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Thermal and Isotopic Anomalies when Pd Cathodes are Electrolyzed in Electrolytes Containing Th-Hg Salts Dissolved at Micromolar Concentration in C₂H₅OD/D₂O Mixtures.

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Abstract

Discussed in this paper is the evolution of work that started by using the M. Fleischmann and S. Pons method and ended by using thin palladium wires electrolyzed in an electrolyte consisting of slightly acidic heavy alcohol-water solution containing thorium (Th) and mercury (Hg) salts at micromolar concentrations. The resulting large and dynamic loading of the Pd wires was studied. The recent use of thorium instead of strontium resulted in thermal anomalies and detection of new elements in larger amounts. The results with Sr are qualitatively in agreement with what was found by Y. Iwamura (Mitsubishi Heavy Industries) using multilayers of Pd-CaO-Pd-Sr in flowing deuterium gas. Most results seem to be in agreement with a "multi-body resonance fusion of deuterons" model recently developed by A. Takahashi (Osaka University).

1 Introduction.

1.1 From heavy water D_2O -LiOD to hydro-alcoholic Th-Hg electrolytes .

Since 2000, we have employed a very particular electrolyte for loading Pd with D. This electrolyte is an acidic hydro-alcoholic mixture with small additions of uncommon ions like strontium (Sr) at very low concentrations (10^{-5} - 10^{-4} M) and mercury (Hg) at even lower concentrations (10^{-6} - 10^{-5}). Recently (January 2003) we replaced the strontium with thorium at a concentration near 10^{-5} M.

To explain why we used such a “strange” electrolyte, let us begin with a short history of our experimental approaches, with both key results and turning points.

1.2. Deep underground measurements and fracto-emission phenomena.

Just three days after Martin Fleischmann⁽¹⁾ and Stanley Pons⁽¹⁾ (Univ. of Utah, Salt Lake City, USA) announced their discovery, we constructed our first electrolytic cells based on the Fleischmann-Pons description.

Since April 15, 1989, studies were made in the deep-underground “Gran Sasso Laboratory” of INFN-Italy. The Pd rods were sometimes replaced by thin-walled Pd tubes in order to reduce the deuterium loading time and to induce the deuterons to flow from the outer surface in contact with the electrolyte to the empty inner surface. In addition, we tested Ti bars as described by S. E. Jones⁽²⁾. We^(3,4) were looking mainly for neutrons from D-D fusion using a very low background in the Gran Sasso, typically near 10^{-6} n*cm⁻²*s⁻¹, which is about 1000 times lower than at sea level. We detected neutrons at 10^{-23} - 10^{-20} n/s, the so called “Jones level”, with up to 10^{-17} n/s during some burst emissions. These effects were found when the electrolytic cell was operating in a variety of nonequilibrium conditions. A procedure consisting of first loading (about one hour after the start-up), rapid on-off cycles of the electrolysis current, AC electrolysis using high frequencies, cell irradiated by intense pulsed light sources, and fast cooling of the electrolyte by immersion of the cell into a vessel containing liquid nitrogen were used.

We also found neutron emission from Portland cement cured with heavy water and during the superconducting transitions of deuterated high temperature, YBCO type, superconductors⁽⁵⁾. S.E. Jones⁽⁶⁾ also reported similar results. We tried to stimulate “extra neutrons” from deuterated YBCO using a weak (2200 n/s) Am-Be neutron source. This produced “extra neutrons” at high multiplicity (3) mainly during the superconductivity transitions⁽⁷⁾, as in previous experiments⁽⁵⁾.

All these experiences convinced us that most of the neutron emission results could be produced by the fracto-emission phenomena⁽⁴⁾, well known since 1938 (with pioneering work in Germany), which is of high scientific interest but of no practical use because most of the positive results are associated with irreversible phenomena.

After 2 years of experiments in the Gran Sasso Laboratories, we realized that the D-Pd system could be thought of as “working” just like an Otto-Benz engine cycle. First, the Pd lattice is filled with the proper fuel (deuterium). Second, the deuterium is stuffed into the lattice, for example through electrolytic loading. Third, a triggering spark must occur, induced by transient phenomena, which will provide for the nuclear “firing”. Finally, nuclear ashes are produced. Unfortunately, at that time (1991), both the necessary D-loading threshold value and the nature of a “really effective trigger” were unknowns that require a direct determination of the actual D/Pd loading ratio.

1.3. Search for excess heat: the A. Takahashi L-H electrolysis procedure.

Beginning in 1992, we started a search for anomalous heat generation by adopting the so called “saw-tooth, low-high current” electrolytic loading cycles as developed by Akito Takahashi⁽⁸⁾. We used LiOD 0.3M in D_2O , Pd plates of 25mm x 25mm x 1mm, and a maximum current density of about 0.5A/cm². During the experimental work with this technique, and after extensive discussions with A. Takahashi, we concluded that excess heat was related to mechanical hardening and to the type of surface texture present on the Pd plates. The experiments were performed in a “normal” (not underground) laboratory where we measured⁽⁹⁾ by flow calorimetry excess heat up to 5-10% of applied power. We propose that “anomalous excess heat” is “triggered”

by applying to the cell a low-high electrolysis current. We believe that the effectiveness of Takahashi procedure is caused by non-equilibrium conditions even during weeks of operation.

1.4. μ s pulsed electrolysis (INFN-LNF method) and use of thin Pd wires.

After these pioneer activities (1993), we came to the conclusion that the necessary and sufficient conditions for the Cold Fusion phenomena to occur can be expressed as follows:

- a) Loading of D in the Pd lattice to give a D/Pd ratio >0.9 .
- b) "Motion" of deuterons at the cathode surface and/or into the Pd lattice without deloading.

Regarding the condition a), we set-up and tested (1993) a very interesting and original method: the "High Power, High Frequency, Pulsing Electrolysis" (HPPE), which could operate at a very high current density up to $12\text{A}/\text{cm}^2$ using "Takahashi type" plates and several hundred A/cm^2 when applied to thin wires. This current produced a high cathodic overvoltage because, according to the Tafel law, the overvoltage is proportional to the logarithm of current density.

