 MJ. These results would violate the second law of thermodynamics unless there is a hidden source of energy, which is 1000 times greater than any conceivable chemical heat sources in the cell. [3] Neutron emission is also positive, but its rate is only about 1 n/s/source. However, we see correlation with the evolution of excess heat: H-mode gave larger excess heat and larger neutron counts compared to L-mode. In H-mode, when excess heat level increased, the neutron count rates usually decreased. If excess heat were generated by the usual d-d fusion, we should observe 10^{14} n/s. Consequently, observed excess heat can not be due to d-d fusions. A hypothetical interpretation [3] was given based on the multibody deuteron fusion reactions, which emit only high energy charged particles (α, d, t, ^{3}He) as direct products. This mechanism would be expected to produce very low level neutrons as secondary products. Fig. 4 shows the results of tritium observation. We observed meaningful tritium generation in Exp. C [13] (Runs No. 86 & 87) to give (n/t) $10^{-5} \sim 10^{-6}$. In Exp. D (Run No. 115), we find an increase in tritium, but one blank sample (fresh D_2O) also showed an increased level so that we cannot conclude that tritium generation actually occurred.

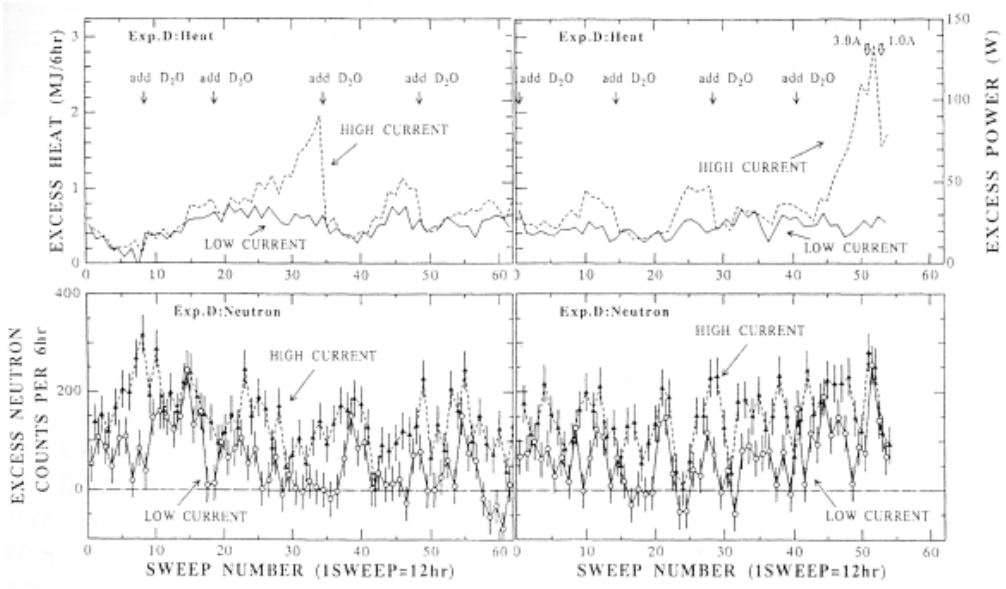

Fig. 3. Evolution of excess heat and neutron yield as a function of sweep cycle number of L-H mode electrolysis for Exp. D. [3] Left: first month. Right: second month.

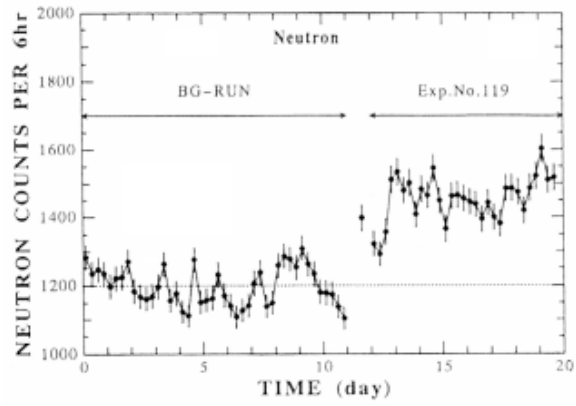

Fig. 4. Observed variation of tritium levels in electrolyte (solid points), compared with background runs (white points).

