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New Kinds of Electrolytic Regimes and Geometrical Configurations to Obtain Anomalous Results in Pd(M)-D Systems

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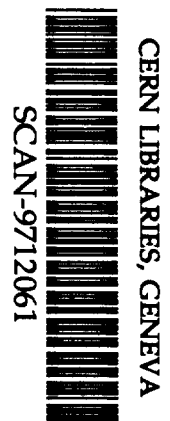
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1 – Abstract

Electrolyses of long and thin Pd (and PdY alloy) wires, in dilute solutions of LiOD-D₂O and LiOH-H₂O at large operating voltages, were made. An innovative kind of geometrical set-up to improve the efficiency of electromigration effect in proton conductors was developed: the usual "single-ended" geometry at the most cathodic point of the wire changed to the "central wire" geometry. The detected excess heat seems to be related to: (H/D) isotopic effect, lattice characteristics, geometrical set-up, dynamic variation of concentration inside Pd wire, anode-cathode and inter-cathodic voltages.

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2 – Motivation

The rationale of the experiments were:

- A) development of new experimental procedures in order to determine the *origin* of any anomalous effects (excess heat and/or nuclear ashes) during and after the electrolysis of Pd(M)–Pt in LiOD–D₂O solution. Because these reasons, we selected 3 control parameters:
 - A1) on–line resistance ratio R/R_0 (loading);
 - A2) excess heat (by *isoperibolic* and *flow* calorimetry);
 - A3) off–line detection of "new" elements at the cathode surface (by SEM analysis);
- B) making large efforts in order to improve the *reproducibility* of the anomalous effects, even though at *low intensity*.

3 – Experimental set–up and procedure

In respect to our previous experiments [1], we developed a new geometry of the system named "*wires, twisted pair*" [Fig. 1]. The Pd wires were very long (160 cm) and thin (100 μm), faced (1 cm distance) to Pt wire (1 mm diameter). The Pd geometrical dimensions and physical parameters were: $78 \cdot 10^{-6} \text{ cm}^2$ of cross–section, 5 cm^2 of total surface area, $12.5 \cdot 10^{-3} \text{ cm}^3$ of volume, 150 mg of weight and 20Ω of initial electrical resistance. In case of PdY alloy, see later, the initial resistance was 50Ω at NTP.

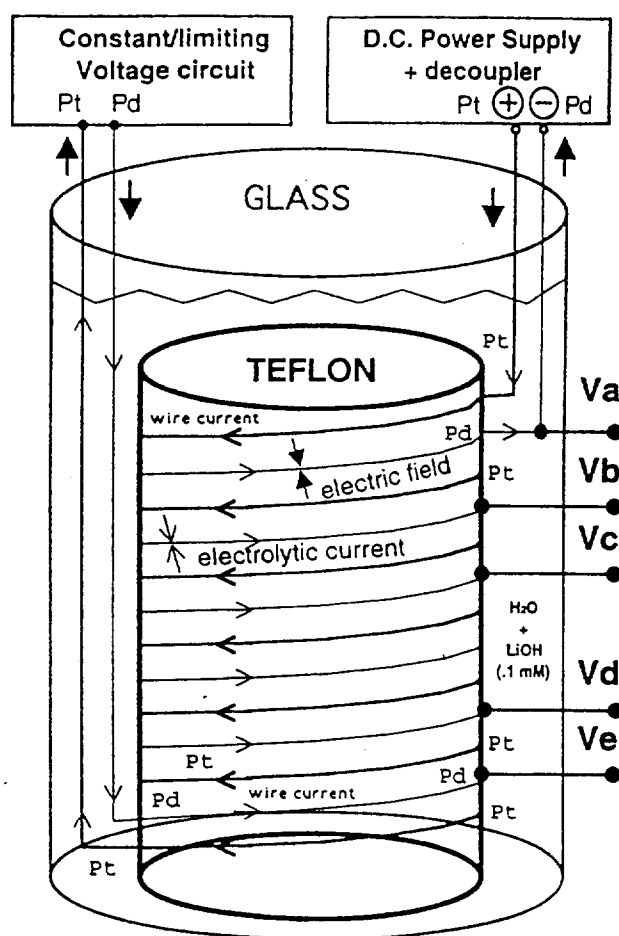


FIG. 1 – Electrolytic cell, Pd/Pt double twisted wires on Teflon cylinder sample–holder.

The main drawback of this kind of geometry is the electrolyte resistivity. Usually, this parameter is enough low (few $\Omega \cdot \text{cm}$), at the LiOD concentration typically used in Cold Fusion experiments (0.1 – 1 N), and changes over time because temperature and several ageing effects. It can strongly affect the measurements of wire resistance because of unpredictable paralleling effects.

