INNOVATIVE PROCEDURE FOR THE, IN SITU, MEASUREMENT OF THE RESISTIVE THERMAL COEFFICIENT OF H(D)/Pd DURING ELECTROLYSIS; CROSS-COMPARISON OF NEW ELEMENTS DETECTED IN THE Th–Hg–Pd–D(H) ELECTROLYTIC CELLS

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Abstract

In the framework of cold fusion studies one of the most important parameters is the deuterium (D) to palladium (Pd) ratio, D/Pd. It is well known that the value of this parameter is related to the normalised resistivity (R/R_0) of the D–Pd system. When at high D/Pd ratios (i.e. at low R/R_0 values) some excess heat occurs, the Pd wire temperature increase and, as a consequence, the apparent R/R_0 value also increases. This effect might give raise to ambiguous data interpretation: similar results are in fact expected in case of a Pd wire degassing (i.e. decreasing of D/Pd ratio). To solve this problem, we developed an innovative procedure and a suitable experimental set-up for the in situ measurement of the Resistive Temperature Coefficient (which is affected only by the real D/Pd ratio) during electrolysis. We will report the results on the hydrogen and deuterium loading of thin (50 μm), and long (60 cm) Pd wires, immersed in a solution of C_2H_5OD (or C_2H_5OH) and D_2O (or H_2O), with addition of thorium (Th) and mercury (Hg) salts at micromolar concentrations. Evidence of "transmutations" of some elements occasionally present on the Pd surface, and sometimes also in the electrolytic solution, have often been claimed in cold fusion experiments. In the present work, unexpected elements have been detected by high-resolution ICP-MS analysis. Some of these elements have also an isotopic composition different from the natural one.

1 Introduction: Reasons to Measure, In Situ, the Resistive Thermal Coefficient of the Pd Cathode

To detect excess heat in cold fusion experiments one of the most important parameters is the deuterium (D) over palladium (Pd) ratio, D/Pd.

It is well known that the value of the D/Pd ratio is related to the normalised resistivity (R/R_0) of the D–Pd system: e.g. its maximum value, 2.0, is equivalent (at room temperature) to a D/Pd ratio of about 0.75. By further increasing the D/Pd ratio, the R/R_0 starts to decrease.

If at high D/Pd ratios $(\gg \text{about } 0.90)$ there is some excess heat, the Pd temperature increases; as a consequence, the apparent R/R_0 value also increases, which is the same result that would be obtained if degassing occurred (a decrease of D/Pd ratio). This effect might give raise to ambiguous data interpretation and fruitless discussions.

To try to solve such a problem, we developed an innovative experimental set-up and a specific procedure for the in situ measurement of the Resistive Temperature Coefficient. As such a parameter is affected *only* by the real D/Pd ratio, any ambiguous interpretation in case of sudden variations of the D/Pd ratio will be avoided.

We will show, and discuss in some detail, a test that lasted about 2 days, made during a typical loading–unloading experiment. The results were obtained on deuterium loading of thin (50 μm), and long ($\sim$60 cm) Pd wire, immersed in a solution of ultrapure, vacuum distilled and ultrafiltered C_2H_5OD and D_2O with addition of thorium (Th) and mercury (Hg) salts at *micromolar* concentrations.

2 The Unconventional Frascati-INFN Procedures for Electrolytes, Electrolysis and Cathode Shape and Preparation

Here are some of key points regarding the Frascati-INFN electrolysis procedure.

The aims of experiments were essentially:

(a) To develop innovative and reproducible electrolytic techniques capable to maximise the values of hydrogen (H) and deuterium (D) concentrations in palladium (Pd) (i.e. the so-called "overloading": $H(D)/Pd \gg 0.90$ as mean value).

(b) To shorten the time from beginning of experiment to reach overloading ($<$50 h).

(c) To maintain the stability of the overloading for a long time ($>$4 h).

2.1 Electrolytes and Electrolysis Procedures

We decided first to employ hydro-alcoholic electrolytic solutions.

Table 1: Summary of the composition of the nine experiments performed, date and some comments about results.

Experiments	Date: begin $\rightarrow$ end (dd/mm/yy)	Electrolyte composition (mol)	Comments on results OVL = overloading (D/Pd > 0.9) S/N = signal/noise Pr = 1 count = 6E10 atoms
1	20/12/02 $\rightarrow$ 16/01/03	$CsNO_3$ (5E−5) $SrCl_2$ (1E−5) $LiOD$ (1.5E−5) H_2SO_4 (5E−6) NH_3OH (1E−4)	Almost no OVL Anode = Pd wire 250 μm Pr = 80 $\Rightarrow S/N = 2$
2	17/01/03 $\rightarrow$ 14/02/03	$CaCl_2$ (21E−5) $SrCl_2$ (1E−4) $HgCl_2$ (2E−4) H_2SO_4 (1E−5)	Two times OVL Residual Cs? Pr = 170 $\Rightarrow S/N = 4$
3	18/02/03 $\rightarrow$ 05/03/03	$CaCl_2$ (1E−5) $SrCl_2$ (1E−4) $HgCl_2$ (2E−4) H_2SO_4 (1E−5) $Th(NO_3)_4$ (8E−6)	Three times OVL $R/R_0 = 1.706$ Pr = 370 $\Rightarrow S/N = 9$
4	04/04/03 $\rightarrow$ 14/04/03	$HgCl_2$ (1E−5) Hg_2SO_4 (E−4) $Th(NO_3)_4$ (21E−6)	No OVL
5	15/04/03 $\rightarrow$ 19/05/03	$Th(NO_3)_4$ (34E−6) Hg_2SO_4 (2E−6)	Several times OVL; excess heat Pr = 300 $\Rightarrow S/N = 6$
6	29/05/03 $\rightarrow$ 31/07/03	$Th(NO_3)_4$ (65E−6) Hg_2SO_4 (5E−6)	Several times OVL; excess heat Pr = 1.4E3 $\Rightarrow S/N = 21$ ^{208}Pb anomaly; ^{203,205}Tl = 4.6E3 and ^{209}Bi = 9E3
7	31/10/03 $\rightarrow$ 08/12/03	$Th(NO_3)_4$ (21E−6) Hg_2SO_4 (3E−6)	Few times OVL: Na contamination Pt deposit on Pd Q = 40E+3C
8	29/01/04 $\rightarrow$ 15/03/04	C_2H_5Od = 740 cm^3 D_2O = 61 cm^3 $Th(NO_3)_4$ (30E−6) Hg_2SO_4 (8E−6)	Few times D overloading ($R/R_0 < 1.8$) Na contamination Pt deposit on Pd
9	15/03/04 $\rightarrow$ 21/05/04	C_2H_5OH = 710 cm^3 H_2O = 37 cm^3 D_2O = 12 cm^3 $Th(NO_3)_4$ (21E−6) Hg_2SO_4 (7E−6)	Almost "light" experiment $\rightarrow$ BLANK Large current adopted for long time (Q = 125E+3C) Few times H overloading ($R/R_0 < 1.45$) Pt deposit on Pd