The home made pulsed power supply could deliver to the cathode high voltage and high current pulses up to 250V and 150A. In addition, these pulses had a rise-time of $<100\text{ns}$ at a peak current of less than 40A, a duration of 500--5000ns, and a repetition rate of 100-30000Hz. The overall maximum duty-cycle was 5% and the power was 80W.

The first tests using this technique were applied to cathode plates^(10, 11, 12). Unfortunately, continuous monitoring of the D loading could not be obtained using the electrical resistance of the cathode (see below, Ref. 13) because the resistance of the plates was too low. On the other hand, Coulomb-metric measurements^(9, 10, 11, 12) give accurate results only at the beginning of the loading, when the deuterium absorbed is relatively large with respect to the total discharged D. When the loading ratio is high and the loading rate is low, i.e. when it is most interesting to know exactly what is happening, the accuracy becomes unacceptably low.

Later on, considering the capital importance of a direct and continuous evaluation of D/Pd ratio, and after profitable discussions with Giuliano Preparata⁽¹⁶⁾ and Emilio del Giudice (University and INFN at Milan-Italy), we used thin cathodes (50-100 μm thick) and long Pd wires because of their sufficiently high resistance.

Thin wires give a number of advantages.

- Continuous monitoring of the actual loading ratio in the Pd cathodes is possible. In fact, it is known that a precise relationship exists between the Pd electrical resistivity and the loading ratio x (at fixed temperature), the so called "Baranowsky curve". The Pd electrical resistivity is usually expressed as R/R_0 , where R is the resistivity at a H/Pd ratio and R_0 is the initial resistivity. Therefore, it is possible to follow the progress of the loading process by measuring the cathode resistance .
- A flux of deuterons can be created. When a dc or ac current flows through a thin Pd cathode, the voltage drop forces the deuterons to move inside the Pd lattice (ref. 13, 14, 15). Because of the skin effect, this variation on the Cohen effect is magnified when a square wave, i.e. one having a fast rise time, is used instead of the sinusoidal current pulse.

By operating with thin Pd wires, both of the above conditions could be met.. The typical energy gain obtained with this technique^(13, 14) ranged from 5 to 40% of applied power. Our best result was an energy gain of the order of 200% lasting over 12 hours, with an input power of about 50W⁽¹⁵⁾. The HPPE technique also allowed for better reproducibility. Occurrence of excess heat was found less dependent on the purity and metallurgy of the Pd cathodes and had a success between 20% and 30%.

Besides these interesting results, a serious drawback appeared when we started to use long thin Pd wires. The self-inductance of the wires could produce sudden undershoot and overshoot voltage spikes that were difficult to manage even by using ultra-fast power diodes. In many cases, such spikes caused catastrophic failure of the data acquisition system in addition to generating high-power and high-frequency "noise". The time and expense of repairing the measuring equipment forced us to suspend most of the research program using this powerful method (1998). We now use the method only for some explorative tests. Meanwhile, the use of thin Pd wires as cathodes gave us the idea to develop, in parallel with the HPPE technique, a completely new approach to meet the above mentioned requirements.

1.5. The impurities problem.

When thin wires are used as cathodes, it is necessary to use very dilute electrolytes, i.e. around 10^{-4}M . At such low concentrations, the purity of D_2O becomes crucial. We found that certain metallic impurities, usually dissolved in D_2O , are galvanically deposited on the cathode and formed an impervious layer, which could seriously hinder the loading process. Such problems were known since 1994 after several Pd plates used during the HPPE technique were examined by SEM. Some our unpublished results were shown, discussed, and video-recorded at the Minsk Symposium⁽¹¹⁾.

1.6. Proper poisoning of Pd surface.

High deuterium loading of Pd can be achieved by altering the physical-chemical properties of the cathode surface instead of using HPPE. The following main processes occur at the cathode surface:

- a) $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{H}_{(\text{adsorb.})} + 2\text{OH}^-$ local alkalization in proximity of the cathode
- b) $\text{H}_{(\text{adsorb.})} \rightarrow [\text{H}]_{\text{Pd}}$ loading reaction
- c) $2\text{H}_{(\text{adsorb.})} \rightarrow \text{H}_2$ parasitic reaction (bubbling out of H_2 gas)

First, reaction c) should be inhibited as much as possible. This can be done by reducing the catalytic properties of the surface by forming a thin, continuous, but not impervious layer of some appropriate substance. Our first idea was to add to the electrolyte small amounts of metallic ions capable of precipitating insoluble hydroxides on the cathode surface using the local alkalinity to initiate the process. The pH values at the cathode surface can be controlled by changing the current density. Unfortunately, most of the metallic ions (i.e. Fe^{+3} , Cu^{+2} , Ni^{+2} etc.) capable of precipitating as insoluble hydroxides tend to form compact and almost impervious metal layers on the cathode surface.

1.6.1. Searching for new electrolytes, acid environment.

It is known that an alkaline environment promotes the precipitation of alkaline-earth carbonates. It is also known that alkaline-earth ions, because of the strongly negative value of their standard potentials E_0 , cannot be galvanically deposited as metals. Accordingly, we found^(17, 18) that small amounts of SrCl_2 (10^{-5} – 10^{-4}M) added to an acid (pH=4) electrolyte, produce a thin and porous layer of SrCO_3 on the surface of the cathode, when, and only when, the electrolysis current density exceeds a certain threshold value. The small amount of CO_3^{2-} ions normally present in water are largely sufficient to insure precipitation of SrCO_3 .

Operating with light water and with this type of electrolyte, H/Pd ratios greater than 0.97 ($R/R_0 < 1.4$) were achieved⁽¹⁷⁾.

1.6.2. The micromolar Hg addition and discovery of new “heavy water” bacteria.

It is known that Hg exhibits a very high cathodic over-voltage of 1.21V in 1N HCl at $10^{-2}\text{A}/\text{cm}^2$, which is thought to reduce H^+ loss and H-H recombination at the electrode surface. Accordingly, we decided to test whether the addition of Hg ions could increase the Pd overloading. It was found that in the presence of even very small amounts (10^{-6} – 10^{-5}M) of mercury ions (Hg^+ , Hg^{2+}), the loading ratio (H/Pd) was strongly increased to give our best result of $R/R_0 = 1.15!$ ⁽¹⁷⁾.