4. Replication Experiment: Exp. D2

The procedure of this replication experiment is shown in Table 1. To do this, we used a new electrolyte, a new Pd cathode sheet (same batch of Exp. D, batch No. 1 from Tanaka Precious Metal Co.), added one thermocouple (see Fig. 1) in the 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, we started the saw-tooth run. After 2 days of applying the saw-tooth, we found a clear increase in the neutron count rates (see Fig. 5, and continued the saw-tooth mode for a total of seven days. Time-dependent calorimetry within the 20 minute saw-tooth period is difficult since it takes 30 minutes to reach thermal equilibrium, so we took the average value from 3 cycles of saw-tooth-periods to obtain an averaged input and output temperature. The results are shown in Fig. 6, compared with neutron emission rates. We saw excess heat after one day, which gradually increased and reached 6 watts (29% of input) in 7 days.

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)20days
L/H = 0.4 A / 5.0 A14 days
L/H = 0.4 A / 6.0 A20 days
L/H = 1.0 A / 7.0 A20 days
Exp.No. 121 ;Step up Mode (same with Calibration)2 days
Exp.No. 122 ;L/H = 0.4 A / 3.0 A20 days
Exp.No. 123 ;L/H = 0.4 A / 4.0 A50 days

(Electricity in Campus was off for one day btw. Run-1 and Run-2 of Exp. 122.)

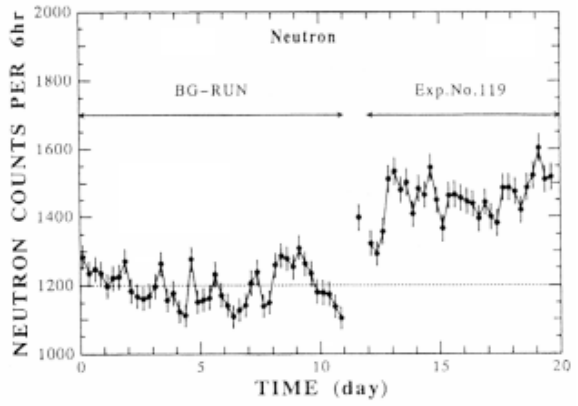

Fig. 5. Neutron generation by sawtooth current mode electrolysis.