In our experimental conditions we used an electrolyte concentration in the range 0.1 – 1 mN. Overall, a quite innovative electronic circuitry and experimental set-up [Fig. 2] was developed: in principle, it *eliminates* all the problems related to electrolyte variations because the anode is almost not connected to reference ground for AC signals (used for measurement of cathode resistance) and the effective AC current flowing at the wire end is also measured. Moreover, this circuitry is able to detect sources of errors, in the computing of Pd wire resistance, arising from: instabilities and/or leakage of "voltage to constant current converter" [Fig. 3] and "high impedance booster" [Fig. 4].

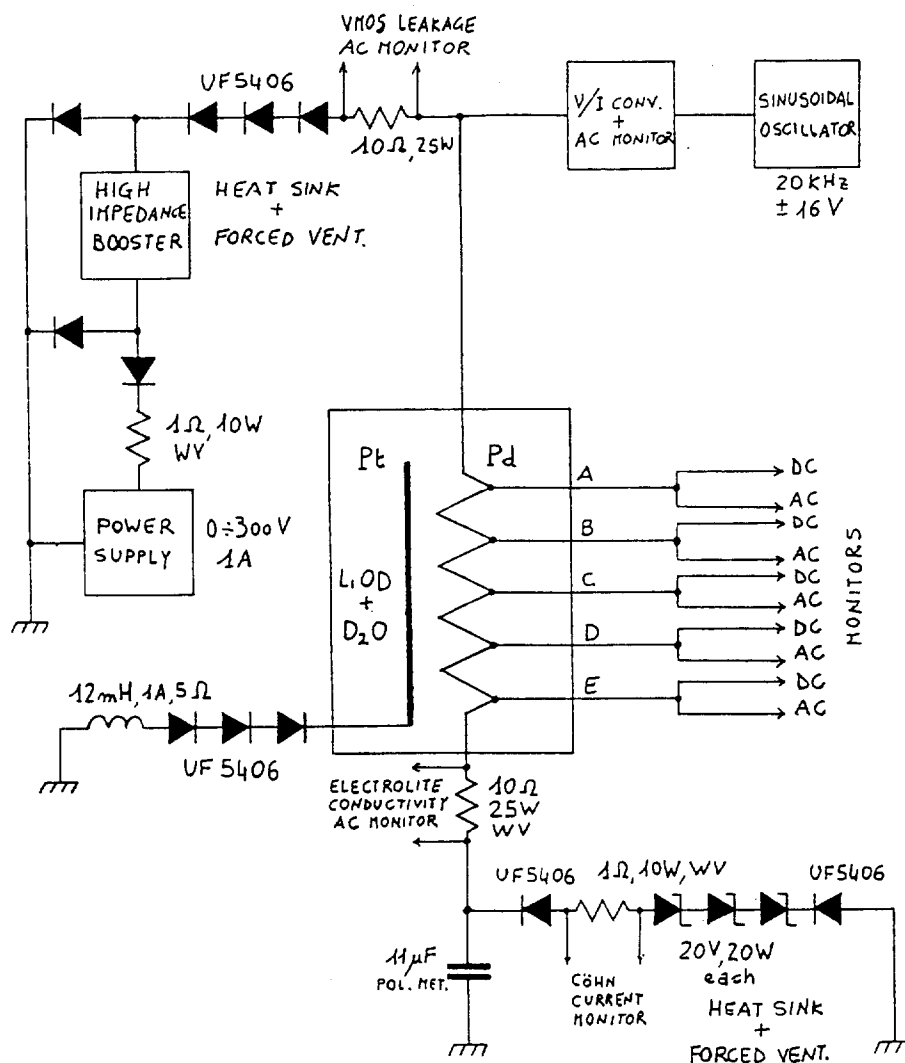


FIG. 2 – Electronic circuitry and innovative experimental set-up devoted to avoid errors in Pd wire resistance measurement due to electrolyte paralleling effects.

