Measurements of Excess Heat and Tritium during Self-Biased Pulsed Electrolysis of Pd-D$_2$O

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ABSTRACT

After Takahashi reported large excess heat with pulsed electrolysis, we built a gas-closed flow calorimeter to perform pulsed current electrolysis. Blank tests using Au plate cathodes were carried out to characterize the system. Four cold-worked Pd sheets were tested, and two of them produced 7.5% and 6% mean excess heat for many weeks. The others Pd sheets did not produce excess heat in most tests, although one of them, after deuterium reloading, produced up to 25% excess heat, but only for few hours. Tritium analysis was carried out and some coincidence between tritium production and excess heat was found.

1. APPARATUS

We constructed an electrolytic system [Fig. 1] using a cylindrical polyethylene vessel (12 cm diameter, 7 cm high, 1 cm thick) as an improved type of that reported by A. Takahashi. [1]

To cool the cell we installed a double ring (two coil) copper coil, which is coated with nickel and covered by acrylic resin). An electric heater (1.2 kW maximum power) was placed on the bottom of the vessel; like the cooler, it was nickel coated and covered by acrylic resin. The use of this particular insulation is required to avoid contamination of the electrolytic solution due to the aggressive concentrated base (0.3 M/l of LiOD or LiOH). The cathode was a sheet (2.5 cm, 2.5 cm, 0.1 cm), and the anode was Pt wire (100 cm long, 0.05 cm of diameter) wound in a spiral around the cathode. The electrodes were separated by 1 cm Teflon bars and located at the center of the bottom of the vessel; a diagonal Pt wire (0.05 cm diameter), 0.3 cm from the surface of the sheet, was used as the voltage reference electrode.

A 1 cm thick Ni rod, similar to the inner temperature sensor, was put very close to the electrodes. Three Pt short wires (1, 1.5 and 2.5 cm long) were put on the top of the vessel and used to sense the solution level.

All the materials used into the vessel were tested against unwanted poisoning of the solution.

The vessel was thermally insulated from environment by 5 cm thick polystyrene and 7 turns of aluminized Mylar.
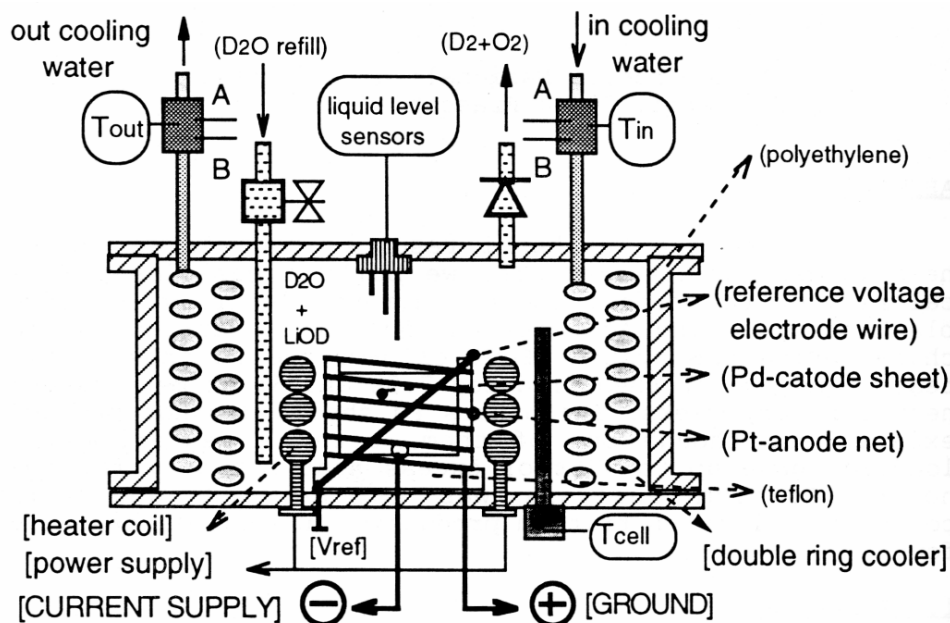
Figure 1. Inner vessel.

The cooling system [Fig. 2] consists of an inner coil, a peristaltic pump and a water bath; the cooling liquid is ordinary water.

The inner coil (0.5 cm of diameter and 4 m long) was modified to improve the cooling efficiency of the cooling fluid. The computer-controlled peristaltic pump was used to provided constant cooling, which can remove heat at different rates by varying the flow rate 0.5 and 30 ml/s.

The water bath keeps the input cooling water at a constant 17°C.