The required amount of Hg ions is very critical. In fact Hg ions are reduced to metallic Hg on the cathode surface, thereby forming an amalgam, which beyond a certain concentration of Hg becomes impervious and stops the loading and deloading processes.

Once the correct amount of Hg salt was established, the loading ratios of H/Pd were in most cases excellent and reproducible with $R/R_0 \ll 1.3$ being currently achieved⁽²⁰⁾. Our results were reproduced by Pirelli Labs⁽²¹⁾ (Milan-Italy) and SRI- International⁽²³⁾ (Stanford-USA). All things considered, it seemed we were dealing with a pretty good loading protocol in 1999.

When we tried to apply such a protocol for D loading using D_2O , the results were consistently worse⁽¹⁸⁾ and less reproducible. The reasons for such failures were:

- The impurities concentration usually present in the “as received” heavy water is too large. Double distillation of D_2O is a necessary but not a sufficient pre-treatment.
- Heavy water contains bacteria belonging to two new species. One of these, *Ralstonia* type⁽¹⁹⁾, was found to form colonies on the cathode surface, which hinder the proper formation of the Sr carbonate layer. Moreover, such bacteria can metabolize almost any kind of heavy metals, including Hg and uranium, thereby removing them from the electrolyte. Finally, they can change the pH of the solution up to about 9. A bulk precipitation occurs at such a pH, thus preventing formation of a very thin precipitate on the cathode surface. Our loading procedure works properly only when the mean pH value of the solution is about 4 and the pH is expected to rise up to 10 only in the proximity of the cathode as a consequence of the applied current density⁽²²⁾.

This bacteria has been submitted for registration in June 2000 (DDBJ –Japan and NCBI-USA) with the name of *Ralstonia detusculanense* and accepted on October 2001. The potential for bio-remediation has yet to be fully explored.

We found that a particular and very complex procedure was required for satisfactory D₂O sterilization⁽¹⁸⁾. This includes double distillation in presence of KMnO₄, firstly in acid and then in alkaline, while operating in dry nitrogen at 95°C.

We tried to eliminate at least part of the time consuming and troublesome pre-treatments needed not only to “kill” the bacteria but also to free the heavy water of inorganic and organic pollutants.

1.7. Use of alcohol-water solution and Sr-Hg salts. Possible “intrinsic” production of Pd nanoparticles. Replication Iwamura experiment.

The main controlling parameter of the D-Pd loading is the ratio between the total amount (not the concentration) of the impurities present in the electrolyte and the surface area of the cathode. Consequently, we propose two simple ways to solve the problem.

- a) A small cell can be used containing only 50 ml of electrolyte.
- b) The cell currently used in our experiments, whose volume is about 1000ml, can be filled with a new electrolyte that is prepared by diluting the impure heavy water with a suitable organic solvent.

The reduction to 50ml is equivalent to a 20 times reduction of the impurities. However, the second approach is more attractive because it does not require construction of a new cell and the ratio between organic solvent and heavy water can be varied over a wide range.

As far as the choice of the organic solvent is concerned, the following requirements should be satisfied:

- large miscibility with water;
- very small amount of H₂O present as residual impurity (to avoid isotopic contamination in D loading);
- negligible acid properties with no isotopic contamination for partial dissociation in H⁺ ions;
- boiling point not far from 100°C.

Alcohols, ketons and esters seemed to be the most promising solvents.

After several experiments we found that the partially D substituted ethyl alcohol (C₂H₅OD) was the best choice. It does not exhibit significant isotopic contamination and it is available at a reasonable price of about 1100Euro/l. Nevertheless, for our purposes distillation was necessary before use (see below). Moreover, distillation of the D₂O was also very effective in improving reproducibility and eliminating unexpected impurities. This requirement became clear when the cathode was subjected to ICP-MS analysis after the study.⁽²⁶⁾

We performed a series of experiments with hydro-alcoholic solutions containing small amounts of Sr salts and Hg ions during which we found excess heat⁽²²⁾ and tritium⁽²⁴⁾ well above background. We found that in the hydro-alcoholic environment, during the anodic phase of our loading cycles, the Pd electrode is eroded. Significant amounts of very fine Pd particles are found at the bottom of the cell at the end of the experiments. ICP-MS analysis after electrolysis showed the presence of Pd in this black powder⁽²⁶⁾. After several loading-deloding cycles, the Pd wire could absorb deuterium quickly and without applied current to give D/Pd up to 0.75. Such a behavior appears to result from increased activity of the Pd surface. We would like to point out that Yoshiaki Arata (University of Osaka, Japan) has stressed the importance of *nano-structures* in order to get loading of Deuterium in Pd (even over 1/1). As consequence, very large amounts of “anomalous excess heat” and ⁴He⁽²⁷⁾ are observed. It is possible to suggest that the increased activity exhibited by our Pd wires is caused by formation of *nano-structures* on its surface, similar to those obtained by Yoshiaki Arata.

Y. Iwamura⁽²⁵⁾ showed that Sr is apparently transmuted into Mo (molybdenum) in a gas loaded system. We tried to check whether such a transmutation could occur also after the repeated D-Pd loading/deloding cycles in our experimental set-up. In July 2002 we were ready to perform an independent variant of the Iwamura experiment. Before starting, we analyzed by ICP-MS all the components present in the cell including the electrolyte (C₂H₅OD, D₂O, SrCl₂, DCl, HgCl₂), and pieces of the Pd cathode and Pt anode. At the end of the repeated D-Pd loading/deloding experiment, the electrolytic solution was vacuum dried. The residue was collected and again analyzed by ICP-MS together with the Pd cathode after it was dissolved in aqua regia. Mo was found in excess of any possible contamination, and the isotopic composition of the Mo was different from the natural one⁽²⁶⁾. It appears that the phenomenon first discovered by Y. Iwamura in a flowing deuterium gas system also occurs in our electrolytic cell when operated using our loading-deloding procedure.