The reasons for this *unconventional* choice were described in detail in our previous papers of ICCF series (Refs. 7 and 8). In short, we used, and are still now using, a solution of 90–95% heavy ethyl alcohol (C_2H_5OD) and 10–5% heavy water (D_2O). The main dissolved cations were strontium (as $SrCl_2$) and mercury (as $HgCl_2$) ions, at some micromolar concentrations (10–100 μM and 1–10 μM, respectively). The pH was kept at about 4 (acidic) by addition (if needed) of few drops of concentrated HNO_3.

For the sake of comparison, most of the electrolytic "cold fusion" experiments carried out in other laboratories use 0.1–1 M $LiOD/D_2O$ solutions, i.e. strong basic solutions (pH around 13/14), and a cathode current density between 60 and 600 mA/cm^2. Such procedure follows the pioneer teachings and long experimental work of Fleischmann and Pons[9] (Univ. Utah, USA), since 1989.

We emphasise that in our experiments, because of the mildly acidic electrolyte (pH $\sim$4) and the very low current density (only 5–20 mA/cm^2at the cathode surface and five times less at the anode) it is possible to reduce, to a large extent, the corrosion of components inside the electrolytic cell, borosilicate glass beaker included. Corrosion effects are typical of "conventional" electrolytic experiments: they are usually operated at high current for long time at strong basic pH. We anticipate that despite our efforts, problems coming from Pt dissolution on the anode are still not solved in a reliable way.

2.2 Elemental Analysis

As a consequence of our procedure, at the end of the experiment it is possible to make accurate elemental analysis by inductively coupled plasma-mass spectroscopy (ICP-MS); inductively coupled plasma-optical emission spectroscopy (ICP-OES); scanning electron microscopy (SEM) with micro-analysis. The following were analysed: the residual powder filtered off from the electrolyte (by vacuum distillation), and the components of the Pd wire itself.

The deleterious "matrix effect" in ICP-MS analysis is strongly reduced. After proper (long) background subtractions and inter-calibrations just after each ICP-MS measurements, the results were quite accurate and reliable. The results were "safe" because they did not call for special, sophisticated (and always dangerous) mathematical elaboration. Refs. 5–7 give a detailed overview and a general discussion on the interpretation of ICP-MS results.

As a historical note, because of obvious economic considerations, we developed our experimental procedure with hydrogen overloading using low cost light hydro-alcoholic electrolytes at different concentrations. In the next step, we tried to adapt, and transfer, the most successful methods to the heavy water and heavy alcoholic solutions, which are

about 400 times more expensive.

In our deuterium-based experiments, we were looking for anomalous production of excess heat, tritium and particularly "transmutations". Very recently in fact, "transmutation" phenomena received a significant acceptance in the scientific community mainly because of the *reproducible* experiments carried out at Mitsubishi Heavy Industries Laboratories (Yokohama, Japan).[1−4] We would like to remark that some of the Mitsubishi Group results (headed by Yasuhiro Iwamura) were independently confirmed also by our experimental group at INFN Frascati National Laboratories, by using with respect to that of Iwamura a complementary methodology: wet electrolytic environment instead of dry gaseous one. A detailed description and comments on the results can be found in Refs. 5–7.

2.3 Cathode Shape and Preparation

Based on suggestions made by Giuliano Preparata and Emilio Del Giudice (University and INFN Milan, 1994), in our loading tests we use Pd cathodes consisting of wires 50–100 cm long with diameter as thin as 0.05 mm. Generally, researchers use rods (following the example of Fleischmann and Pons) or plates ($25 \times 25 \times 1$ mm, following Akito Takahashi, Osaka University, Japan, 1992).

Before use, the Pd wires were carefully cleaned by dipping them in sequence in organic solvent, water, nitric acid, and water. Afterwards, by means of a specific protocol of joule heating and subsequent slow cooling down to room temperature, the wires are stress relieve annealed and, at the same time, properly oxidised as to form a thin film of Palladium oxide on the wire surface.

Such a complex protocol for treating wires was developed and continuously improved by our group since 1996.

By the way, we note that since 1993, we have exploited the peculiar characteristic of PdO at surface of palladium plates. The plates (Takahashi type geometry) were air oxidized at about 700°C, with a butane gas flame in a proper alumina crucible. Results from fast deuterium loading were presented at the ICCF4 and ICCF5 conferences. At that time the understanding of phenomena, although quite intriguing and reproducible, was not deep enough to justify further research.

2.4 Effects of Electrolysis Procedure on Results

As reported in our papers presented at previous ICCF conference, JCF Meetings and Asti Workshops, we performed a series of experiments with hydro-alcoholic solutions containing small amounts of Sr and Hg salts. We found excess heat (see Ref. 8) and

tritium (see Ref. 10) well above background. We also found that in the hydro-alcoholic ambient, during the anodic phases (that is for some hours every 1–3 days) of our loading cycles, the Pd electrode was partially eroded, producing small solid debris. Significant amounts of very small Pd particles are found at the bottom of the cell at the end of the experiments. In such black coloured powder ICP-MS analysis showed the presence of Pd together with some unexpected elements (see Ref. 5).

Moreover, after several electrolytic loading–unloading cycles, we could observe a very unusual phenomenon: the eroded (and therefore *very active*?) surface of the Pd wire was able to rapidly absorb the small amount of the deuterium gas dissolved into the solution without applying any electrolytic current. In our cell the maximum overpressure is only 50 mbar. Such spontaneous absorption was remarkable: a D/Pd ratio up to 0.75 was often reached.

