Anomalous Excess Heat by D_2O/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_2O/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_2O/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 (~200 mA/cm^2) are being clarified[2),4)] .

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 the source of excess heat is , 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_2O+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

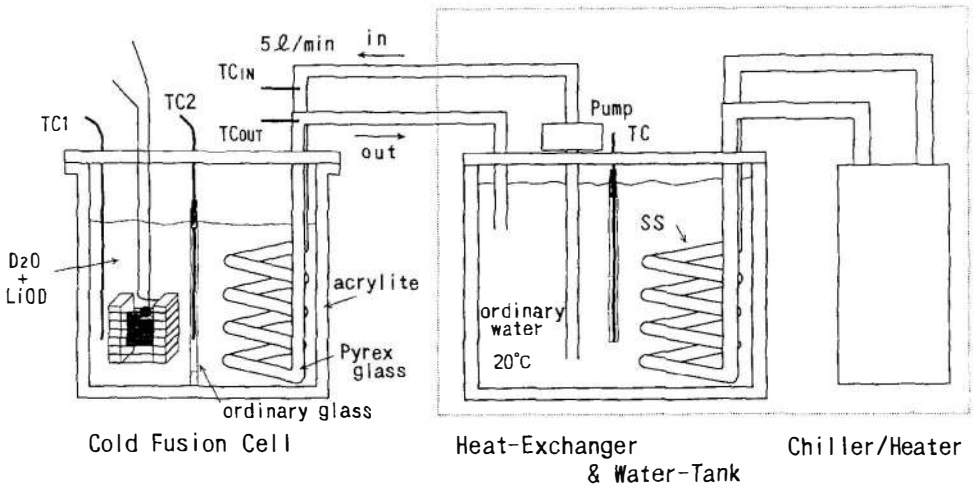


Fig.1 : Schematic view of electrolysis cell for L-H mode operation and cooling system .

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_2O by dissociation , we add fresh D_2O 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 $Q^{+}=kS(T_e-T_c)$, where Q^{+} is the heat source by joule-heating of electrolysis (+"nuclear" heating), T_e 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_2O addition cycle of 7 days).

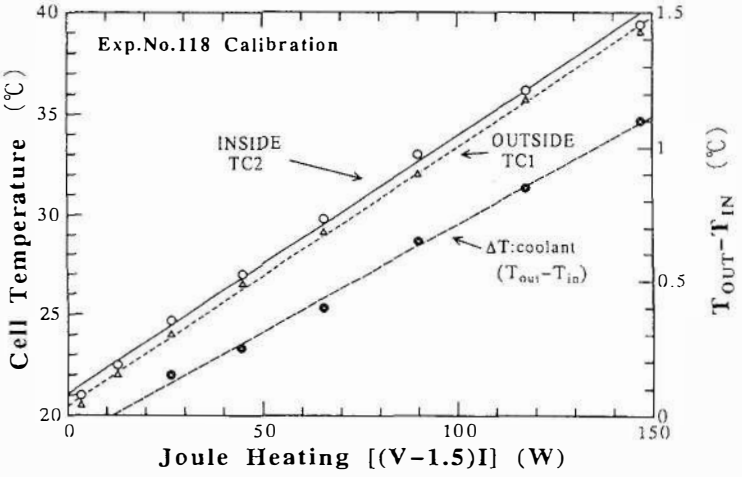


Fig.2 : Calibration for calorimetry for Exp.D2 .

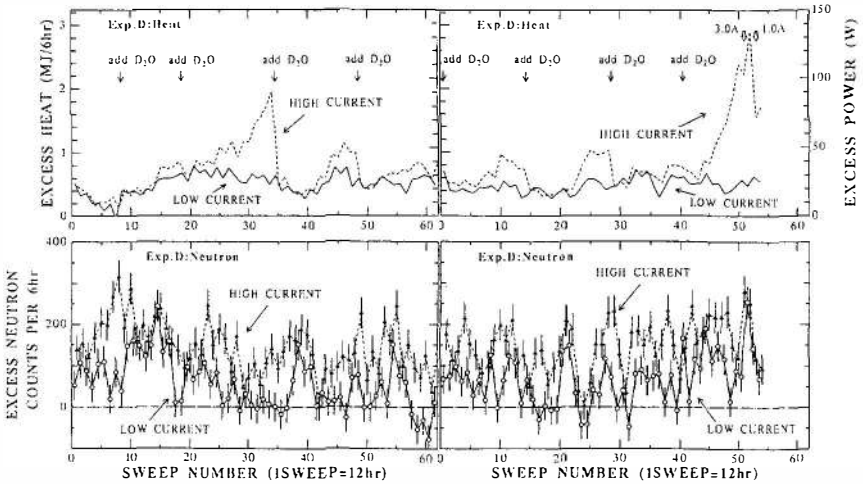
For calorimetry calibration , we used a "dead" Pd plate (Exp.D) or a fresh Pd plate (Exp.D2 , regarding no excess heat at beginning). Calibration run was done by step-wise changing of current for every one hour . Calibration curves for Exp.D2 is shown in Fig.2 , which proves that the linear relation 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_2O 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



a) First one month b) Second one month
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].