1.8. Thorium salts as electrolyte.

In January, 2003, we substituted Th salts for the Sr salts used previously. We decided to test whether something similar could happen in our experiments, based on some 1998 results indicating possible Th transmutations during high-power AC (50Hz) electrolysis with zirconium electrodes⁽²⁸⁾. Like Sr, Th ions can form an inorganic precipitate on the cathode surface as Th(OH)₄ (solubility product K_s = 10⁻⁵⁰), by action of the

current density. Another similarity to Sr^{+2} is that Th^{+4} ions cannot be galvanically deposited because of the highly negative value of their standard potential ($E_0 = -1.899\text{V}$).

Accordingly, as objectives of the present work, the following were sought:

- a) occurrence of excess heat,
- b) presence of foreign elements in both the cathode and the cell after electrolytic loading.

The operations were performed with electrolytes containing small amounts of Th and Hg salts.

2 Experimental set-up

2.1 Electrolytic cell and flow calorimeter

The cell configuration is shown in Fig. 1. The sample holder, a PTFE tube, is placed in a 1000 ml borosilicate glass (type 3.3) cylinder (\varnothing 67mm, height 460mm). 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 (\varnothing 50 μm) long (60cm) Pd wire (total surface $\approx 1\text{cm}^2$). In the lower part of the "U", at its center, a small weight (6g PTFE cylinder) keeps the wire tense during the Pd loading so as to compensate its 4 - 6% elongation. The anode is a Pt wire (\varnothing 250 μm , length 60 cm, purity 99.99%). A third Pt wire (\varnothing 250 μm , 30 cm long) is put exactly in the middle of the "U" shaped cathode for reference purposes.

To measure cathode resistance, an AC current (16mA, 10KHz, square wave) is superimposed on the electrolysis DC current, and the resistance value is continuously monitored using the resulting AC voltage drop.

A high quality LM135H thermometer (sensitivity 0.05 $^{\circ}\text{C}$), inserted in a PTFE tube, is placed in the middle of the cell, perpendicular to the cathode and anode. A Joule heater (max. 20W) is used to calibrate the calorimeter and is located between the electrodes in a peripheral position. It consists of a chain of 20 resistors inserted in a PTFE tube (\varnothing 8mm, length 30cm) filled with thermal conducting grease.

The cell is pressurized (50mbar) and thermally insulated. The electrolysis gases and vapors are made to flow through a silicon oil bubbler and through a twin cold trap before reaching the atmosphere. The correction for this loss of energy is not yet applied, consequently all the data about excess heat are underestimated.

The heat exchanger within the cell consists of a 500cm long PTFE pipe, outer/inner diameter 4/2mm, wound around the PTFE holder through which water flows. 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 computerized peristaltic pump (Masterflex 7550-62) provides a constant flow of distilled water (0.200ml/sec, with day-to-day stability of $\pm 1\%$, routinely measured every 12 hours). Water is picked up by the pump from a 2-liter reservoir to which it returns from the cell. The cell, water reservoir, and pump, are placed in a container held constant at 24 $^{\circ}\text{C}$.

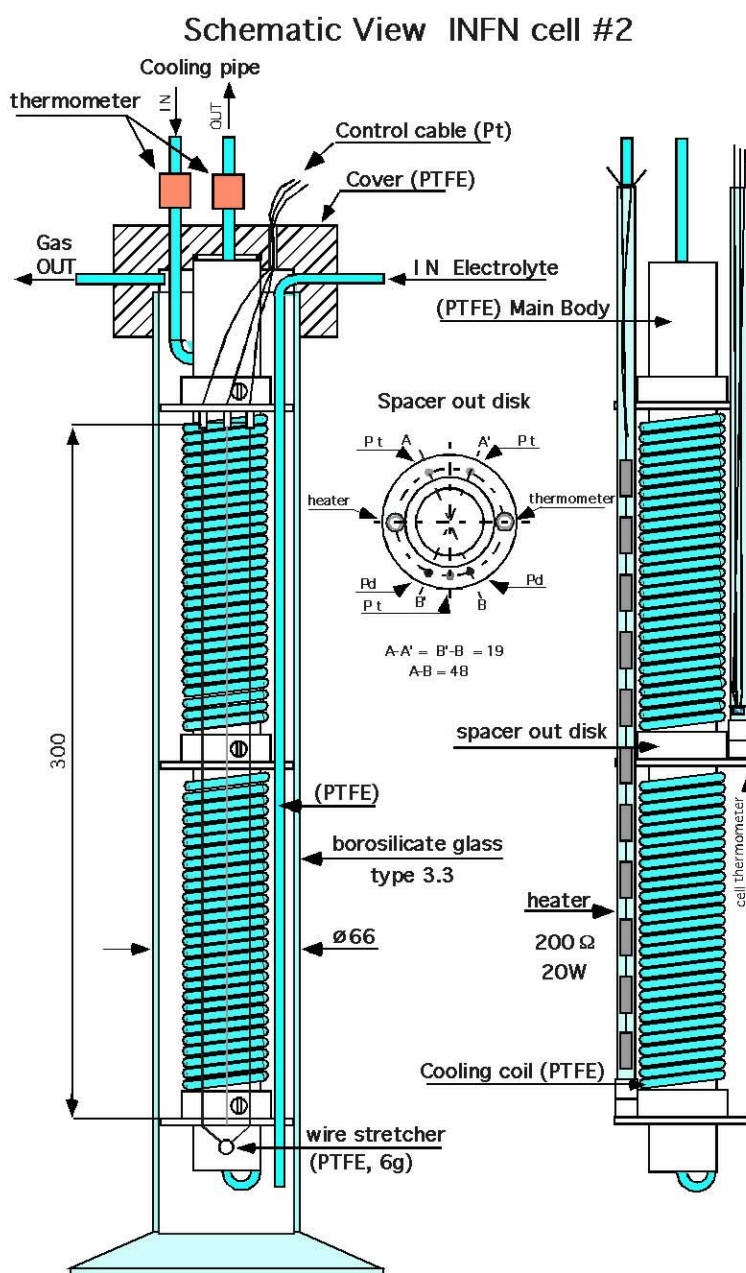


Figure 1 – Schematic view of the electrolytic cell.

2.2 Composition of the electrolyte

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

The ethyl alcohol was previously vacuum distilled at $35^\circ C$ in order to eliminate mainly sodium and iron and ultra-filtered using a 100nm, MILLIPORE PTFE filter. The density was routinely measured (Mettler Toledo

DA-110M) before and after distillation, to confirm that no significant H₂O contamination occurred during the operations.