The observed D self-loading of the Pd wire up to a value equivalent to a gas pressure of over 10 bar, is obviously connected to our new and specific electrolysis procedure.

Because the observation of such experimental effect, we designed a new electronic circuit able to manage, at will, the cathodic → anodic → cathodic cycles, in a continuous way. Such circuitry worked well and is under consideration for a patent application.

Coming back to the Pd cathode, we observed by SEM analysis that the surface after electrolysis, was deeply modified; many small bubbles and holes were sprayed over the surface, suggesting the formation of a nanostructural and/or fractal geometry. See Ref. 11 for further comments about the importance of nano-structure in cold fusion experiments as pointed out by Yoshiaki Arata (Osaka University, Japan).

Based on Arata's views, we are also convinced that *the formation of nano-structural and/or fractal geometry at Pd surface plays a key role in the production of all the anomalous effects detected in cold fusion experiments.*

3   Analysis of New Elements

Another important result in cold fusion studies is the experimental evidence of "transmutations" of some elements present on the cathode surface (Th and/or Hg in the present work), along with the Pd itself.

In our experiments, we used both light and heavy water electrolytic solutions. In some experiments, characterised by *high deuterium loading* over long periods (days) and repeated loading–unloading cycles, unexpected elements (sometimes in quite large amounts) have been detected by high resolution ICP-MS analysis. Some of these elements have also an isotopic composition different from natural one.

We would like to recall that in 2001, Iwamura et al.[1] was the first to show, in a very

elegant experiment, that strontium (Sr) is apparently transmuted into molybdenum (Mo), or cesium (Cs) into the rare earth praseodymium (Pr) when:

(a) D_2 gas is forced to flow for enough long time (several hundreds of hours),

(b) the D_2 gas flow is at a high enough rate (>2 sccm),

(c) the D_2 gas flow through a proper *multilayer* of Pd/Pd–CaO/Sr or Cs.

We recall that proper *multilayer* was fully developed by Iwamura's team at Mitsubishi Heavy Industries (Yokohama Laboratories, Japan), starting in 2000, and later patented at International level.

We tried to check whether such a "transmutation" can also occur after repeated D–Pd loading/unloading/loading cycles in our experimental set-up. In July 2002, we were ready to perform an independent variant of the Iwamura experiment.

Before starting we performed ICP-MS analysis of all the components present in the cell (C_2H_5OD, D_2O, $SrCl_2$, DCl, $HgCl_2$, and Pd), and pieces of the two Pt wires (anode and reference electrodes, taken from the same batch). At the end of the D–Pd loading/unloading experiment, the electrolytic solution was vacuum dried, the residue was collected and again analysed by ICP-MS together with the Pd cathode, all dissolved in hot-concentrated aqua regia. Excess Mo was found in amounts far above any conceivable contamination. The isotopic composition of the Mo was different from the natural one (see Ref. 5).

It appears that the phenomena previously discovered by Iwamura in a flowing deuterium gas system also occur in our electrolytic cell, operating for a time length of 500–1000 h, according to our loading–unloading–loading procedure.

3.1 Thorium Salts as Electrolyte

In January 2003, we decided to substitute the strontium salts, previously used as electrolytes, with thorium salts.

The two main reasons for such the change were as follows:

(a) Some results published also by our group in 1997–1998, seemed to show Th "transmutations" during high-electric power, at high temperatures and pressure, with AC (50 Hz) electrolysis with massive zirconium electrodes (both anode and cathode, see Ref. 12). Accordingly, we decided to test whether something similar could happen in our new experimental apparatus based on thin Pd wires and a very strict control of impurities.

(b) Th ions (like Sr^{2+}), because of the local alkalization produced by the passage of the electrolytic current, can precipitate on the cathode surface as $Th(OH)_4$ (solubility product $K_s = 10^{-50}$). Th ions (like Sr^{2+}) should not be galvanically deposited on the cathode because of the high negative value of their standard potential ($E_0 = -1.899$ V). In any case, as we want Th to be present on the Pd surface, even though this element could be co-deposited as Th deuteride (instead of as Th hydroxide) through some unknown process, no incompatibility with the aim of our specific experiment should occur. Taking into account that very low values of current density are required to deposit the proper $Th(OD)_4$ and/or ThD_x layer(s) on the cathode surface, the occurrence of some anomalous excess heat, should be easily detected.

Operating with Th containing electrolytes, we intended to assay the following:

(a) the occurrence of anomalous excess heat;

(b) the presence of foreign elements: at the Pd cathode surface and/or into the bulk, into the liquid solutions, in the insoluble agglomerates generally present at the end of the experiment in the electrolytic cell.

4 Short Description of Experimental Set-up: Electrolytic Cell and Flow Calorimeter

In order to understand the resistive thermal coefficient (RTC) measurement procedure (see Chapter 5) and experimental results obtained, we report some of key points of our electrolytic cell.

The configuration of the cell was shown in Fig. 1 of Ref. 6. The sample holder, a PTFE tube, is placed in a 1000 ml borosilicate glass (type 3.3, brand FORTUNA) cylinder (diameter 67 mm and height 460 mm). The cathode and anode are both "U"-shaped and are located on the opposite walls of the holder, facing each other. The cathode is a thin (diameter 0.050 mm) long (60 cm) Pd wire (total surface about $1 cm^2$). In the lower part of the Pd "U"-shaped cathode, at its centre, a small weight (6 g PTFE cylinder) keeps the wire tense during the loading so as to compensate its 4–6% elongation. The anode is a Pt wire: diameter 0.250 mm, length 60 cm, purity >99.99% (Aldrich Chemicals, Germany; provided with an analysis certificate made with the ICP-MS method). A second Pt wire (length 30 cm, same type of previous one) is put exactly in the middle of the "U"-shaped cathode for purposes of electrolytic tests.