Seven temperature sensors (Si device, AD590) are used. Their sensitivity is 1 μA/°C. Using a 10 KΩ loading resistor in the circuit, we get a value of 10 mV/°C through an operational amplifier (OP227). The most important sensors placed outside the vessel, the input and output of the cooler, are doubled. This configuration gives redundant independent measurements of the output thermal energy.

The outgoing gases from D_2O dissociation are sent into a closed system as shown in Fig. 3. The solution is warmed by electrolysis; a bottle is used to condense the vapor. Two optional large volume rubber balls are used to collect the gases and vacuum/over-pressure pump is used for pressure operating tests. A recombiner (gas diffusion electrode, E-TEK, USA), working at room temperature, is placed into a bottle to recombine the D_2 and O_2 gases into D_2O. The D_2O is routinely collected both for periodic tritium analysis and measurement of dissociated water (to check against self-recombination into the electrolyte vessel). Two pressure sensors (one analog c and the other digital) are used. Two in-line low-drop pressure valves are used to avoid gas return to the vessel from the recombiner (mainly CO_2). A Teflon tube inserted into the vessel is used to refill the D_2O.
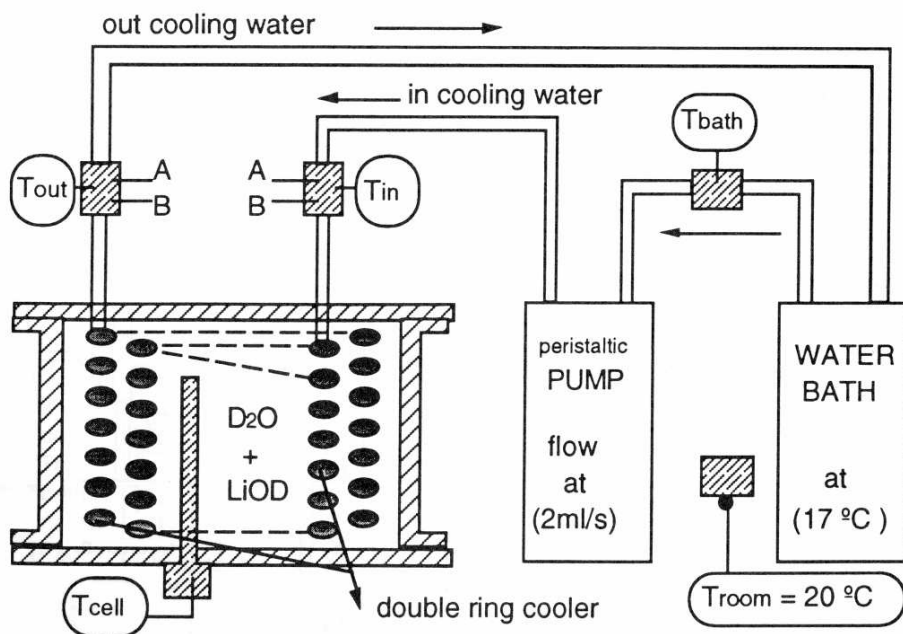
Figure 2. Cooling system.

A custom made circuit [Fig. 4] was used to control the constant-current generator in order to perform time dependent electrolysis. The typical shapes used were a 20 minutes period, 0.25 to 5.1 A; a saw-tooth wave with a half-period of 20 to 360 minutes; and 0.25 to 7 A square wave. The wave controller is auto or manual, with time and amplitude selectable.