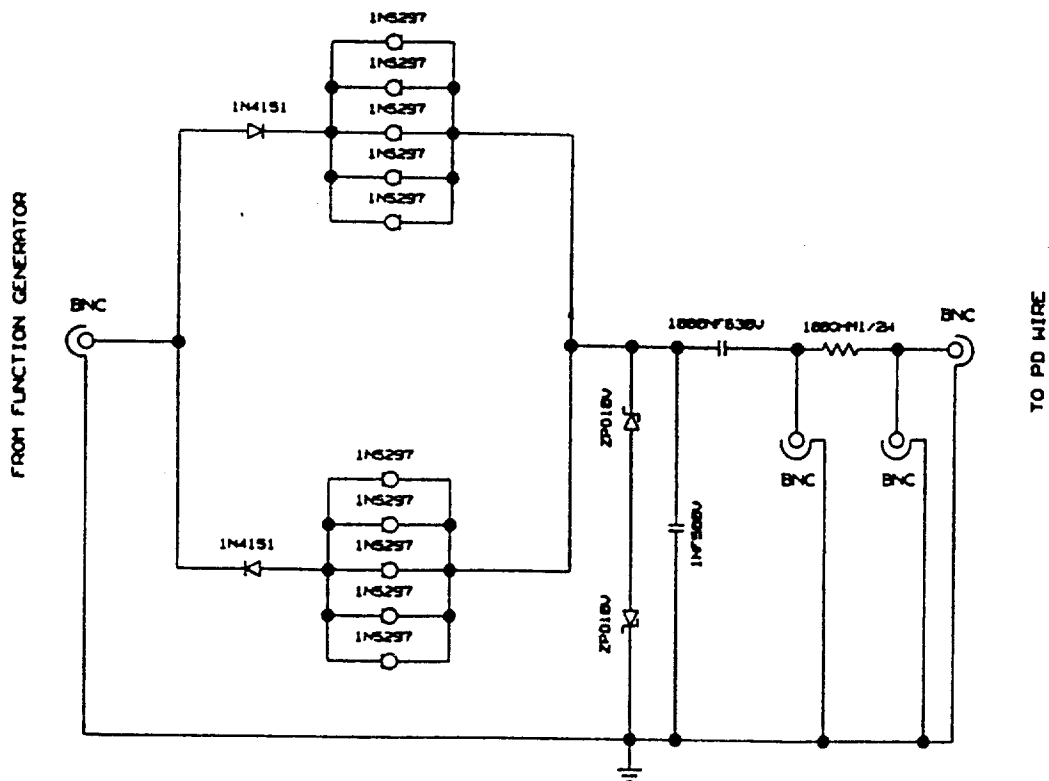


FIG. 3 - Details of "voltage to current converter" electronic circuit.

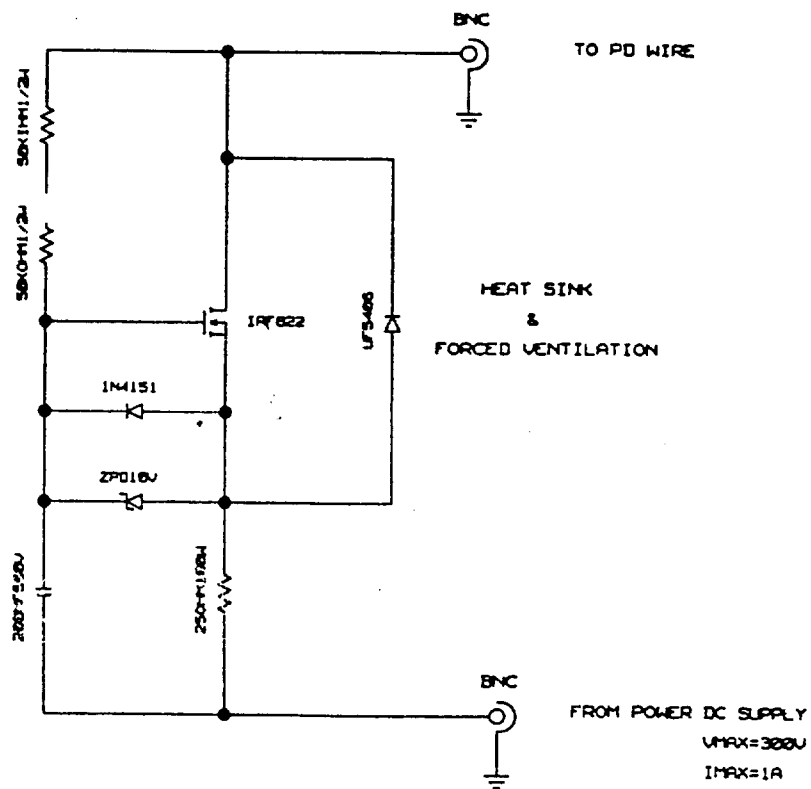


FIG. 4 - Details of "high impedance booster" electronic circuit.

4.1 Innovative approach on electromigration effect

We have performed further studies about the electromigration effect from the point of view of loading and *dynamic storage*. We have developed an innovative geometrical configuration of the Pd wire set-up, called "*collider*" [Fig. 5], that can improve H-D loading and, mainly, the *dynamic storage* in respect to the usual unidirectional one.

The electromigration effect, studied since 1929 [2], is a powerful tool, at least in principle, in order to increase largely the H-D-T concentration in host materials where these elements behave as *proton conductors*. Recently, this kind of effect was used, from several authors, in order to increase the deuterium concentration in Pd (and/or Pd alloys) over the thermodynamic equilibrium condition in the framework of the Cold Fusion studies.

The basic equation related to electromigration effect is:

$$C(x) = C_0 e^{-[eZ^* V(x) / K_B T]} \quad (1)$$

where:

- C_0 is the initial concentration of H-D-T in host material;
- Z^* is the effective charge number of H-D-T in Pd [the value is 1 at low concentrations ($H/Pd < 0.6$), is about 0.1 at high concentrations ($H/Pd > 0.8$) and/or at high temperature ($T > 30$ °C)];
- $V(x)$ is the voltage drop along the host material in the limit of its homogeneity (no large dislocations or fracture);
- K_B is the Boltzmann constant;
- T is the temperature, in Kelvin.