To measure cathode resistance, an AC current (16 mA, 10 kHz, square wave, equivalent to a current density along the wire as high as $800 A/cm^2$) is superimposed by an
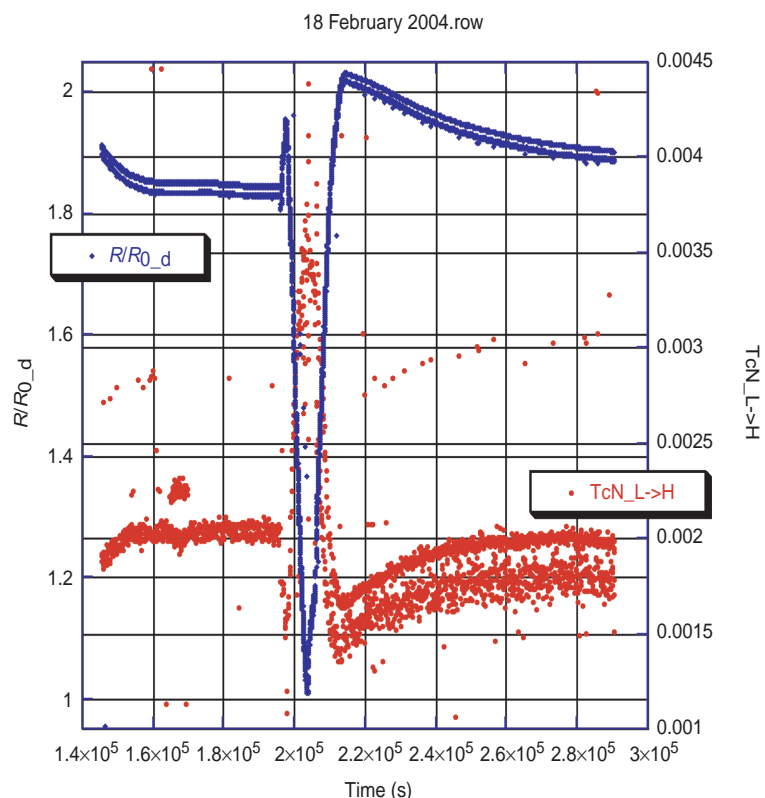
Figure 1: Row data. R/R_0 and Resistive Temperature Coefficient, versus time (s).

array of metallic polyester capacitors to the low intensity electrolysis DC current (2–20 mA). The AC resistance value, resulting from AC voltage drop measurements (about every 10 s), is computed and acquired by a computer.

The square-wave AC current, with a low current of about 15 mA, is kept constant by a proper array of fast (ns response) constant current diodes, kept at constant temperature to minimise their strong thermal dependence.

A high quality LM135H thermometer (sensitivity 0.05°C), inserted in a PTFE tube, is placed in the middle of the cell, perpendicular to the cathode and anode. A Joule heater (maximum 20 W), used to calibrate the calorimeter, is located between the electrodes in a peripheral position. It is inserted in a PTFE tube (diameter 8 mm and length 30 cm). The cell is slightly pressurised (50 mbar at maximum) and thermally insulated. The electrolysis gases and vapours are allowed to flow through both twin cold-traps and silicon oil bubblier before reaching the atmosphere. Corrections for these losses of energy are not yet applied, consequently all the data for excess heat are slightly under-estimated.

The heat exchanger within the cell consists in a 500 cm long PTFE pipe, outer/inner diameter 4/2 mm, wound around the PTFE holder through which the cooling water flows. The temperature of the distilled water flowing in the pipe is continuously measured at the inlet and outlet of the heat exchanger with two LM135H thermometers. A comput-

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erised peristaltic pump (Masterflex 7550-62) provides a constant flow of distilled water (0.200 ml/s, with day-to-day stability of $\pm 1\%$, routinely measured every 12 h). Since November 2003, the water is pumped from a 4-l temperature-stabilised bath (brand Thermo NELSAB, model RTE 201), through thermally isolated tubes, kept usually at $24\pm0.1°C$, to which it returns from the cell. Cell and pump are placed in a small volume temperature stabilised chamber (kept at $24\pm0.15°C$) to further improve the accuracy and reliability of the calorimetric measurements.

4.1 Composition of the Electrolyte and Cleaning Procedure

A mixture, typical 93% volume of heavy ethyl alcohol (C_2H_5OD) and 7% water (D_2O), with a total volume of 750 ml, was used as electrolyte.

The ethyl alcohol (Aldrich) was previously vacuum distilled at 30–35°C with a vacuum distillation system (Buchi, Model 134, Switzerland) to eliminate mainly sodium and iron. It was also ultrafiltered on line using a 100 nm, Millipore PTFE filter. The distillation system was significantly modified in our Frascati Laboratory in order to keep vacuum conditions in a static state. The density was routinely measured by densimeter (Mettler Toledo, Model DA-110M, Japan) before and after distillation, to confirm that no significant H_2O contamination occurred during the distillation operations.

Heavy water (99.97%) isotopic purity, reactor grade (Ontario-Hydro, Canada) was distilled at 40–45°C in vacuum and ultrafiltered before use, in a procedure similar to that used with the alcohol. Density was measured before and after distillation.

$Th(NO_3)_4$ (5/15 mg) was added to the electrolyte and the pH of the resulting hydro-alcoholic solution was adjusted to a value of about 3 by adding few drops of (highly concentrated, 14.5 M) HNO_3 (diluted in pure D_2O), in order to avoid uncontrolled precipitation of $Th(OD)_4$.

The cell was cleaned after each experiment using repeated cycles of water/organic solvents/water/nitric acid/water in an ultrasonic bath. After experiment #2 (February 14, 2003; see Table 1 in Ref. 6), we increased the duration of the immersion of the cell in concentrated (65%) warm (60°C) HNO_3 from 2 min to 14 h (all night) because we suspected that residual traces of Cs might remain trapped around the strictly connected spires of the cooling serpentine.

5 RTC Measurement: Principles of Operation

The innovative procedure developed for the, in situ, measurement of the RTC, is based on a regular (every 60–200 s) changing of the intensity of AC current (at 10 kHz) along the

wire, from the "low intensity" (15 mA) normally used to measure the R/R_0 values, to the "high intensity" (about 120 mA).

The change of current intensity affects the power dissipated in the wire (i.e. from about 7–15 mW at low intensity regime, to about 800 mW at high-intensity regime). Obviously, the dissipated power depends on the wire resistance variation, due to H/D absorption. When the "high intensity" is on, the wire increases its temperature. The variation is large enough (although the wire is immersed in a good thermally conductive solution, like alcohol–water) to be detected, with accuracy of the order of some percent by our R/R_0 measuring system.