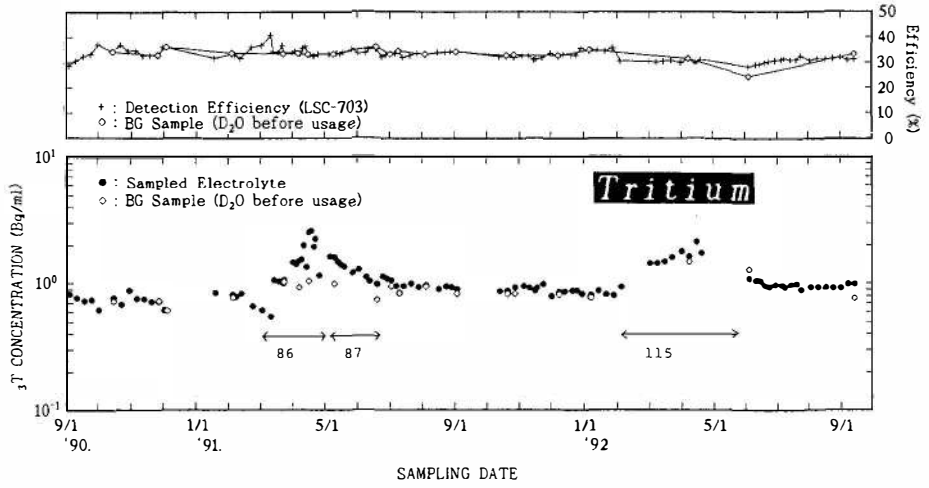


Fig.4 : Observed variation of tritium levels in electrolyte (solid points), compared with BG runs (white points) .

observe 10^{14}n/s/source so that observed excess heats could not be due to d-d fusions . A hypothetical interpretation[3] was given based on the multibody deuteron fusion reactions which emitted only high energy charged particles (α,d,t,^{3}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[13](

No.86 & 87 runs) to give (n/t) ~$10^{-5\text{-}6}$. In Exp.D (No.115 run), we find increase of tritium level , but only one blank sample (fresh D_2O) 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

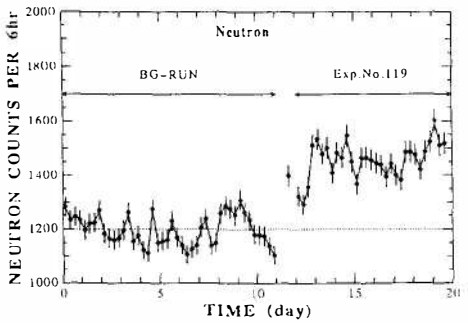


Fig.5 :Neutron generation by sawtooth current mode electrolysis

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.)