From equation (1) it follows that an increase in the concentration gradient results from a large voltage gradient in the cathode wire, once it is provided that some proper concentration C_0 of H-D-T is continuously fed to the Pd (by gas loading or proper electrolytic technique). We will remark that the proper feeding of deuterium to Pd wire (C_0) is an intrinsically difficult task because the diffusion speed of incoming deuterium is only 10^{-7} – 10^{-8} $cm \cdot s^{-1}$ (β phase) while the moving-crossing-escaping has a diffusion speed 100 – 1000 times larger (γ phase).

The easiest way to *maximise* the voltage drop and to *minimise* the power dissipated by Joule effect is to use *long* and *thin* cathode wire [3]:

$$V = I R = I \rho l / S \quad (2)$$

$$W = V^2 / R \quad (3)$$

Equation (2) represents the voltage drop along the cathode wire and equation (3) represents the dissipated Joule power: ρ is the intrinsic resistivity, l is the wire length and S is the cathode wire cross-section area.

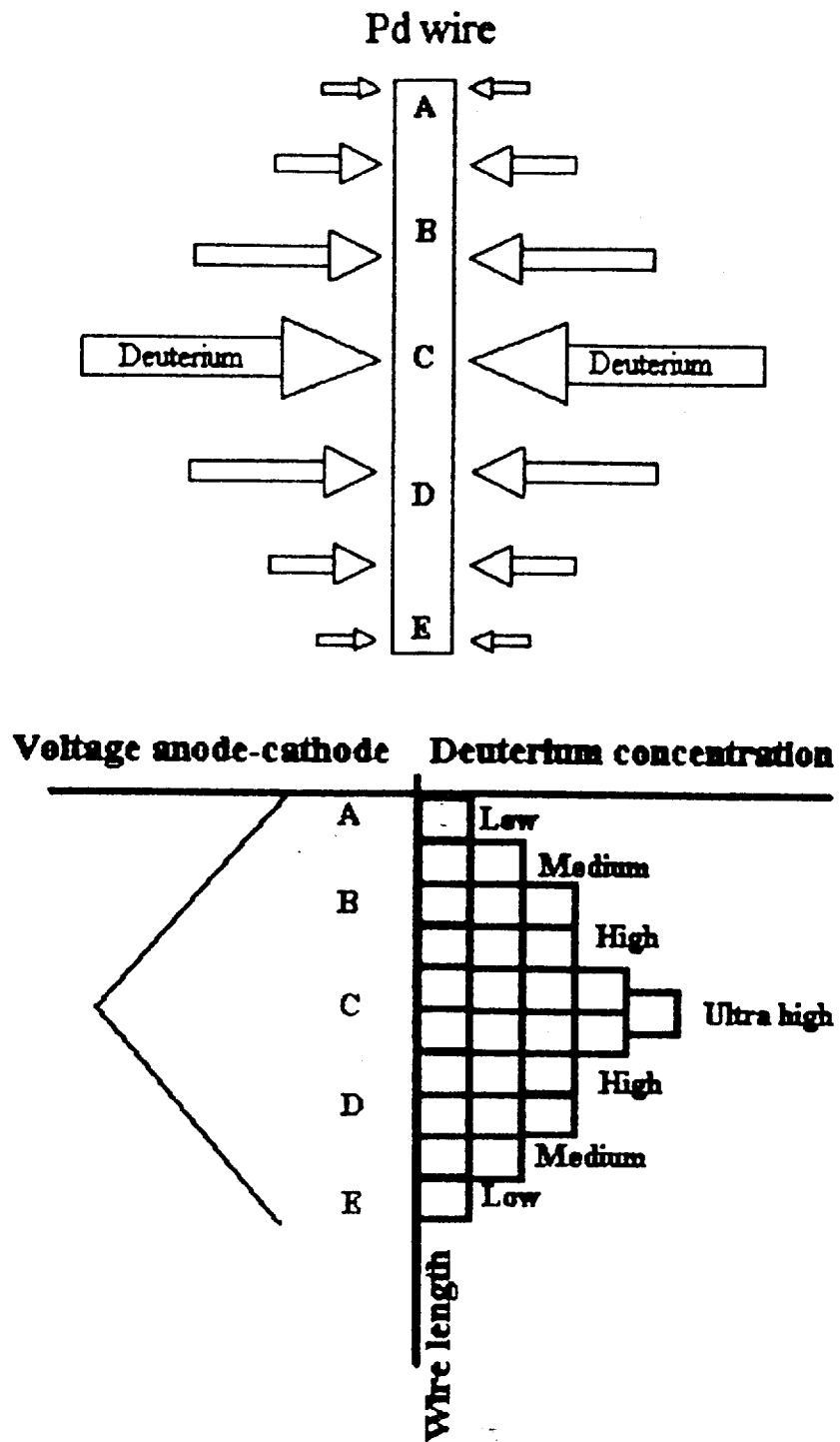


FIG. 5 – Sketch of enhanced electromigration by "central wire geometry" (collider). The point C is the most negative input voltage, the points A and E are electrically connected. $|V_A| = |V_E|$; $|V_C| > |V_{B,D}| > |V_{A=E}|$

4.2 – Limits to electromigration effect

Regarding the electromigration effect, there exists an intrinsic limitation.