The heavy water, 99.97% isotopic purity reactor grade (Ontario Hydro), was distilled at 45°C under vacuum and ultra-filtered before use. Density was measured before and after distillation. Th(NO₃)₄, (5--15mg) was added to the electrolyte and the pH of the resulting hydro-alcoholic solution was adjusted to about 3 by adding a few drops of HNO₃, in order to avoid precipitation of Th(OD)₄.

3. Experimental results

3.1 Excess heat generation and abnormal resistance behavior.

Under “normal” conditions when electrolysis current is switched off, the cathode resistance gradually increases toward its maximum because of D deloading. In contrast, when the electrolyte contains thorium, stopping the current causes the cathode resistance to decrease toward a minimum value (Fig. 2) where it remains stable for a few minutes. Finally, it starts to rise, moving gradually towards its maximum as expected.

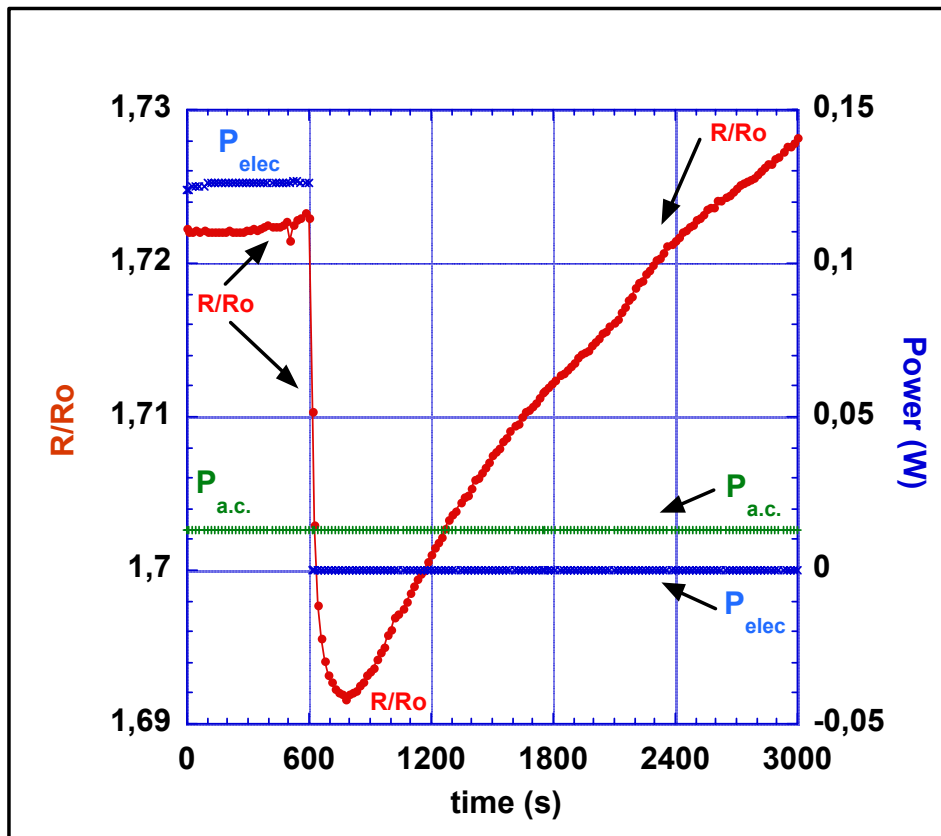


Figure 2 – The fall in cathode resistance when the electrolysis is switched off. R/Ro is the ratio between the actual resistance R and resistance at D/Pd=0. P_{elec} is the power input due to the electrolysis current. P_{a.c.} is the power input due to the a. c. current used to measure the cathode resistance.

We propose that before interruption of electrolysis, the wire was at a temperature higher than that of the solution, and the observed decrease in resistance was caused by cooling of the wire.

It can be easily demonstrated that the observed phenomenon cannot be attributed to Joule heating induced by the electrolysis current flowing into the cathode. In our loading cycles we kept the electrolysis current constant, typically at 10mA. The cathode resistance is about 60 ohm. Power input into the cathode is given by the formula:

$$W=i^2 \cdot R$$

where R is the cathode resistance, and i is the current flowing into the cathode averaged along the wire. By roughly assuming that this current is equal to the electrolysis current, power experienced by the cathode cannot exceed 6mW. This amount of Joule heating has a negligible effect on the resistance. In order to achieve a quantitative evaluation of the observed phenomenon, we performed the tests summarized in Fig. 3.