It is reasonable to assume that during the "high intensity" cycle the actual loading ratio D/Pd remains substantially unaffected.

It is also reasonable to assume that the relationship:

$$W = hS(T_{\mathrm{w}} - T_{\mathrm{s}}), \tag{1}$$

where W is the dissipated power, h the thermal exchange coefficient, S the wire surface, and $T_{\mathrm{w}} - T_{\mathrm{s}}$ is the temperature difference between wire and solution, remains substantially unaffected when the wire resistance changes because of the H/D loading.

The value of the RTC is known for pure Pd ($\alpha = 3.8 \times 10^{-3}$).

It is, therefore, possible to calculate the (1) values at H(D)/Pd = 0 by applying the low–high current intensity:

$$R_{\mathrm{low}} = R_0(1 + \alpha T_{\mathrm{s}}), \tag{2}$$

$$R_{\mathrm{high}} = R_0(1 + \alpha T_{\mathrm{w}}), \tag{3}$$

$$R_{\mathrm{low}}/R_{\mathrm{high}} = (1 + \alpha T_{\mathrm{s}})/(1 + \alpha T_{\mathrm{w}}). \tag{4}$$

In (4) the only unknown is T_{w}: such a quantity can be calculated as a function of W ($T_{\mathrm{w}} = f(W)$) and can be determined at any moment of the experiment (in fact, the actual dissipated power at high level of current intensity is always known; consequently, T_{w} is always known; the only unknown is therefore the value, function of the loading ratio, of the resistive coefficient α).

Taking into account that the change of α as a function of loading ratio is very large (>200%, i.e. from 0.38%/°C at D/Pd = 0 to 0.18%/°C at D/Pd = 0.75) the assumed approximations can be largely accepted.

6 Experimental Results on RTC

Measurements from experiments #8 (deuterium experiment) and #9 (hydrogen experiment) are compared here because the experimental set-up was exactly the same, making cross-comparisons easy.
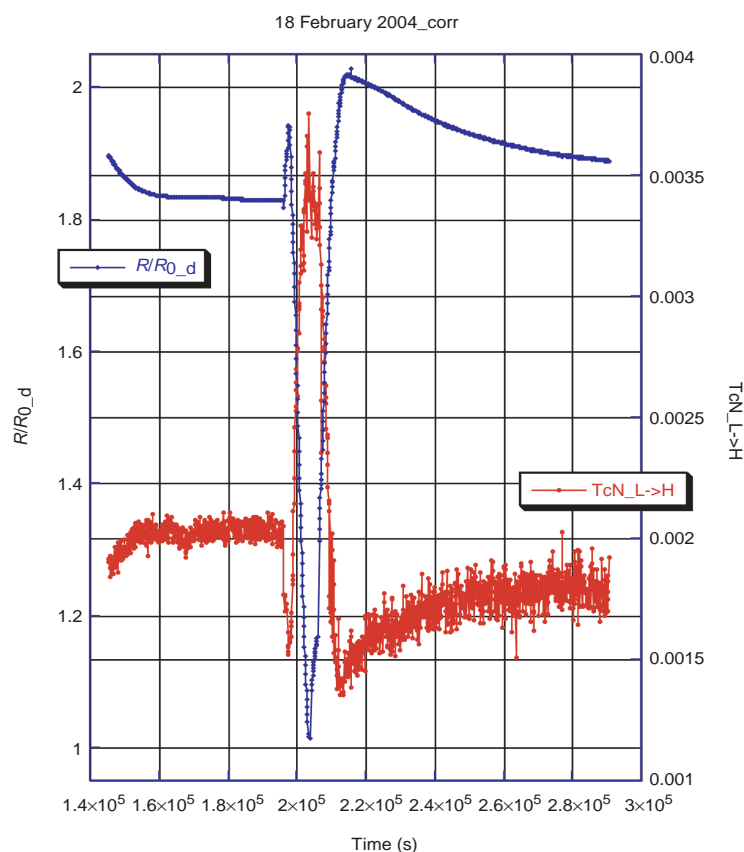
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Figure 2: Same as Fig. 1, except the data are filtered for clarity.

6.1 Exp. 8 (File 18 February 2004) Deuterium

In Fig. 1, the R/R_0 ratio (vertical left axis, from 0.95 to 2.05), shows over time (from 140,000 to 310,000 s), and the Resistive Temperature Coefficient (vertical right axis, from 0.001 to 0.004).

The data clearly show the twin values of R/R_0 due to the cycles of low power (about 7–15 mW) and high power (700–800 mW) because AC (electromigration) currents injected along the Pd wire.

In Fig. 2, the same data of Fig. 1 are shown after off line filtering. This procedure, up to now, has been made selecting the data one-to-one, and is very long time consuming and tedious.

Figure 3 is just a magnification of Fig. 2 around the unloading–loading area.

In short, the cell was kept in cathodic condition up to time 196,000 ($R/R_0 = 1.82$).

At that time the electrolytic current was disconnected and the R/R_0 value, after a small decrease, started to increase again because unloading. About RTC, it was at 0.0020–
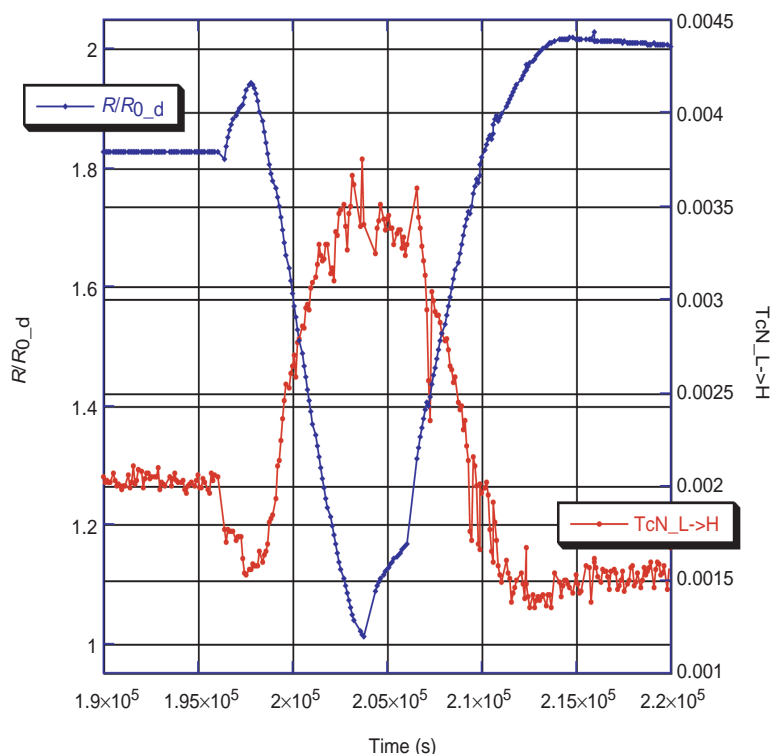
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Figure 3: Magnification around maximum–minimum of R/R_0.