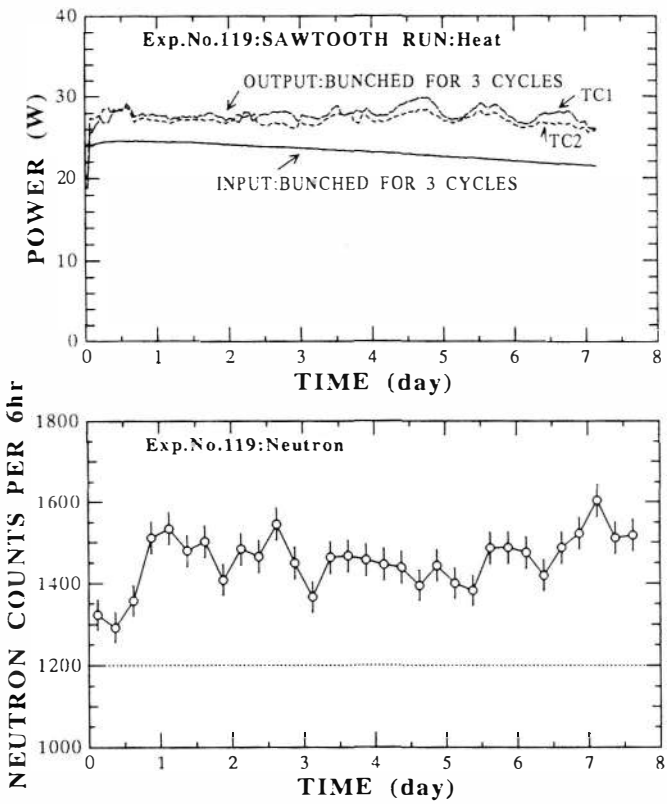


Fig.6 : Evolutions of excess heat and neutron yield by sawtooth current mode electrolysis ; 3 cycles data are bunched and averaged .

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 theory[3]. 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.C[3], which were explained as the consequence of competing process of d-d and d-d-d fusions[13].

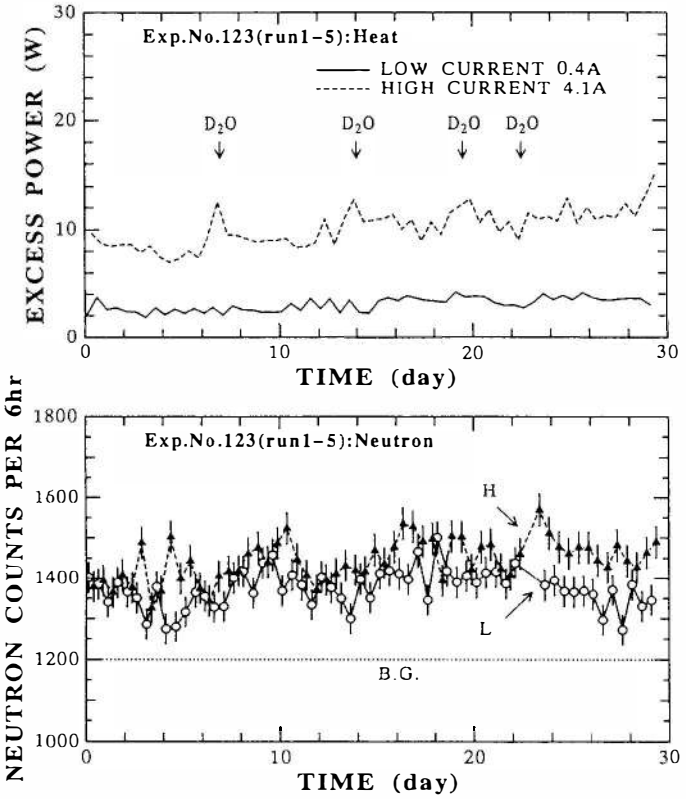


Fig.7 : Evolutions of excess heat and neutron yield for a month of No.123 runs of Exp.D2 .

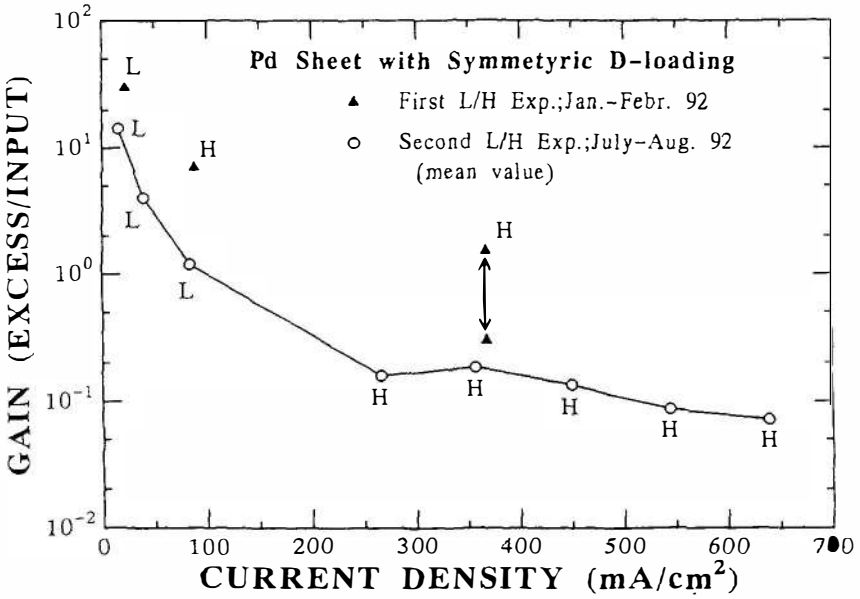


Fig.8 : Net gain (Output / Input - 1.0) of excess heat as a function of electrolytic current density .