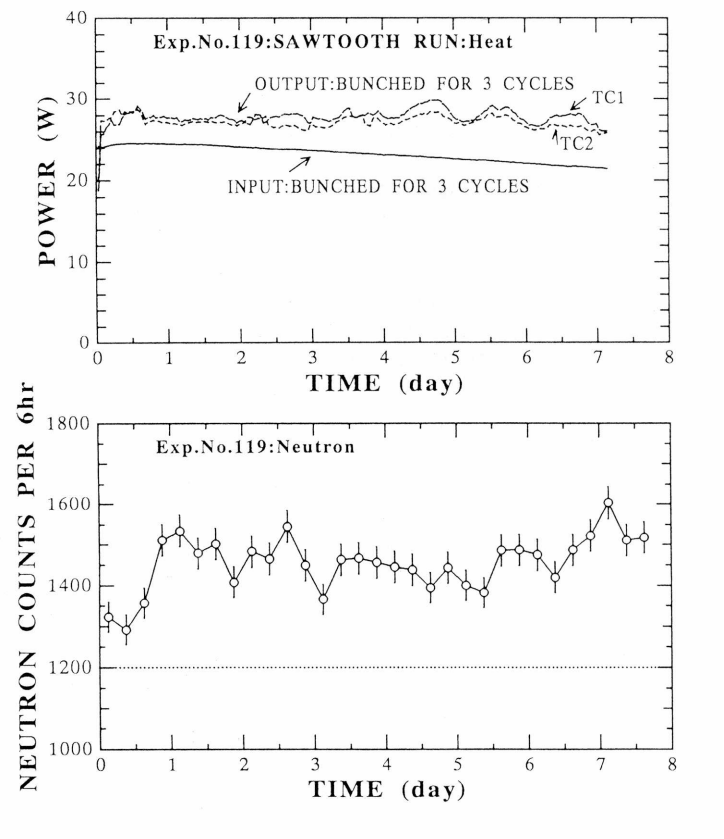

Fig. 6. Evolution of excess heat and neutron yield by sawtooth current mode electrolysis: 3 cycles of data are bunched and averaged.

At the eighth day, we started the L-H mode, which was continued for more than 3 months. During the first month, excess heat was rather constant (6 ~ 10 watts for H-mod and 2 ~ 4 watts for L-mode). We did not see a rapid increase as in the case of Exp. D. The experiment was interrupted twice (in runs No. 122 and No. 123), due to electric power failures at the campus, each lasting about one day. When we restarted electrolysis with L-mode, cell temperature increased slowly from 20.0ºC to a higher value in 6 hours. Excess heat after restart was about half the level before the power failure, and recovered in 2 ~ 3 weeks. After running Exp. D2 for about 3 months, we changed the current level for the L or H modes to measure excess heat at different applied currents, to find out whether there was a systematic connection between excess heat and current density. Typical data is shown in Fig. 7, which shows gradual increase of excess heat over one month. Corresponding excess neutron rates over background (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 one-fourth of that in Exp. D (average). This result is predicted by the multibody fusion theory. [3] Exp. D2 is still running for the 4th month at this writing, 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 fusion. [13]

5. Discussion

To summarize the excess heat observed in Exp. D and Exp. D2, we plotted net gain (output/input - 1.0) as a function of electrolytic current density based on the Pd sheet surface area (~11.5 cm^2), as shown in Fig. 8. The net gain of excess heat decreases as we increase current density, though absolute magnitude of excess heat increases, for both Exp. D and Exp. D2. We observed a 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 calculated excess power per cm^2 of Pd surface to be plotted on the Storms' graph, [14] 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 [15] and burst data of Pons and Fleischmann. [12] It seems that the solid curve by Storms is not the limit. However, high power density (more than 10 watts/cm^2) was observed in bursts and is not controllable yet. We could reproduce excess heat in Exp. D2, but achieving such high magnitudes were different. It seems that we were not aware of essential changes in the 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 the "effective" surface area of Exp. D Pd cathode was much smaller than that of Exp. D2. What is the reason for 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 of the used Pd sheet from Exp. D, and found deposits of Al-27 and Ca-40 in amounts comparable to the amounts of Li-7. Ca-40 might come from Pyrex glass. We do not know exactly from where A1-27 came. Anyway, we can propose that thin MOS-like (metal oxide semiconductor) or MH (metal hydride) layers formed on both surfaces of the Pd sheet. It is interesting that McKubre pointed out the drastic effect of A1 impurity in the electrolyte on causing reproducible excess heat. [16] As shown in Fig. 11, we can speculate that the thin MOS film formation on Pd surface as a "blocking layer" may play a role enhancing cathode over-potential (hence cell voltage) and suppressing deuteron diffusion-out from Pd to cause a locally high D/Pd ratio near the 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, interest has been focused on our recent experiment of deuteron-beam implantation into Pd or Ti foil with thin A1 layer on surface which showed a drastic effect to emitted 8 MeV α-particles (by d-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 the "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.