The deuterium concentration increases at the end of the cathode wire, where the voltage drop is at the most negative value, but it can escape from this side if there is no physical barrier at the end. These barrier can be mechanical (metal covered with gold, copper or nickel) or electrical (deuterium chemical potential on the palladium surface larger than deuterium chemical potential inside palladium). Sometimes this barrier is made just by soldering the Pd (by Sn–Pb alloy) with copper wire, feeding the necessary current to the system [4,6]. This kind of procedure can be likely because the wire for the connection is copper. This element, in proper conditions, can penetrate onto the Pd surface and has the peculiarity (together with nickel) of decreasing the Pd lattice parameter [5]. This alloy, at the skin of the wire, reduces the speed of deuterium deloading, just because it acts as a mechanical barrier. The tickness of copper barrier has some physical limitations and the effectiveness is largely procedure–dependent. One of the main drawbacks arises when it is necessary to reverse the polarity of the electrolysis and the copper can dissolve into the solution, worsening the low conductivity behaviour of the solution (LiOD 250 μ N). Low conductivity is necessary to keep large anode–cathode voltage at enough low current (e.g. 100 V, 500 mA, 160 cm wire length, 1 cm anode–cathode distance, 30° C temperature) in order to get large Deuterium–H–T loading [4].•

In DC conditions it is quite difficult to get an effective *adhesive strength* able to withstand hundred of thousand (or even million) of atmosphere of pressure necessary, speculatively, to get Cold Fusion just by pressure.

The pulsed condition helps to reduce the necessity of using strong barriers at the end of the cathode wire because, in proper conditions, it is conceivable that the *highly concentrated deuterium inside the wire is itself like a dynamic barrier*.

According to the new set–up, at least in principle, it is not necessary at all to have a barrier against the escape of deuterium because the barriers are two, dynamics: they are just the highly concentrated deuterons themselves coming from opposite and symmetric directions, with the (nominal) same intensity.

This kind of geometry can be further improved using *pulsed current* because it is possible to reach larger gradient of concentrations, due to larger voltage drops (up to 100 + 100 V along the length of 80 + 80 cm of 100 μ m Pd wire diameter in our experiment, peak current of about 23 A) during pulsing, in respect to the few volts (typically about 9 + 9 V) achievable in DC conditions with 1 A total current.

Thanks to this geometry, through loading experiments using the Pd resistance measurement, will be possible to clarify whether the *anomalous excess heat* arises from *static* or *dynamic* conditions of deuterium inside palladium. Dynamic condition is equivalent to high speed of D concentration variation.

5 – Pd–Y alloy wire

We studied, since 1994, the effect of elements that contract or enlarge the Pd lattice with endothermic or exothermic behaviour [1]. Now, we experimentally studied the Pd–Y alloy (Y = 3.9% in weight), an exothermic enlarged lattice, from the point of view of isotopic effect (H,D) using both normal wire geometry (*usual electromigration*) and central wire geometry (*collider*): four kinds of different experiments in total.

The PdY alloy was selected for two main reasons. The first reason was that the Y itself is an element that can absorb H–D–T in large amounts (up to 2.8:1) and the hydride is stable even at high temperature (1100 K; 10,000 ns). The second reason was that the intrinsic resistance of this alloy is, noticeably, 2.5 times larger of pure Pd: it is possible to experimentally test, also, the new theory developed from G.Preparata [3] about the "electrical confinement" of H–D–T in Pd due to larger voltage drop along the wire.

6 – Pulsing procedure

We further verified the effect of high power pulsing (peak current in the range as high as 20,000–200,000 A/cm²; pulse width of 500 ns; peak voltage between anode and cathode up to 300 V) about rise time(80 – 300ns) and repetition rate (100 – 50000 Hz) with respect to loading and excess heat.

In our experience, the excess heat detected by proper pulsing, given an experimental set-up and kind of Pd wire used, is about twice in respect to the most effective DC operation conditions that we can adopt.

The main drawback of pulsing operation is that, up to now, we are not able to measure R/R₀ with enough high resolution because large noise intrinsically emitted from the pulse: it affects adversely the low level (5 – 10mA, 20 KHz) sinusoidal signal used for resistance measurement. One of the main advantages (and extra benefit) of pulse procedure is that it can be very effective for *conditioning* the Pd cathode wire to subsequent loadings, with anomalous effects, in high voltage DC conditions.