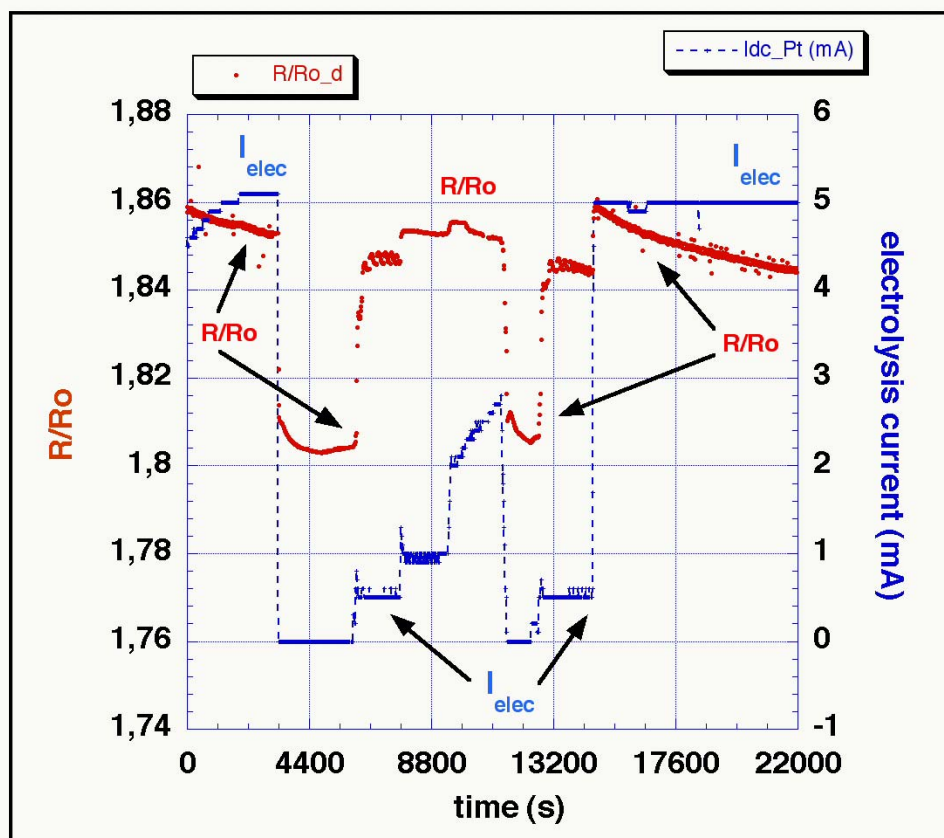


Figure 3 – Evidence of the phenomenon of restoration of the R/R_o value with very low electrolysis currents and consequent demonstration that the drop down of R/R_o is not due to the shut down of the Joule effect. I_{elec} is the electrolysis current.

After power was turned off and cathode resistance decreased, an electrolysis current of 0.5mA was applied again in the circuit. This supplied 15 microwatt of Joule heating to the Pd wire. No resistance rise can be expected from such a small amount of power. Yet, the resistance of the wire jumped up to 90% of the level it had reached before shut-down. Further incremental increases in the electrolysis current up to 3 mA produced progressively smaller increases in resistance. The test were repeated several times and the results were substantially the same.

It appears that the observed fall in cathode resistance was not due to the Joule heating induced by electrolysis current flowing into the cathode. In fact, the only plausible explanation we can find for the observed phenomenon is that the Pd wire generates excess heat once a small electrolysis current is applied. The phenomenon, whatever it is, appears to occur at the cathode surface.

We previously recorded this kind of anomalous decrease in resistance several times during some previous loading experiments with alcohol-free electrolytes containing Sr-Hg. It was observed only once with as great an intensity when the hydroalcoholic Th electrolytes were used. The largest event with non-alcohol electrolyte was reported in Ref. 18, pg. 189, Fig. 8 where we cautiously proposed that the cell was producing excess heat.

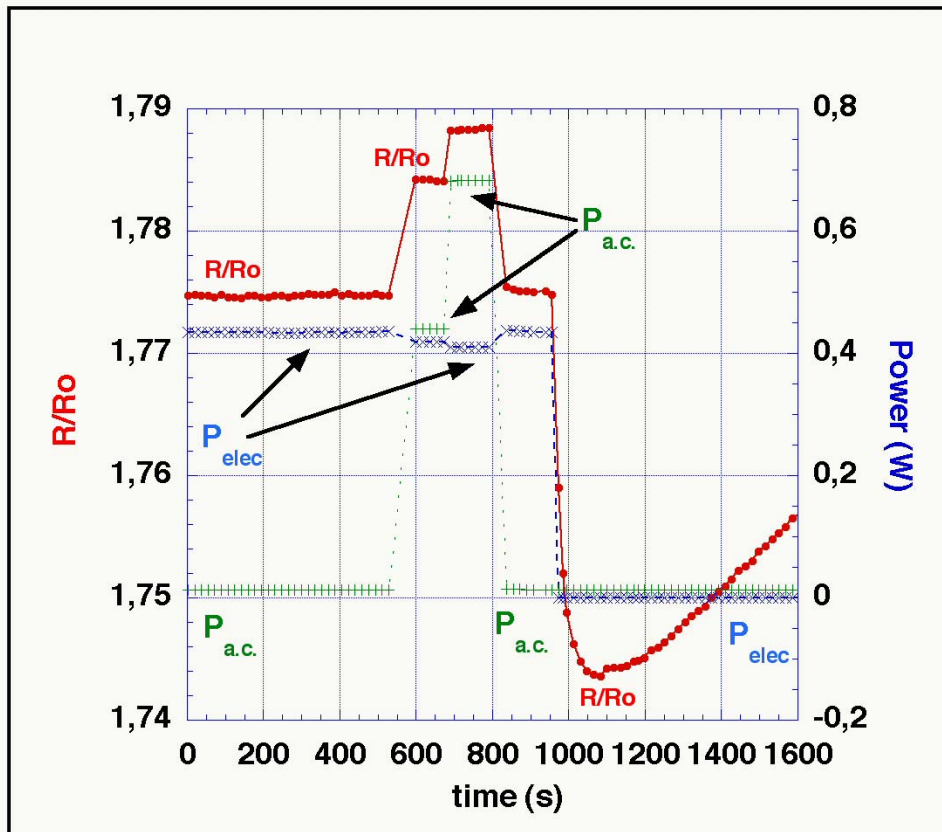


Figure 4 – Self calibration procedure. On the left side it is shown the increase of R/R_o due to the Joule effect produced by increasing the a. c. power input ($P_{a.c.}$). On the right side it is shown the R/R_o drop down when the electrolysis power (P_{elec}) is reduced.

3.2 Self calibration procedure.

As we performed the tests described here, we realized we had on hand a simple method to assess and evaluate the occurrence of excess heat in the cell: the cathode itself can act as an “in situ” micro-calorimeter. Fig. 4 shows how this calibration can be achieved and how the excess heat can be rapidly and precisely estimated.

While DC current is supplied to the cathode, an AC current (about 100mA) is superimposed, which generates additional power of about 680mW. This additional power causes cathode resistance to increase from the initial R/R_o value of 1.775 to the final one 1.788, caused by the resulting temperature change. When the AC current is turned off, resistance returns to its initial value. In other words, a variation of 0.013 in cathode resistance ratio corresponds to an input power of 680mW. After this “calibration” was done, electrolysis current was switched off. We observed that the R/R_o ratio dropped from 1.775 to 1.744. Based on the previous “calibration”, this change in ratio indicates that the cathode was generating $31/13 \times 680\text{mW} = 1621\text{mW}$.

To evaluate the total power balance we have to consider total external power fed into the cell. About 150mW resulted from the DC electrolysis current. The net gain of ~1440mW means the output/input ratio is ~9.5. Because this auto-calibration method may be considered unconventional, we decided to confirm the excess heat using flow calorimetry.