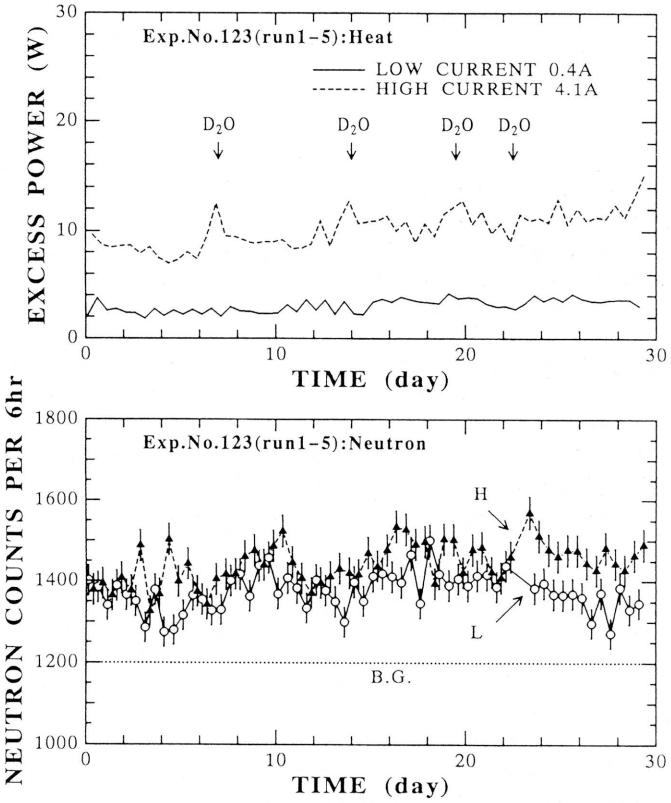

Fig. 7. Evolution of excess heat and neutron yield for one months of run No. 123 of Exp. D2.

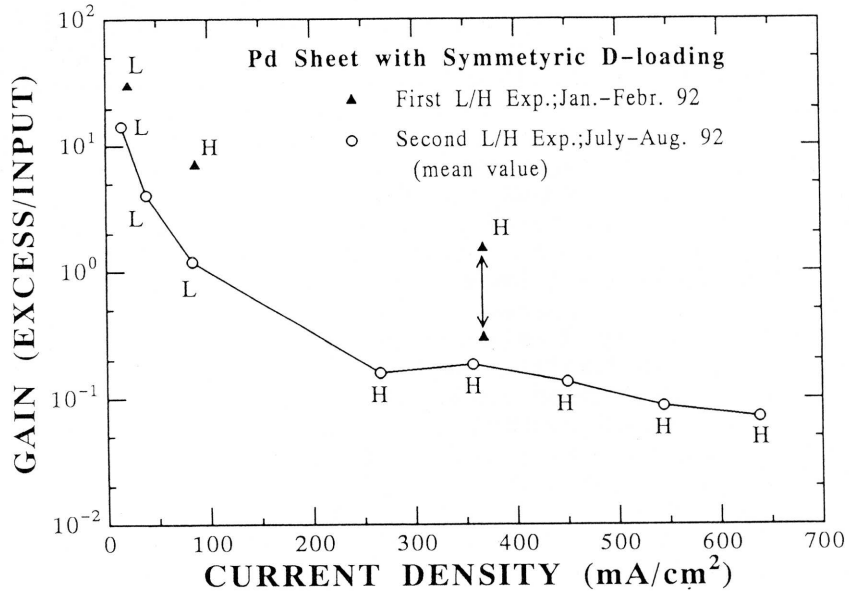

Fig. 8. Gain (output/input -1.0) of excess heat as a function of electrolytic current density.