Two fast recovery-time high power diodes (IR, mod. 40HFL80S05) were inserted between the generator and the electrodes to avoid a deuterium deloading from the Pd cathode during the fast transition current edge[3]: a reverse voltage polarization can occur for short time in this condition.
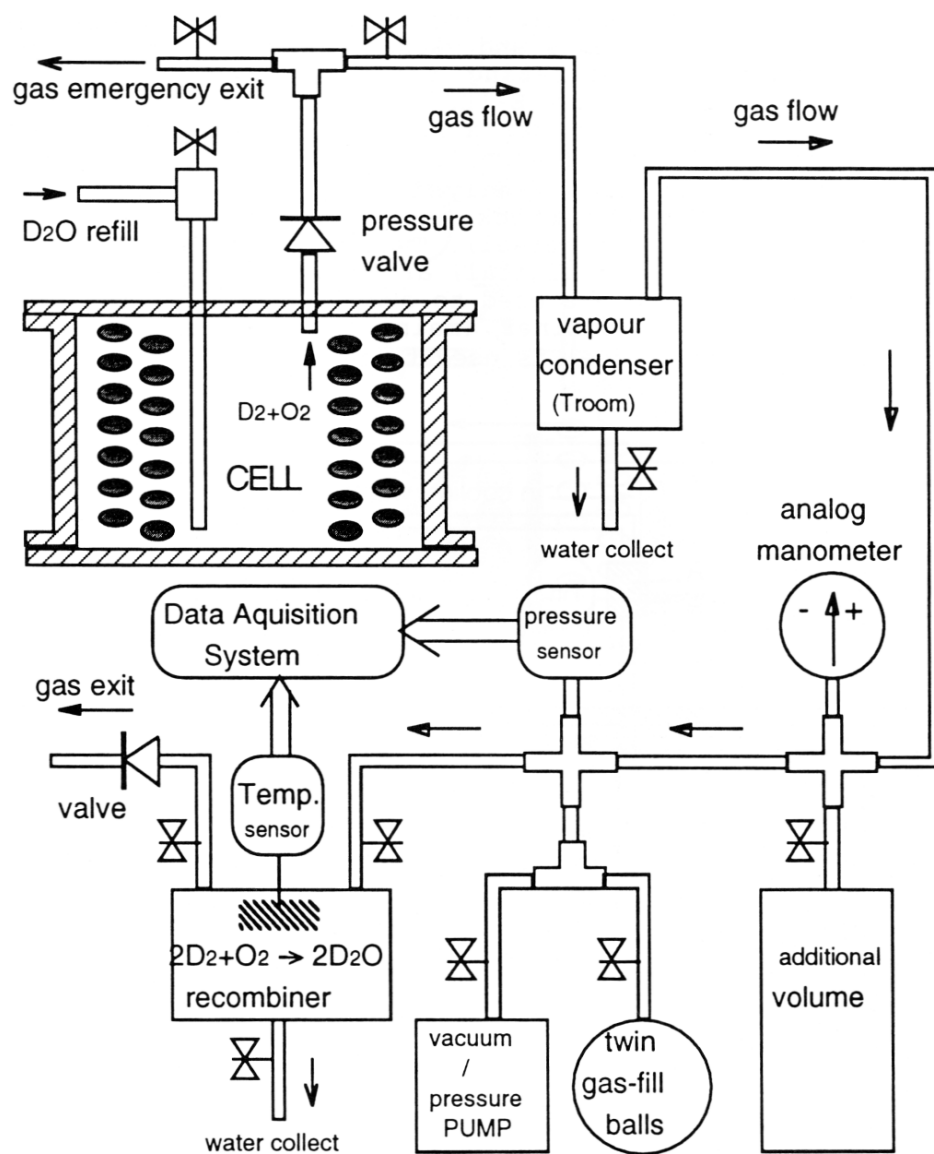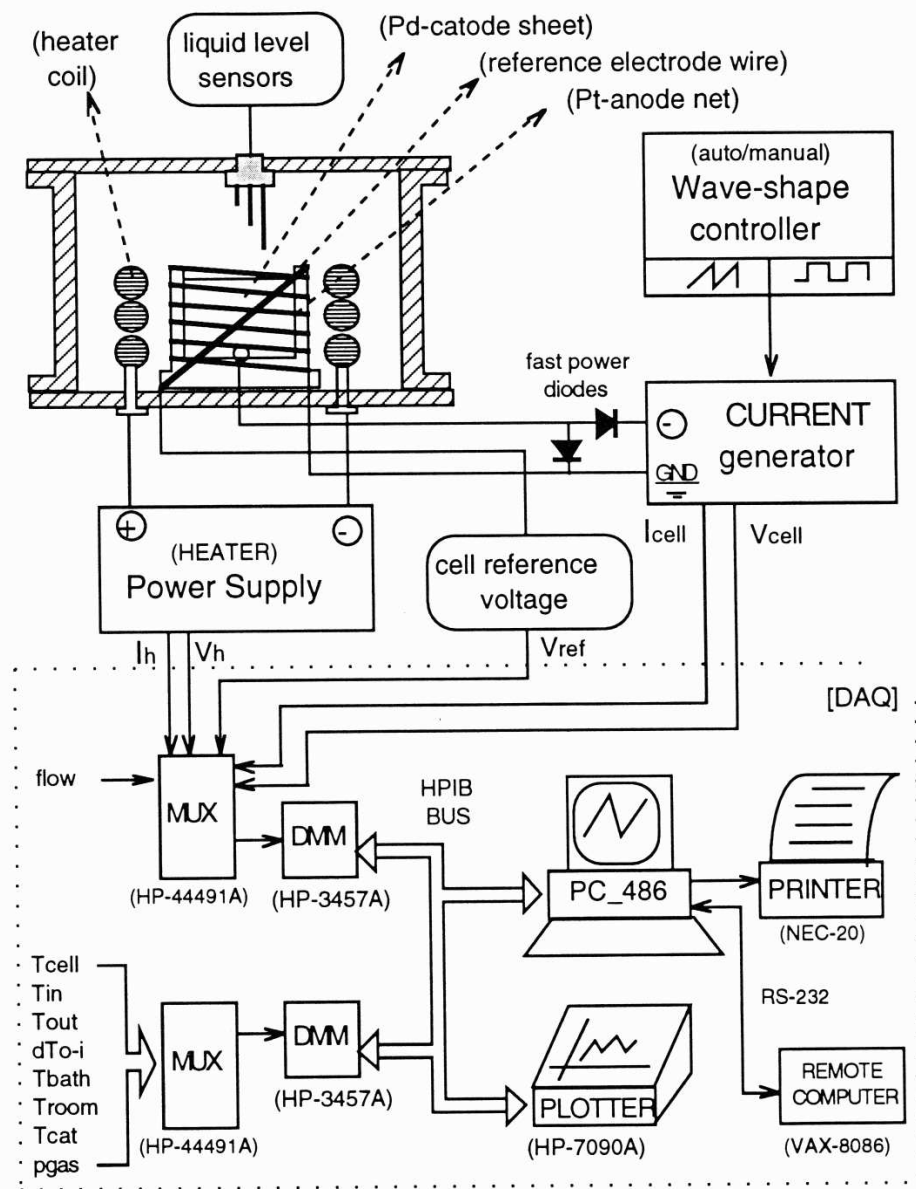
Figure 3. Gas system.