0.0021 during loading condition and decreased to 0.0015 at the point where it reached the maximum of R/R_0.

At time 194,000 unloading was forced by anodic current (2 mA). The maximum of R/R_0 was 1.94 and not 2.0 as expected because the anodic stripping was quite strong and the unloading was not homogeneous along the wire.

At time 204,000 the anodic current was ended and the R/R_0 reached the minimum value of about 1.015. This value is little bit larger then 1.00 because some stress, due to previous loading, was induced into the wire. The RTC reached a value of about 0.0037, close to the value reported in the literature (0.0038 at 293 K).

From about time 204,000 to time 206,000 the wire was in floating condition and absorbed some deuterium dissolved in the alcohol–water solution.

At time 206,000 was given again cathodic current, and it started usual loading.

At time 213,500 the R/R_0 reached the maximum value, about 2.015, larger than 2.00 because previous residual stress. The RTC reached it minimum value, about 0.0014. The value of 0.0014 is clearly different from previous 0.0015 (at time 198,000) found in our experiment because of forced, rapid inhomogeneous unloading.

Such values are lower then that reported in the literature (0.0018). We think that our measurement conditions (electrolysis) are quite different from that reported in the
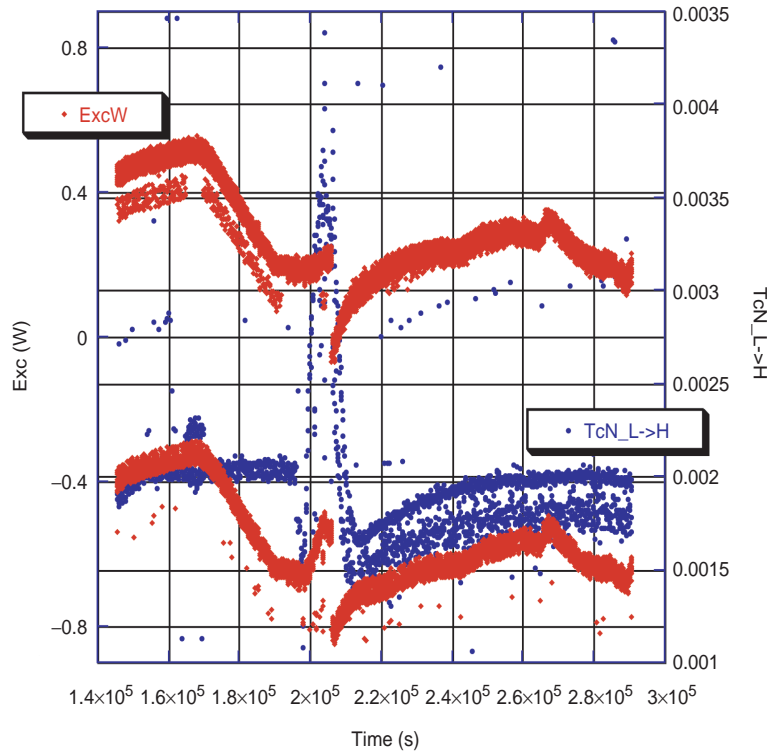
Figure 4: Row data. Evidence of excess heat, at time 150,000, in respect to time 290,000. In fact, the R/R_0 values were the same but RTC were different.

literature (clean gas environment) and can explain the differences. Moreover, we think that the value of heat exchange constant, measured at the beginning of the experiment, increased because of better thermal conductivity. This effect reduced the amount of signal detected. Obviously, more sophisticated analysis and experimental procedures will be needed in the future.

At time 290,000 the R/R_0 value reached the same value of time 145,000, i.e. 1.90. We can observe that the value of RTC was lower at time 290,000 compared to time 145,000. A possible explanation is that at time 145,000 some excess heat occurred that increased the value of R/R_0 of the wire.

The effect of excess heat can be seen in Fig. 4. The value was over 200 mW.

In conclusion, the combined observation of R/R_0 and RTC can help strongly to judge if there is some excess heat, especially at low level of power.

6.2   Exp. 9 (File 25 March 2004). Hydrogen Experiment

In Figs. 5 and 6, similar to Figs. 2 and 3, are shown the behaviour over time (in s) of R/R_0 (vertical left axis, from 0.95 to 1.85) and RTC (vertical right axis, from 0.001 to 0.0045).

The electrolytic current was as low as 5 mA.