3.3 Flow calorimeter measurement.

During the tests shown in Fig. 4, the cell was not thermally insulated because we had to visually observe the inside of the cell during the test to be sure the cylindrical weight kept the Pd wire under enough tension. As soon as we realized that the cathode was producing excess heat, we applied makeshift thermal insulation to the cell, to improve calorimetry. Nevertheless, diurnal temperature fluctuations ($\pm 3^\circ\text{C}$) caused the inlet water temperature to vary over a range $\pm 0.5^\circ\text{C}$. This change caused the calorimetric to oscillate by $\pm 500\text{ mW}$ during the day/night cycle. Despite this variation, measurement of heat generated within the calorimeter is still valid

because the calorimeter was used to make absolute measurements. In fact, the measured values are underestimated because of heat loss through the imperfect thermal insulation of the cell.

The absolute measurement of the heat flow out of the cell is shown Fig. 5. While the power input was maintained constant at $\sim 150\text{mW}$, the measured power output oscillated around an average value of $1400\text{mW} \pm 400\text{mW}$, with a tendency to rise while the R/R_0 ratio slowly decreased, which indicated that the D/Pd ratio had increased during this time. Apparently, the flow calorimeter measurements are in substantial agreement with the "in situ" micro-calorimetric estimations. Further experiments are in progress to optimize electrolyte composition and heat recovery.

Surprisingly, we found that electrolyte consumption was over 5 times larger than predicted by Faraday's law. We suspect that this loss is caused by heat being generated in a few hot spots where temperature is very large. This local heating evaporates the solution so that gaseous D_2O and C_2H_5OD are lost in addition to D_2 and O_2 . We plan to build a new cell made from PTFE, quartz, HDPE, and mylar in order to detect IR radiation from the deuterated Pd wires using a thermo-camera.

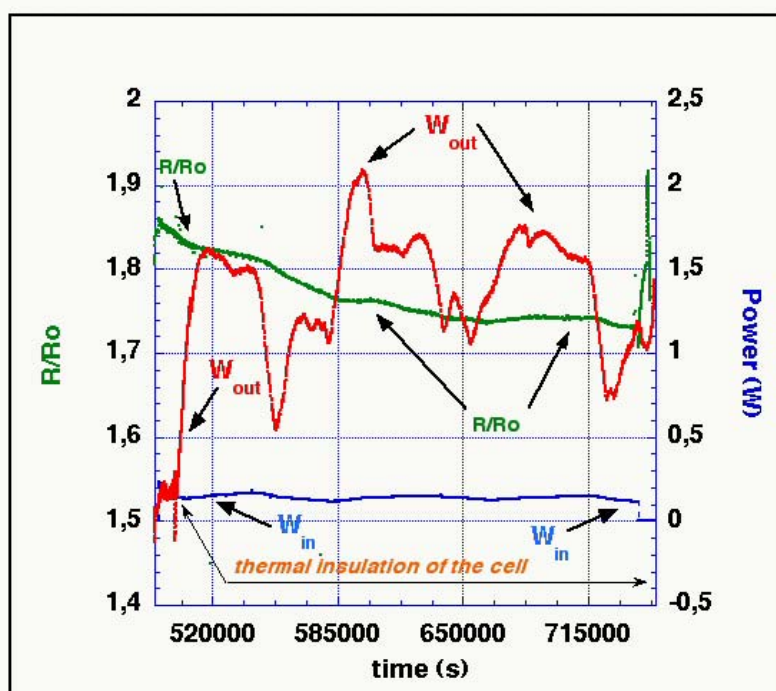


Figure 5 – Flow calorimeter measurements. W_{in} is the total power input. W_{out} is the power flowing out of the calorimeter with the outgoing water flow.

4. ICP-MS Measurements.

4.1 Procedure

ICP-MS measurements were performed in a chemistry laboratory operating under the ISO 9001 quality control protocol. The laboratory is located in the Interdisciplinary Research Area of Castel Romano (Rome), in the "Centro Sviluppo Materiali" building. The ICP-MS used is from HP & YOKOGAWA Analytical Systems, model 4500. It has been in operation since 1996. Calibrations with Atomic Absorption Standards are made every day before starting analysis. Sensitivity is about $6 \cdot 10^{10}$ Atoms/counts. Typical background is 10 - 80 counts, depending both on the mass analyzed and overall condition of the instrument. Background is higher for two well known sources of interference, due to Ar, Cl, O, N, C, H, and impurities dissolved in the deionised "Milli-Q" water and reagents used. The carrier gas is Ar. Because of our specific experimental constraints, we almost always use hot, concentrated Aqua Regia to dissolve the materials in glass beakers (borosilicate 3.3). A concentration of 0.25% is submitted to the instrument for analysis of the main elements in the electrolyte (Pd, Sr, Th, Hg). We make 2 runs, from mass 2 to 260 with a resolution of 0.5 AMU. Each run takes about 200

seconds and sample uptake is 0.5ml/min. Blank and mass tuning (Li, Y, Tl) runs are made at the beginning of analysis, after 3 hours of operations, and at the end of the study. Calibration is done more frequently if an element is at a particularly high concentration. Between each measurement there is a washing cycle of about 10 minutes using HNO₃ at 5% concentration or Aqua Regia if needed. A blank measurement is always performed.

Data are analyzed according to the general recommendation of ICP-MS manufacturer and to our specific operating conditions. We especially want to avoid spurious results caused by double mass and half-mass signals adding to the masses of interest. To solve such problems, we performed a large number of analysis using standard solutions of elements of interest to calibrate the machine. Obviously, D₂O and C₂H₅OD were also carefully characterized.

The cell was cleaned after each experiment using repeated cycles of water and organic solvents in an ultrasonic hot bath. After Experiment #2 (Feb. 14, 2003; see Table 1a), we increased the duration of immersion in HNO₃ (65%, 60°C) from 2 minutes to 14 hours because we suspected that a residual amount of Cs might be hidden somewhere in the cell.