Figure 4. Power supply and data acquisition system.

An independent voltage generator is used to supply the inner heater for calorimetric calibration.

All the electric and thermal parameters were computer acquired by an IEEE488 bus connected to two multiplexed 6.5 digit sensitivity DMM (HP-3457A). The following data were collected: seven temperatures (absolute and differential inlet and outlet cooling fluid, inner vessel, water bath, recombiner and room temperature), current and voltage of the vessel, reference cathode voltage, outgoing gas pressure and peristaltic pump flow. Three of these parameters were independently selected and on-line plotted by a high resolution color graphics plotter (HP-7090A).

A PC-486 computer was used to monitor and acquire the parameters and linked to remote computer (VAX-8086) to store and off-line analyze the data.
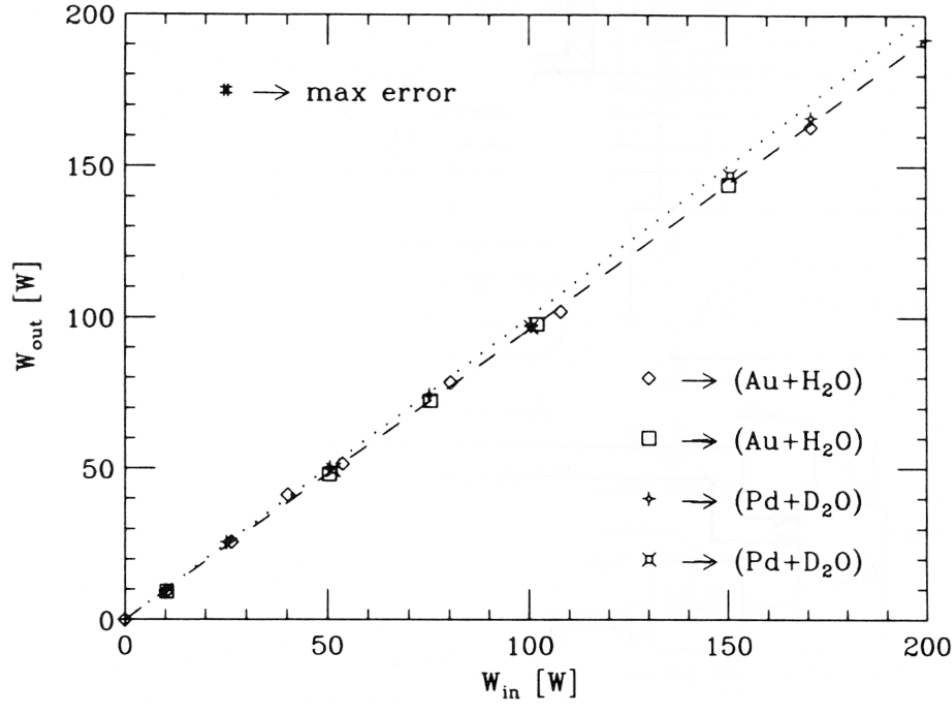

Figure 5. Calorimeter thermal calibration.