The wire was previously almost overloaded because of the combined effects of Th and Hg, apart from cathodic current.
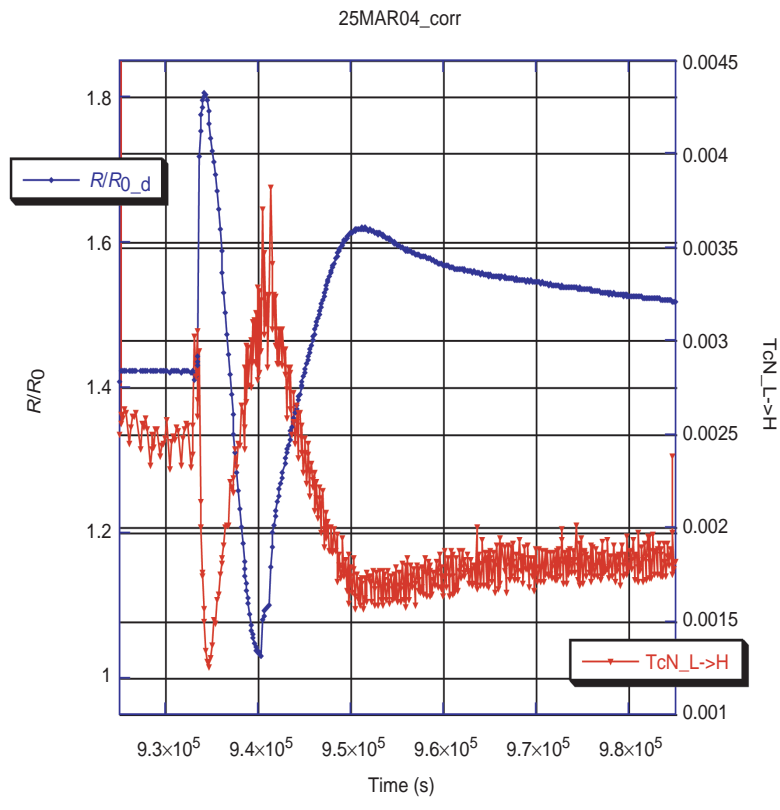
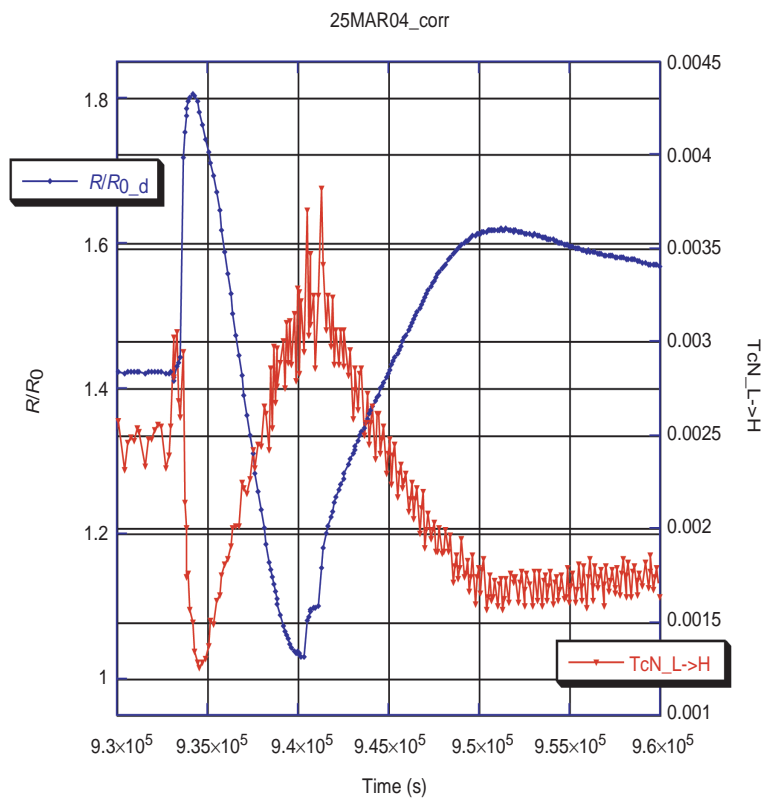Figure 5: Filtered data. Hydrogen loading. Overview of 1 day of experiment.

Figure 6: Filtered data. Hydrogen loading. Magnification around: minimum (relative) → maximum (absolute) → minimum (absolute) → maximum (relative) of R/R_0.

At time 930,000 it was almost steady at $R/R_0 = 1.43$ from several hours and RTC had a value of about 0.0024.

At time 933,000 electrolysis was discontinued, and the wire immediately started to deload.

At time 93,340, because the loading was not very fast, we applied anodic current (2 mA).

At time 934,000 the R/R_0 value reached it maximum (1.80) and RTC its minimum value (0.0013). The value of RTC was 0.0013 lower than the expected value, 0.0018.

As discussed in the previous deuterium experiment 6.1, the differences of values about RTC can be understood if we accept that the *heat exchange coefficient* of wire with the solution *increased a large amount* in respect to "time zero" of the experiment, when we calibrate (keeping the value for data elaboration).

At time 940,500 the R/R_0 reached its minimum value (1.05) and RTC its maximum (about 0.0033): we disconnected the anodic current. We did not wait long in anodic conditions because we were afraid the wire might break from the anodic corrosion effect. The minimum of R/R_0 was larger than 1.00.

At time 941,500, after observing weak self-loading, we restarted the cathodic current at 5 mA.

At time 951,000 the R/R_0 reached it maximum value of 1.62 and RTC its minimum of about 0.0017.

Both values are different from expected. We think that large differences are due to inhomogeneous loading of the wire.

At time 985,000 the loading was still improving (R/R_0 about 1.53) and after about other 30,000 s reached the value of 1.42, similar to the value that we observed at time 935,000 (the beginning of unloading → loading cycle). In other words, the mild unloading → loading cycle did not damage the surface of Palladium wire.

7 Experimental Results with ICP-MS

Experimental conditions and ICP-MS analysis results about the nine experiments, up to now performed that included ICP-MS analysis, are reported in Tables 1 and 2.

7.1 Summary of Experiment #7 (Analysis by ICP-MS, 1 count about 5×10^{10} atoms)

Date: Oct 31, 2003–Dec. 08, 2003.

Current: Usually 10 mA, up to 50 mA along 5 days ($Q = 40 \times 10^3$ C).

Overall results: Only few times overloading.

Table 2: Summary of some of most frequent elements found by ICP-MS in the nine experiments.

Experiments	^{31}P(100)	^{39}K (93.3)	^{63}Cu (69.2) ^{65}Cu (30.8) 63/65 = 2.25	^{64}Zn (48.6) ^{66}Zn (27.9) ^{67}Zn (4.1) ^{68}Zn (18.8)	^{133}Cs (100)	^{206}Pb (24.1) ^{207}Pb (22.1) ^{208}Pb (52.4) 206/208 = 0.46
1	7E3	2.2E6	2.4E6	2.7E6	>3E8	1E4
2	0	0	2.1E6 63/65 = 1.94	1.8E6	6E5	4E5
3	4E5	2.7E6	6.1E6 63/65 = 1.93	1.7E6	1E6	9.5E5
4	2.5E4	1.4E6	2.9E6 63/65 = 2.05	7.5E3	1.94E5	6.9E5
5	1.8E6	2.3E6	2.4E7 63/65 = 2.07	1.2E7	9E4	1.5E6
6	2.72E7	6.4E6	9.3E8 63/65 = 2.08	5.1E8	2.2E5	2E8 206/208 = 0.39
7	0	0	3.9E6 63/65 = 2.0	3.6E6	2E4	1.25E6
8	2.5E5	1.6E8	2.7E6 63/65 = 2.14	1.77E7	3E5	7.1E5 206/208 = 0.49
9	0	0 (found 6.6E6 from C_2H_5OH)	2.3E6 63/65 = 2.12	6.2E6	0	4.5E5

Background subtracted.