7 – Main results

We summarise the main results obtained using Pd 99.92% (from ORIM, isoperibolic calorimetry, 5 months of experiments) and Pd–Y (from Tanaka K.K., flow calorimetry, 3 months of experiments) wires (both 160 cm length and 100 μm diameter):

- a) loading (by R/R₀ absolute value measurements and behaviour observations) show that R/R₀ loading with D is larger than R/R₀ loading with H, as expected;
- b) the maximum loading is achieved with central wire geometry, in comparison to normal wire geometry;
- c) excess heat using LiOD–D₂O solution is larger than LiOH–H₂O solution (Fig. 6, PdY alloy, normal–wire geometry, D₂O and H₂O experiments);
- d) excess heat measured using central wire geometry is larger than using normal wire geometry.

In Fig. 7 are shown the results using pure Pd, central wire geometry.

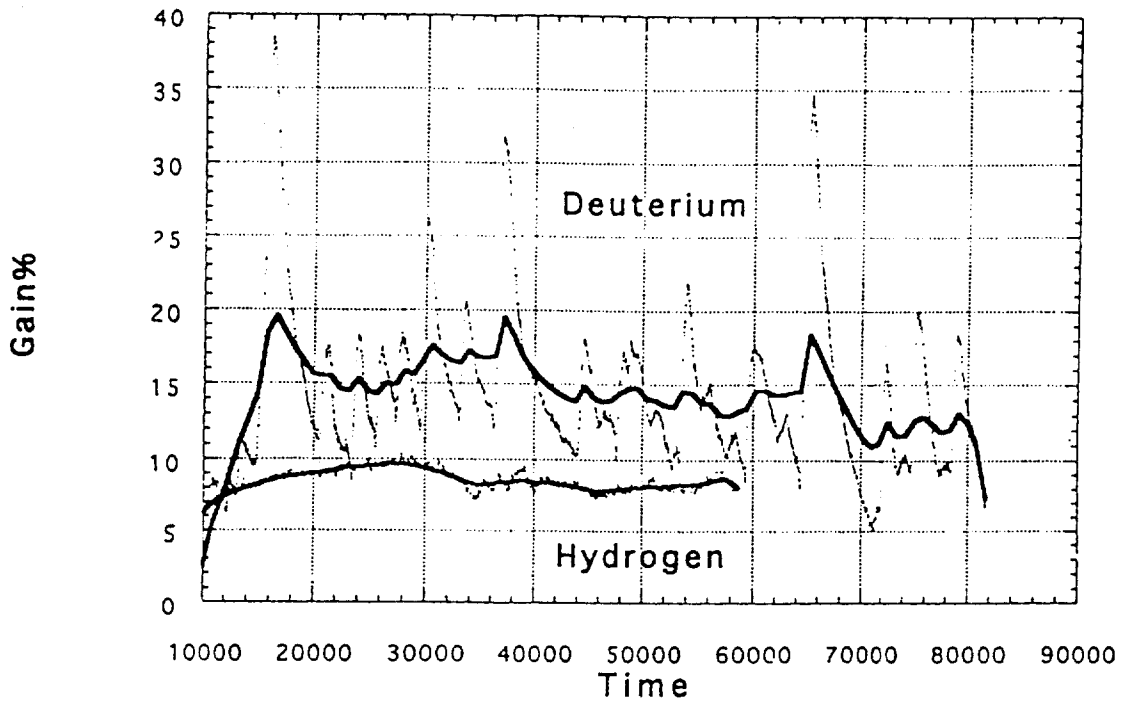


FIG. 6 – Isotopic behaviour of normal wire geometry set-up using flow-calorimetry (1% accuracy). We used the same wire, before loaded by D and later by H. We notify that after six loading/deloading procedure (washing) the excess heat of Pd/Pt/H system decreased to about 3%.