## 2. CALIBRATION AND EXPERIMENTAL PROCEDURES

We performed two different types of thermal calibration: electric calibration, using the inner heater, and electrolytic calibration during the electrolysis with an Au plate cathode. Generally, the calibration was performed before and after an experimental run. Fig. 5 shows calibration data ranging over 1 month performed in 4 different ways, varying the electrode type (Au or Pd) or the electrolyte (LiOH+H_2O or LiOD+D_2O).

The data show the linearity and stability of the calorimeter up to 180 W of input power, calculated as the product of the voltage times the current at the heater, in respect to the output power (watts) calculated as:

$$W_{out} = K \cdot \phi \cdot \Delta T \tag{1}$$

where K= 4.184 J · /(ml · K) is a constant conversion factor taking into account the specific heat of cooling fluid (light water), ϕ is the cooling fluid flow in ml/s, ΔT is the temperature difference between the output and the input of the cooling fluid. The slope difference between the ideal curve when no heat is lost to dissipation (the dotted line in Fig. 5) and the straight interpolation curve of the data is 4 ± 1%, because the thermal conductivity of vessel walls and water vapor. This slope difference is 5 ± 1% in case of electrolytic calibration, with an Au cathode and LiOD+D_2O solution. The increased dissipation is almost all due to the energy loss to effluent gases. The sensitivity of the calorimeter depends on the flow rate. It is 0.418 W/(ml/s)

when the cooling fluid is water; the resolution, dependent on thermometers sensitivity and flow stability, is estimated to be about 1.5%.
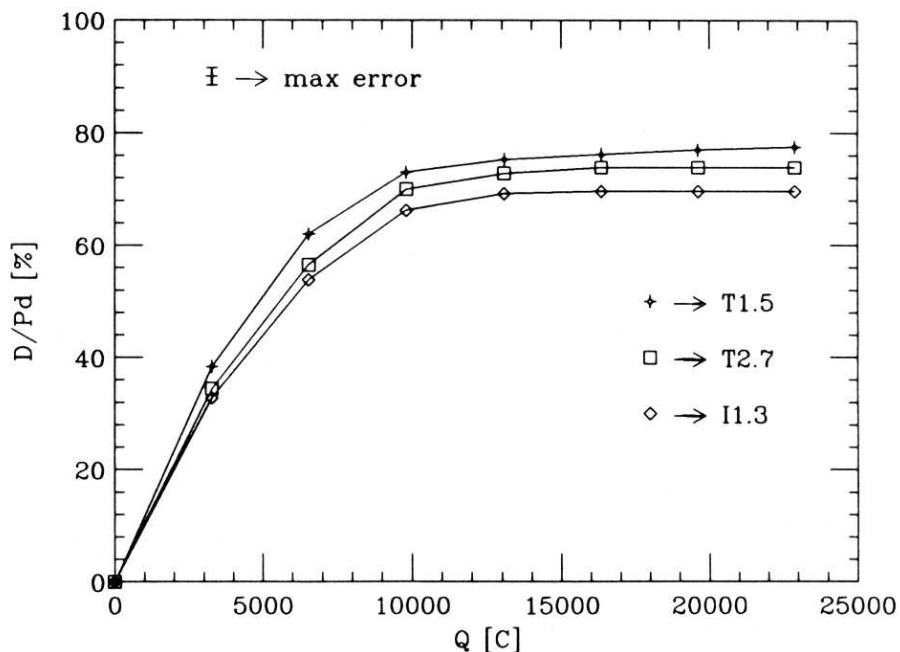
Figure 6. D/Pd ratio for 3 different Pd sheets.

A specific procedure was adopted to measure the quantity of D adsorbed into the Pd cathode. During the first 6 or 7 current saw-teeth, the recombiner was excluded and the pressure of electrolytic gases ($O_2+ O_2$) was collected into a container with a known volume. Some D was absorbed by the cathode, leaving leftover O_2 gas in the headspace. We calculated the charging ratio, D/Pd, based on the gas pressure of this leftover O_2. After the sixth current ramp the sensitivity of the pressure measurement became too low to estimate the D/Pd ratio. After the tenth ramp we opened the recombiner to the gas system. Fig. 6 shows the D/Pd ratio versus the electric charge between the electrodes for three different Pd sheets: each data point in the plot corresponds to the D/Pd value cumulated during a ramp. A later D/Pd independent check, based on D_2 gas evolution during Pd discharging at the end of the experiment (with no current applied to the electrode) gave similar results. We estimated, based on the latter, that the equilibrium ratio is 0.67 at STP.