Reasons: Large ^{23}Na in C_2H_5OD (poor vacuum distillation); excessive Pt deposition from anode.

Electrolytes (750 cm^3 solution: C_2H_5OD 93%, D_2O 7%):

- $Th(NO_3)_4 = 21.5 \times 10^{-6}$ mol ($\rightarrow 2.6 \times 10^8$ counts) recovered 70%.

- $Hg_2SO_4 = 3 \times 10^{-6}$ mol ($\rightarrow 3.6 \times 10^7$ counts) recovered 3%.

Main elements detected by ICP-MS:

- Cu = 3.9 $\times 10^6$; ^{63}Cu/^{65}Cu = 2.0; Cu from Hg?

- Zn = 3.6 $\times 10^6$; Cu/Zn = 1.08.

- Rb = 2 $\times 10^4$.

- Cs = 2 $\times 10^4$.

- Pb = 1.25 $\times 10^6$; Pb from Hg and/or Th?

- Bi = 8 $\times 10^3$.

7.2 Summary of Experiment #9

Date: March 15, 2004–May 21, 2004.

    Current: Usually $20\,\text{mA}$, up to $50\,\text{mA}$ along $15\,\text{days}$ ($Q = 125 \times 10^3\,\text{C}$).

    Overall results: Only few times H overloading ($R/R_0 < 1.45$).

    Reason: Excessive Pt deposition from anode.

    Electrolytes:

1. $760\,\text{cm}^3$ solution: $C_2H_5OH = 712\,\text{cm}^3$, $H_2O = 36\,\text{cm}^3$ i.e. commercial 95% concentration, ethyl alcohol; $D_2O = 12\,\text{cm}^3$;

2. $Th(NO_3)_4 = 21.5 \times 10^{-6}\,\text{mol}$ ($\rightarrow 2.6 \times 10^8$ counts) recovered 60%;

3. $Hg_2SO_4 = 7 \times 10^{-6}\,\text{mol}$ ($\rightarrow 8.4 \times 10^7$ counts) recovered 58%.

Main elements detected by ICP-MS:

- $Cu = 2.3 \times 10^6$; $^{63}Cu/^{65}Cu = 2.12$; Cu from Hg?

- $Zn = 6.2 \times 10^6$; Cu/Zn = 0.37; Zn from Pd?

- Rb = 0.

- Cs = 0.

- $Pb = 4.5 \times 10^5$; Pb from Th and/or Hg?

- Bi = 0.

8 Key Parameters and Comments

After a lot of tests in different experimental conditions we have identified the following key parameters and experimental conditions to be fulfilled:

(a) *Deuterium*, must be carefully purified, especially if it comes from a liquid compound.

(b) *Large overloading,* for long time (days) and *flux* of deuterium through the Pd surface. At present the stability of the D overloading in our experiment is not yet completely satisfactory.

(c) Presence of "*nanostructures*" on the Pd surface (Pd + Th + Hg + "impurities").

(d) *Pt dissolution should be avoided.* Pt ions are galvanically collected on the Pd surface and inhibit the loading process (a drop in the cathodic overvoltage): at present this important item is not fully controlled in our experiments.

(e) *Cleaning* the Pd surface during the loading process by means of short periods of anodic stripping.

9 Comments on Transmutations

- *Pb seems to be related to Th*: enhanced decay of Th by deuterium? (also according to *Cincinnati Group* preliminary experiments, by Zr–H, in 1997);

- *Cu seems to be related to Th, Hg and Pd*: fission, according to Takahashi model and, very recent, specific results using Y. Iwamura multilayer device (test on D–Hg–Pd, Japan–Italy joint Collaboration, this Conference);

- *Zn seems to be related to Pd*: fission, according to Takahashi model;

- *It is necessary to increase*, in a large amount, the *equivalent cross section*. At present, it is about 1 barn on Iwamura Cs to Pr (ion beam deposition) gas experiments, reproducible; up to 600 barn in our electrolytic (Th–Pb, experiments #6 reported in Tables 1 and 2) *but not fully reproducible*.

9.1 Comments about Th–Hg Addition

- The Th–Hg solutions, at micromolar concentration, give transmutations results "better" than Sr–Hg solutions.

- The main drawback is the criticality of Th addition because, quite frequently, it form a thick layer at Pd surface that decrease largely the H (or D) absorption into Pd, at least at room temperature.

- The main advantage is the increased mechanical properties of Pd wire: our historic problems of thin wire ruptures disappeared.

- The combined effect the previous two points can be very useful in the case of *technological application* of *cold fusion effect*: high temperature and over-all reliability are needed.

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10 Conclusions

By comparing the results of nine experiments, it can be argued that *transmutations are real and not an instrumental artefact.*

In fact, the appearance of new elements depend on:

(a) deuterium presence (not hydrogen) in the Pd lattice;

(b) deuterium overloading for a long time together with inward–outward deuterium flux trough the Pd surface;

(c) elements added to the electrolyte that are capable of being fixed and/or absorbed at the Pd–electrolyte interface.

Work is in progress at INFN-LNF to build a special calorimeter and electrolytic cell transparent to IR radiation. Such radiation will be detected from a IR thermo-camera, model TH7102MX (from NEC, Japan), provided also with a special optical instrument (Nikon) able to detect our thin wire ($50\,\mu$m) up to 2 cm of distance. Our goal is to get a "full movie" of the "excess heat" coming out from the Pd surface, along the experiment, starting from the beginning when no excess heat exists, up to its eventual occurrence.

Further work is necessary in order to reduce the dissolution of Pt at the anode in our cell.

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