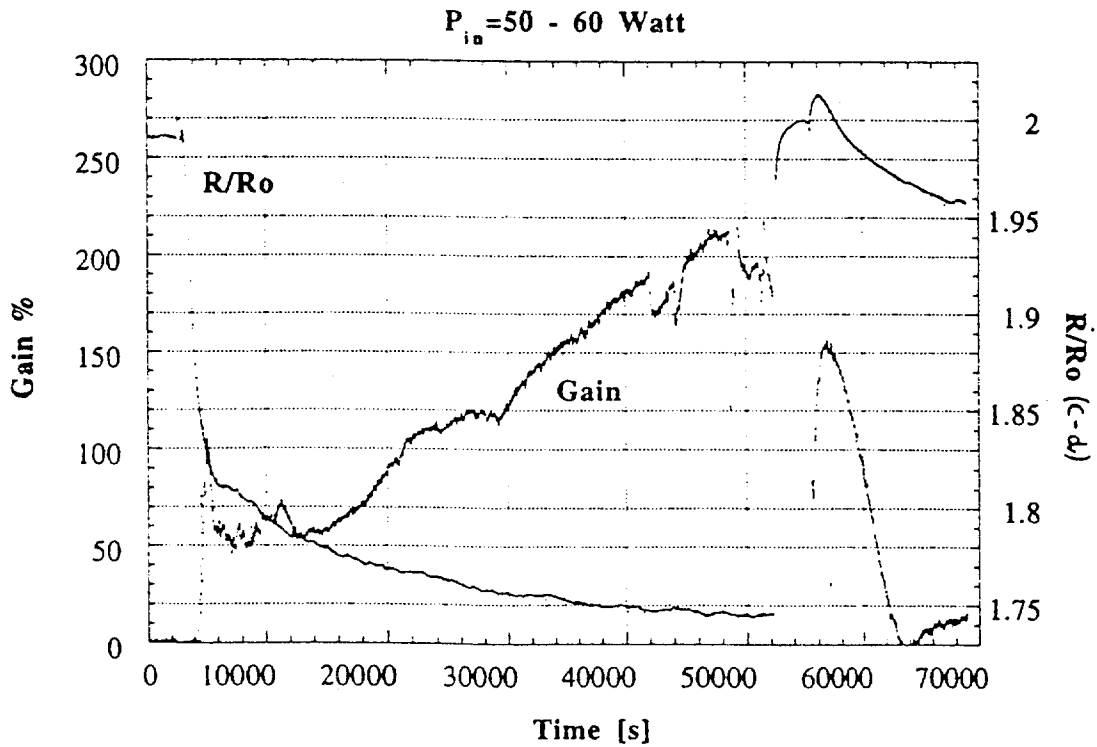


FIG. 7 – Pure Pd "central wire geometry" results. Isoperibolic calorimetry (15% accuracy).

The input power was about 50W and in this specific experiment, lasted about 20 hours, after the procedure of FLOATING (2 minutes) and subsequent restart (at the same electrical parameter, constant current), it was detected a very large amount (up to a maximum of 200 W) of excess heat. The amount of excess heat seems related to the *speed of loading*, as shown in Fig. 7 (time 4,000–6,000 seconds), and not to the absolute value of loading (time 48,000 – 52,000 seconds): although the R/R₀ value (at time 50,000) is lower than at the beginning of the experiment, the excess heat begins to vanish because the speed of variation of loading is very low.

In our opinion, this specific experimental result is quite significant to understand (and hopefully to control in the future) the phenomenology of Cold Fusion, at least from the point of view of excess heat generation.

The behaviour of loading of PdY (Fig. 8, 9) seems to have 2 components: the first seems related to pure Pd (R/R₀ increases and after, in proper condition, can decrease), the second seems to be related to Y (R/R₀ increases linearly with the time, up to some limiting value).

The detection of excess heat even with this lattice expanded material (with normal wire geometry) can support the idea that large cathode–anode voltage (because large resistivity of this alloy) is quite effective to *confine* the H/D inside lattice [3].

8 – Some general conclusions and further developing.

The PdY alloy has the peculiarity of very large resistivity and good mechanical properties (not brittle even after several cycles of loading–deloading). In proper experimental conditions, it seems that this material always gives anomalous excess heat, although at limited value (15 – 25%) in comparison with pure Pd. As main advantage, the generation of excess heat does not need of any kind of *special* pre–treatment of the wire (used, as received, from Tanaka K.K., just cleaned by organic solvents), as generally necessary for pure Pd (at our experience) like conditioning by high current or pulsing.

The beneficial effect of central wire geometry (developed at INFN–LNF since February 1995 and extensively studied from October 1995), from the point of view of both larger loading and excess heat generation, also in this lattice expanded material, seems confirmed.

Comparison of experimental results between *normal* and *central* wire geometry suggest that the origin of anomalous excess heat can be related to the *movement* of D (H?) in Pd. It can remember the original idea of A. Takahashi [7] with Low–High current electrolysis, in order to get some moving of D in Pd plates. The pulsing obviously is effective for this purpose, at least in order to increase the overall efficiency of excess heat generation