Several tests were performed to study the electrolytic processes and characterize the calorimetric system.

Blank tests were performed using an Au cathode sheet, and an electrolytic solution of 0.3 M H_2O+LiOH or D_2O+LiOD. Power input was pulsed current, as described above: ramp current from the beginning of the test (for a half day maximum) and then square wave current (for several days).

The D_2O from the recombiner was periodically collected and its tritium contents was analyzed.

A neutron detector (REM counter) was located very close to the vessel to monitor large neutron emissions, only for safety reasons.

3. RESULTS

During two months of experimentation, 4 cold-worked Pd sheets made by two different Japanese Firms were tested: Tanaka Kikinzoku K.K. batch #1 (designated here Tl.2 and Tl.5, with Vickers hardness 155+170 at 200g-10s) and batch #2 (designated T2.7) production (Vickers hardness 145), and IMRA Industries batch #1 (11.3) production. Similar Pd sheets from Tanaka batch #1 and #2 were tested by E. Storms. [2] Table 1 shows a list of all the tests.

No excess heat (±2%) was ever detected during the blank runs.

No excess tritium (±3%) was detected during the blank runs apart the enrichment due to electrolysis, computed with a value of 2 for the isotopic separation factor. The Tl.2 Pd sheet gave excess heat up to about 12% maximum (=4 W of =30 W mean input power), two days after the beginning of the run [Fig. 7]. At the beginning, the current was ramped for 1 day and the excess heat occurred just some hours after the start run. During the following 5 days, with square wave current, the mean excess heat was about 7.5%. After that we retried ramp current, hoping to increase the excess heat by a D over-loading into the Pd, but the excess heat decreased.

Table 1. List of Tests Performed

TEST	DENSITY G/cm^3	DATE d/m/y	CURRENT A	ΔE/E %	TRITIUM (excess)	NOTES
HEATER	----	2/8/92 3/8/92	DC	----	----	calib
Au/Pt LiOH+H$_2$O	----	3/8/92 4/8/92	ramp+sqr max (4A)	----	----	blank
Au/Pt LiOD+D$_2$O	----	4/8/92 6/8/92	ramp+sqr max (4A)	----	± 3%	blank
Pd/Pt [T1.2]	= 11.8	6/8/92 25/8/92	ramp+sqr max (5A)	12% max < 7.5% >	(26%)	D/Pd >0.75
Au/Pt LiOD+D$_2$O	----	7/9/92 12/9/92	Ramp+sqr max (5A)	----	± 3%	blank
Pd/Pt [11.3]	11.99	12/9/92 22/9/92	Ramp+sqr max (7A)	< 2% (25% peak)	(18%)	D/Pd=0.69 (=0.84)
Pd/Pt [T2.7]	11.99	23/9/92 2/10/92	Ramp+sqr max (7A)	< 2%	unknown	D/Pd=0.72
Pd/Pt [T1.5]	11.75	3/10/92 24/10/92	Ramp+sqr max (7A)	8% max < 6% >	(36%)	D/Pd=0.79 running

After 3 days of ramp current we switched again to square wave current and the excess heat returned to an average value of 7.5%, lasting for 10 days. The test was interrupted abruptly when an extended power blackout occurred. Overall excess heat of about 3 MJ were produced in 19 days. Because we did not measure the maximum D/Pd charging value at the beginning, we estimated this value (>0.75) when the plate was discharged. A total of +26% excess Tritium

(+240 dpm/ml) was measured from the recombined D_2O water collected, taking into account the enrichment factor (≈2) of the tritium in the solution.