4.2 Experimental results

4.2.1 Sr → Mo

Results using Sr within the electrolyte were reported in Ref.26. We observed that some of the Sr was transmuted to elements with mass 94 and 96, qualitatively in agreement with the Y. Iwamura results. Moreover, the total amount of Mo atoms we found ($1-2 \cdot 10^{15}$), normalized to Pd electrode surface (about 1cm²), is very similar to the Iwamura gas experiments.

4.2.2 Cs → Pr

Transmutation of Cs to Pr (according to Y. Iwamura) was not observed when we used concentrated Cs because we were not able to achieve a sufficiently high deuterium concentration in the cathode. Much to our surprise, results were better when a Th salt was used with a “proper mixture” of Ca and Sr salts. Using these mixtures, we apparently transmuted Cs and, in smaller amounts, Pr. We note that the thorium salt did not contain measurable impurities of Cs or Pr, according to both the assay from the chemical company (Aldrich) and our routine analysis by ICP-MS. In the best experiment in which apparent transmutations have been detected, the signal is nine times background.

Later (in experiments #5 and #6) we refined the method using only Th and Hg salts to increase the deuterium concentration in Pd. In experiment #6 we observed a signal to background ratio as large as 21. Experiment #4 did not achieve the necessary deuterium concentration, making it a very useful blank for ICP-MS analysis.

In other words, apparent transmutations of Cs into Pr occurred in an electrochemical environment, similar to those reported by Y. Iwamura in a gaseous environment^(25, 29) and recently confirmed by A. Takahashi *et al.*⁽³⁰⁾

4.2.3 Thorium results

We performed a total of 4 experiments with Th salts, in amounts ranging from 8×10^{-6} to 6.5×10^{-5} moles in the total volume of electrolyte. The pH for the Th solution was 3 compared to 4 for the Sr solution.

4.2.4 ICP-MS: results

Some results are summarized in Tables 1 and 2. We list masses that are relatively easy to interpret and for which reproducible results were obtained. We observed several other anomalies that are not yet fully understood. We anticipate that most of such anomalies are in the range of masses 46 - 60, 107 - 116, along with some isotopic anomaly for Pd.

Table 1: Results of ICP-MS analysis. Please note that "overloading" is defined here as D/Pd>0.9.

Exp	Date: begin→ end [dd/mm/yy]	Electrolyte composition: [moles]	Comments on results OVL=Overloading S/N=Signal/Noise Pr=1count=6·10 ¹⁰ Atoms;
#1	20/12/02 → 16/01/03	CsNO ₃ [5·10 ⁻⁵] - SrCl ₂ [1·10 ⁻⁵] LiOD [1.5·10 ⁻⁵] - H ₂ SO ₄ [5·10 ⁻⁶] NH ₃ OH [1·10 ⁻⁴]	Almost No OVL ; Anode=Pd wire 250μm Pr=80=>S/N=2
#2	17/01/03 → 14/02/03	CaCl ₂ [21·10 ⁻⁵] - SrCl ₂ [1·10 ⁻⁴] HgCl ₂ [2·10 ⁻⁴] - H ₂ SO ₄ [1·10 ⁻⁵]	2 times OVL, Residual Cs?? Pr=170=>S/N=4
#3	18/02/03 → 05/03/03	CaCl ₂ [1·10 ⁻⁵] - SrCl ₂ [1·10 ⁻⁴] HgCl ₂ [2·10 ⁻⁴] -H ₂ SO ₄ [1·10 ⁻⁵] Th(NO ₃) ₄ [8·10 ⁻⁶]	3 times OVL R/Ro=1.706 Pr=370=> S/N=9
#4	04/04/03 → 14/04/03	HgCl ₂ [1·10 ⁻⁵] -Hg ₂ SO ₄ [1·10 ⁻⁴] Th(NO ₃) ₄ [2.1·10 ⁻⁵]	No OVL
#5	15/04/03 → 19/05/03	Th(NO ₃) ₄ [2·10 ⁻⁶] Hg ₂ SO ₄ [2·10 ⁻⁶]	Several times OVL; Excess heat; Pr=300=>S/N=6
#6	24/05/03 → 14/07/03	Th(NO ₃) ₄ [2·10 ⁻⁶] Hg ₂ SO ₄ [5·10 ⁻⁶]	Several times OVL; Excess heat. Pr=1.4E3=>S/N=21 ²⁰⁸ Pb anomaly

Table 2: shown here are the counts of the main mass found; the natural abundance is in paranthesis. The composition of the solution is described in Ref. 26.

Exp	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=.46
#1	7·10 ³	2.2·10 ⁶	2.4·10 ⁶	2.7·10 ⁶	>3·10 ⁸	1·10 ⁴
#2	0	0	2.1·10 ⁶ 63/65=1.94	1.8·10 ⁶	6·10 ⁵	4·10 ⁵
#3	4·10 ⁵	2.7·10 ⁶	6.1·10 ⁶ 63/65=1.93	1.7·10 ⁷	1·10 ⁶	9.5·10 ⁵
#4	2.5·10 ⁴	1.4·10 ⁶	2.9·10 ⁶ 63/65=2.05	7.5·10 ³	1.94·10 ⁵	6.9·10 ⁵
#5	1.8·10 ⁶	2.3·10 ⁶	2.4·10 ⁷ 63/65=2.07	1.2·10 ⁷	9·10 ⁴	1.5·10 ⁶
#6	2.72·10 ⁷	6.4·10 ⁶	9.3·10 ⁸ 63/65=2.08	5.1·10 ⁸	2.2·10 ⁵	2·10 ⁸ 206/208=.39

3 Conclusions

After a large number of experiments during 14 years of research aimed at finding anomalous effects in systems forced to a high concentration of deuterium, we are confident that most of the observed effects occur at the interface between the solution and the Pd bulk. A properly formed layer of a third element is necessary.

Nonequilibrium is also necessary to trigger the effects. Recently, we found that using a deuterated hydro-alcoholic solution made slightly acid works very well. Addition of Th and Hg salts at micromolar concentrations improve the effects even at very low electrolytic current density ($<10\text{mA/cm}^2$).

We think that the model developed by Akito Takahashi about multi-body resonance fusion of deuterons⁽³¹⁾ can explain most of the thermal and isotopic anomalies, including foreign elements, that we have recently observed.

Further work is necessary to fully characterise the system and increase the magnitude of the effects.

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