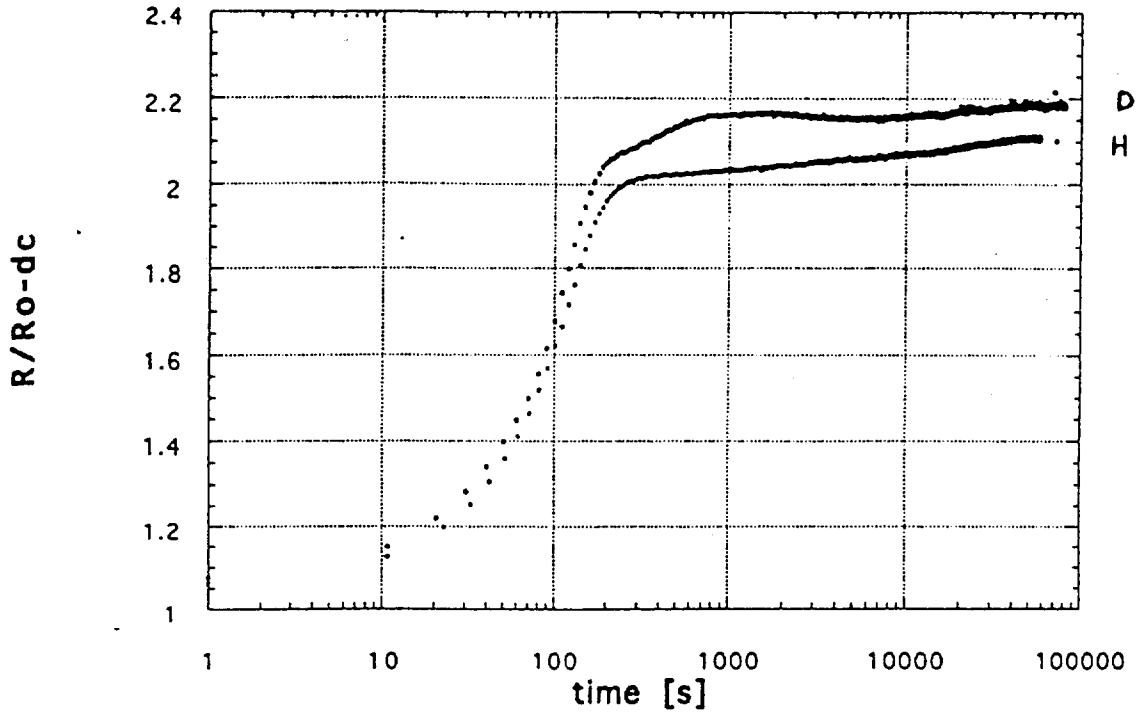


FIG. 8 – Normal wire geometry resistance behaviour of PdY. Isotopic effect clearly detected.

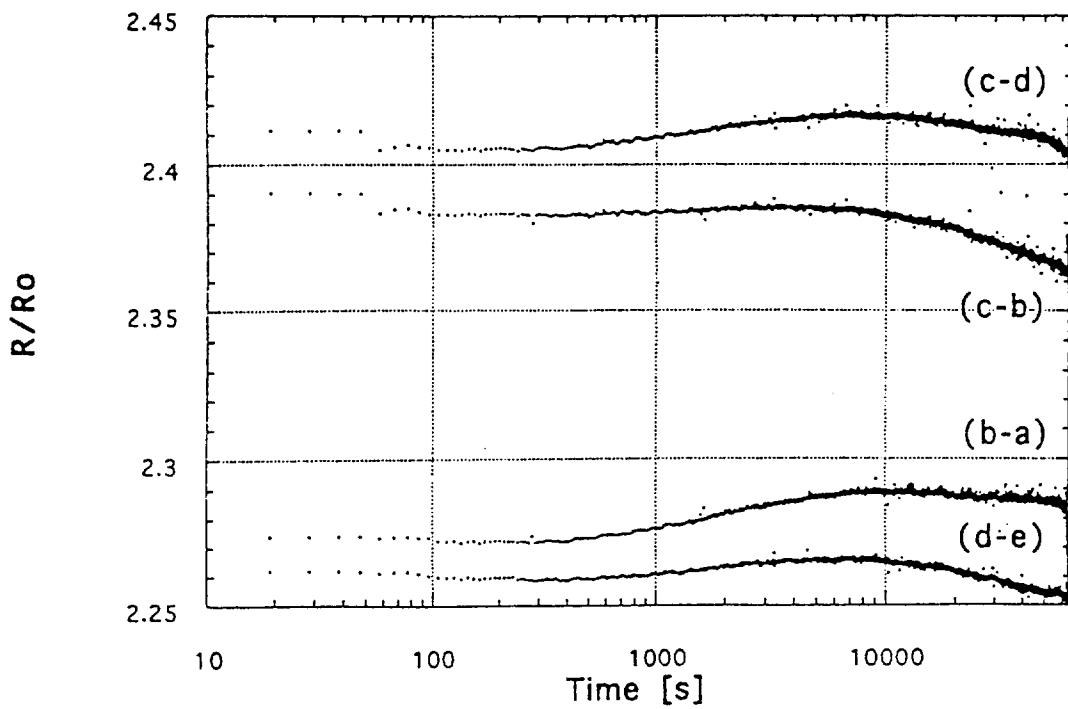


FIG. 9 – Central wire geometry resistance behaviour of PdY-D: details of the wire 4 different sections.

Acknowledgements

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Prof. Akito Takahashi (Osaka University) gave us very useful warnings and suggestions about behaviours of isoperibolic and flow calorimetry in our unusual electrolytic cell geometry.

Obviously, we never can forget the illuminating idea about the thin wire geometry and its peculiarity that Prof. Giuliano Preparata (Milano University) gave us continuously.

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