The 11.3 Pd sheet did not produce significant excess heat up to 7 days so we decided to stop the current supply for 12 hours, letting the Pd electrode deload the overcharged deuterium. After that, we restarted the deuterium loading with some current ramps: the D/Pd reached the value of 0.84 ±0.04 starting from 0.67 (D/Pd value at equilibrium at STP); we note that the previous first charging up D/Pd value was 0.69. After this reloading, we used square current further increasing the high level from 5.1 up to 7.2 A. After this operation the excess heat reached the 25% peak value lasting just some hours. During the 2 days following no significant excess heat appeared [Fig. 8]. We added borosilicate to check if glass contamination can help the D adsorption on Pd surface, but it did not produce significant effects. The overall excess tritium produced was estimated be around +18% (+172 dpm/ml).
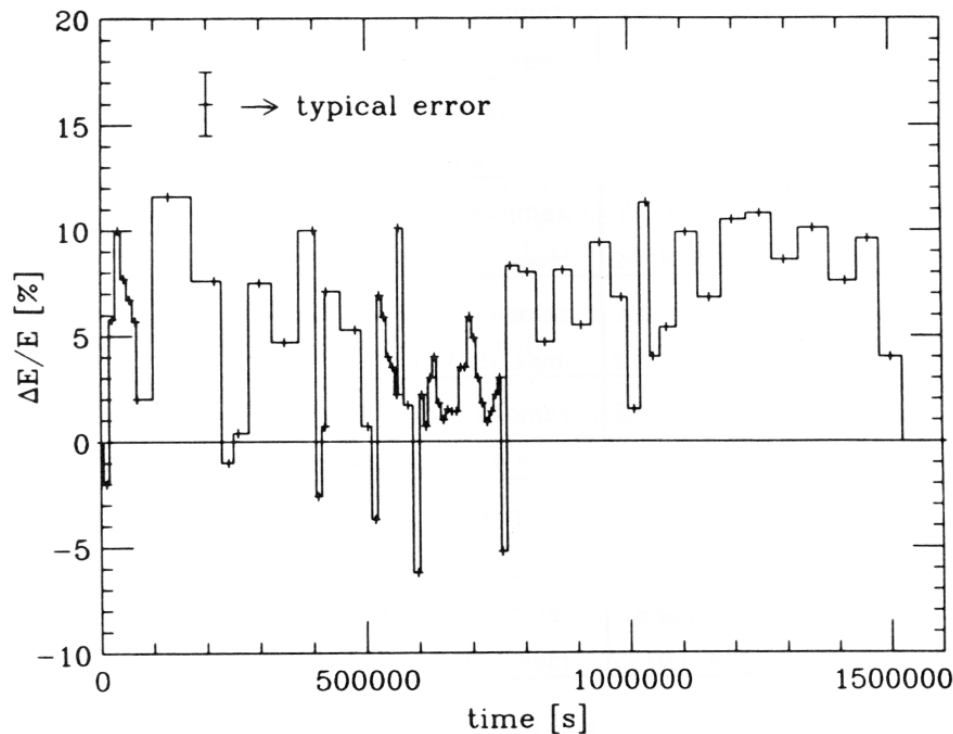
Figure 7. The T1.2 Pd sheet gave excess heat up to +12%.

The T2.7 Pd sheet, operated in the same conditions of the previous sheets, produced no significant excess heat (<2%) during 9 days of experiments.

The Tl.5 Pd sheet gave the highest D/Pd value on the first charging up (D/Pd =0.79). After 2 days of current ramp, the current square wave was selected and the excess heat started from 4% (+2.5 W of about 60 W mean input power) increasing to about 6% in about 67 hours [Fig. 9]. After this time a peristaltic pump failure occurred, so that the current was put to low value (0.25 A) for many hours. Excess tritium, measured until the pump failure, was +36% (+340 dpm/ml).

After the pump was fixed, the test was restarted and the Pd sheet continued to produce about 5% mean excess heat for many days. This Pd sheet is still running at this writing.