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[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-Fleischmann[12] . 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

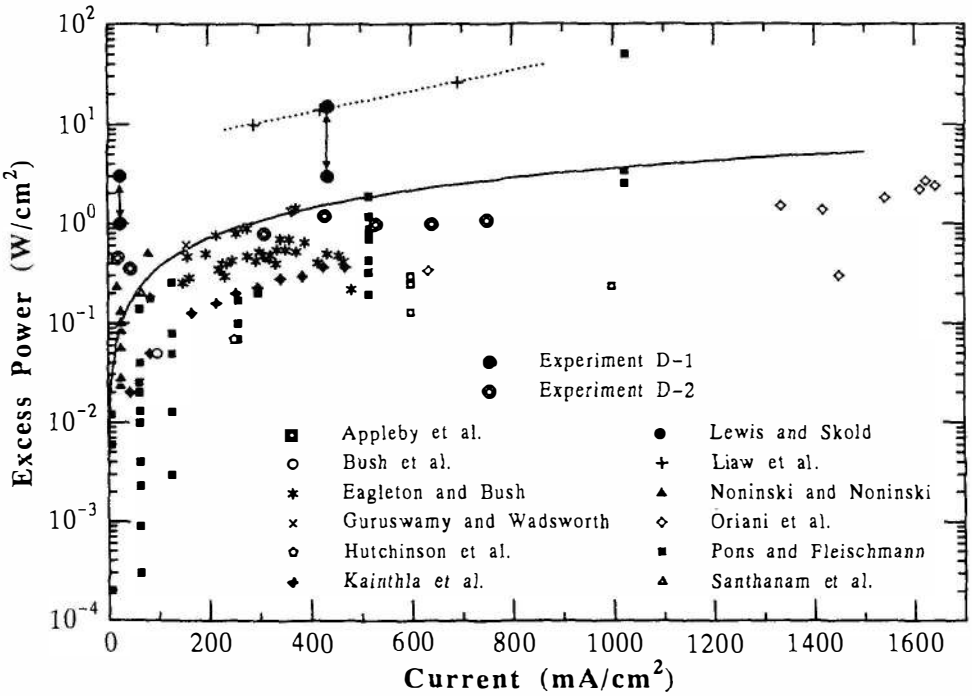
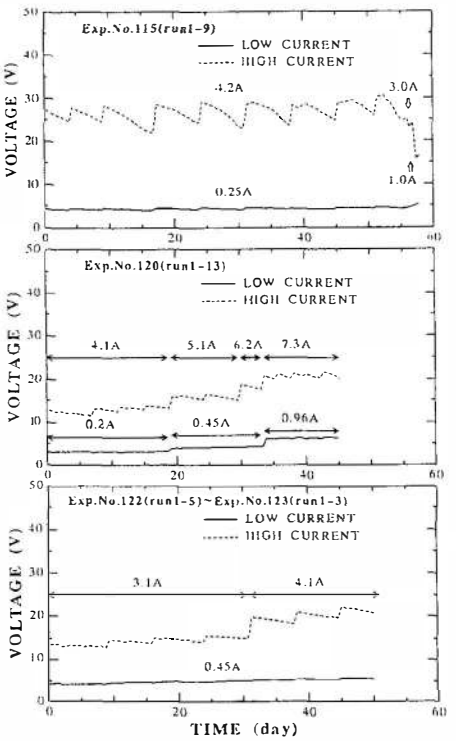


Fig.9 : Trends between excess power per surface area (cm²) and electrolytic current density . (see Ref.14)

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-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 .



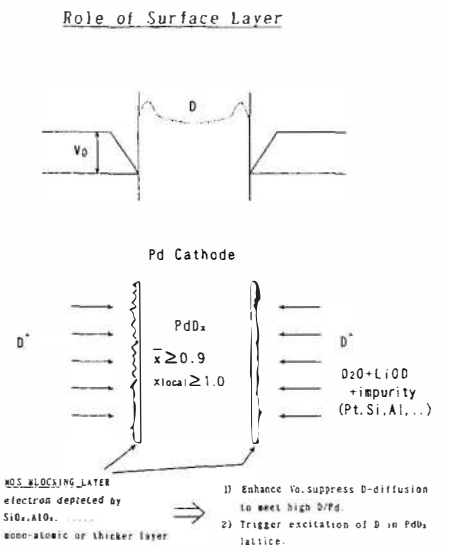


Fig.11 : Role of MOS (metal oxide semiconductor)-like film on surface of Pd cathode .

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

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