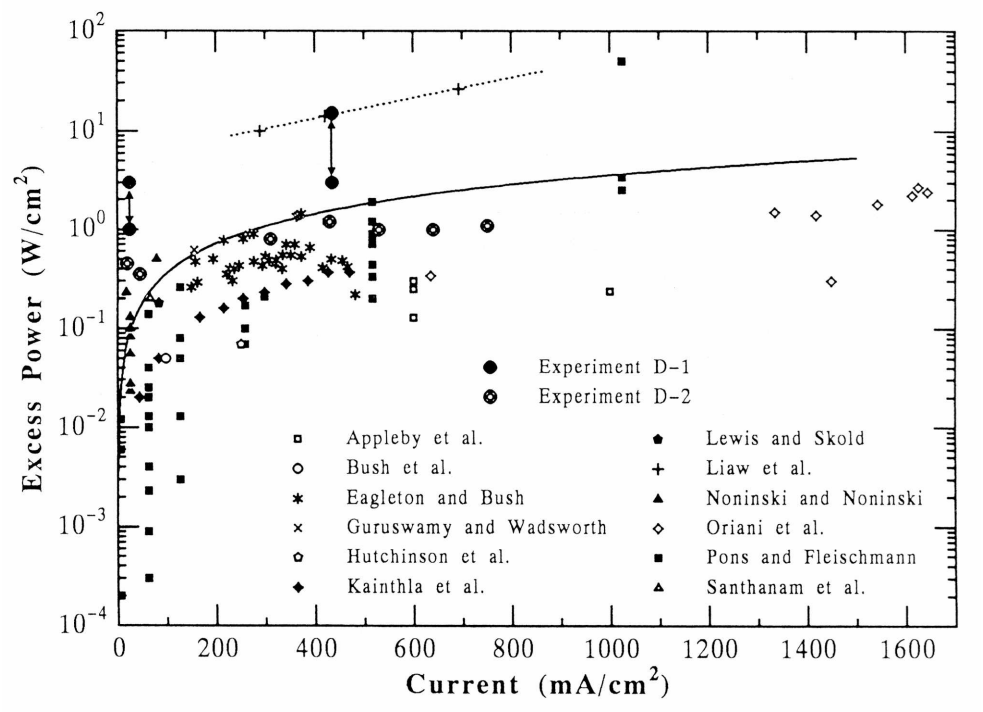

Fig. 9. Trends between excess power per surface area (cm^2) and electrolytic current density. (see Ref. 14)

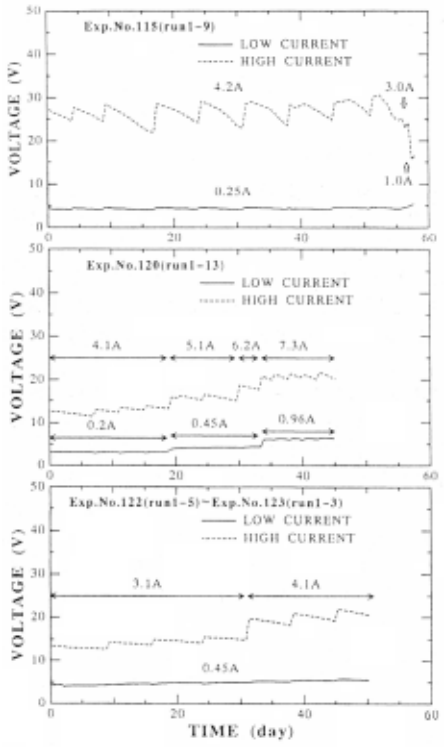

Fig. 10. Evolution of cell voltages for Exp. D (upper graph) and Exp. D2 (middle and lower graphs).

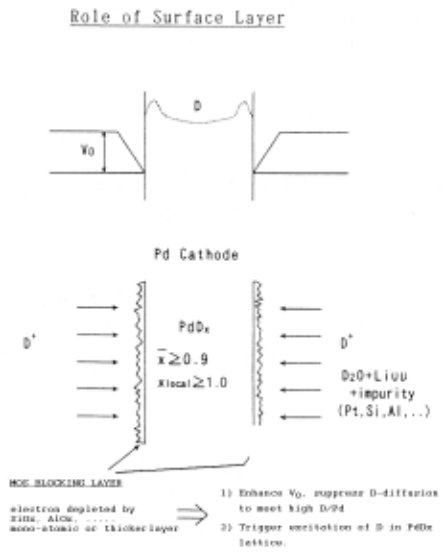

Fig. 11. The role of the MOS-like (metal oxide semiconductor) film on the surface of the Pd cathode.

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