The reference voltage, from the diagonal Pt wire in front of the cathode, was always acquired and under study. It has been observed a sort of correlation between this parameter and the deuterium adsorption into the Pd.
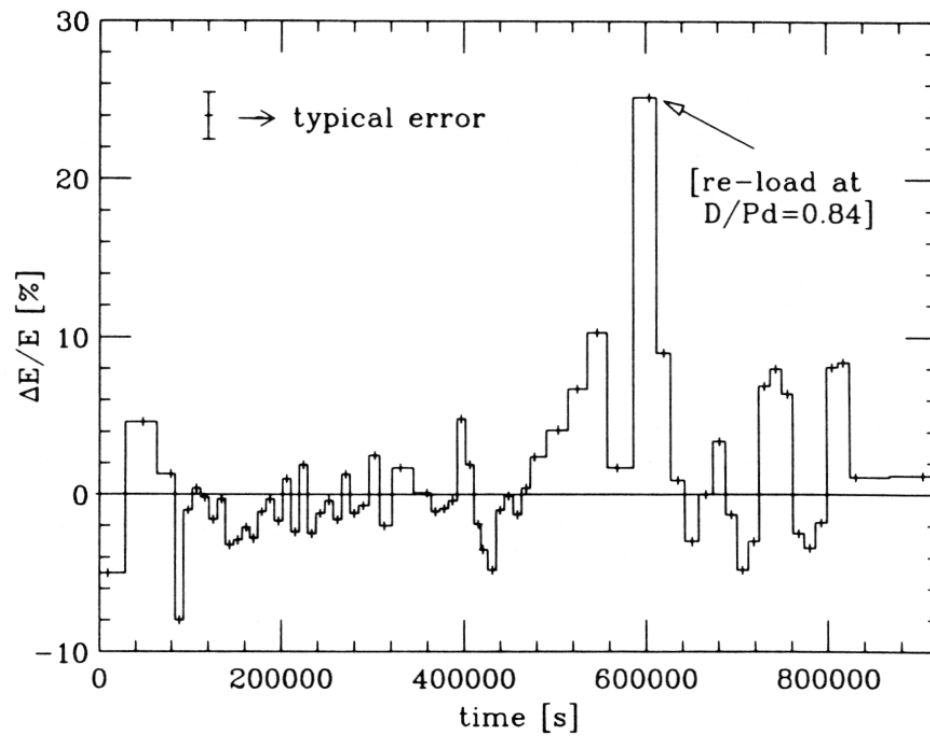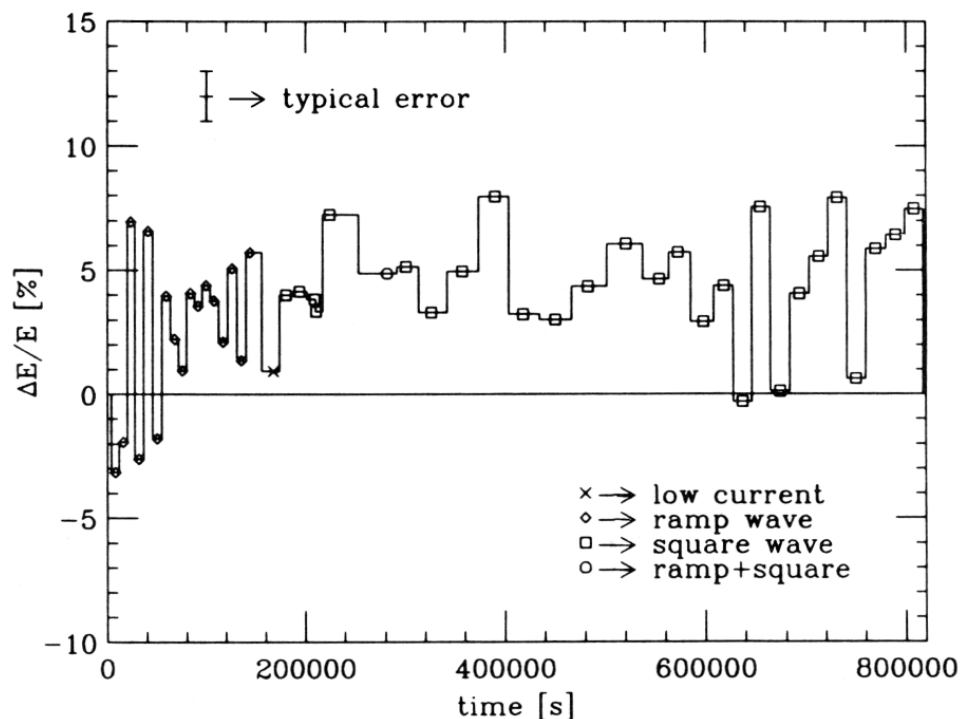

Figure 8. The I1.3 Pd sheet gave once excess heat of +25% for a short time.

Figure 9. The T1.5 Pd sheet gave excess heat of about +5% for a long time.

Because this parameter involves the conductivity and the temperature of solution, apart the electric charge status of Pd-Pt pile, the correlation with the D/Pd parameter is not yet completely clear.

Looking at table 1, the D/Pd seems correlated to the mass density of the Pd sheet in this way: the D/Pd ratio increases if the mass density decreases.

4. CONCLUSIONS

Based on the tests we performed with our cold-worked Pd sheets, we can say that a high sensitivity flow calorimetry is required to observe excess heat with certainty at low levels (5%).

The self-biased pulsed electrolysis, with a proper circuit, seems able to reduce the long deuterium charging time to a few hours and the excess heat generally appears some hours later; the excess heat is strictly correlated to a high D/Pd charging ratio (> 0.75)

Our data appears to show some correlation between excess heat and low mass density (lower then the 12 g/cm^3 "standard" value) in the two Pd sheets.

Excess tritium seems to be produced when excess heat is obtained, albeit in small amounts.

In conclusion, the metallurgy of the Pd electrodes plays a very important role for both high D/Pd ratios and large excess heat. Moreover, the deuterium charging methods (pulsed current) strongly helps the production of excess heat.

ACKNOWLEDGEMENTS

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