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**HIGH HYDROGEN LOADING INTO THIN PALLADIUM WIRES
THROUGH PRECIPITATE OF ALKALINE-EARTH CARBONATE ON THE
SURFACE OF CATHODE: EVIDENCE OF NEW PHASES IN THE Pd-H
SYSTEM AND UNEXPECTED PROBLEMS DUE TO BACTERIA
CONTAMINATION IN THE HEAVY WATER**

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Abstract

A new procedure has been developed at INFN Frascati Laboratory in order to achieve a very high Hydrogen or Deuterium electrolytic loading into a long and thin Palladium wire. This technique consists in the addition of a very small amount of alkaline–earth elements into a very diluted acidic solution.

Because of enhancing pH values around the cathode, during the electrolysis, carbonates are able to precipitate onto the cathode's surface forming a thin layer which strongly increases the Pd loading; a computer simulation has been developed to find out the proper working conditions for the carbonates precipitation.

Loading results of Hydrogen were excellent ($H/Pd \cong 1$). The evidence of a new phase in the Pd–H system was inferred from the basis of the variation of the thermal resistivity coefficient of the Pd wire as a function of the H/Pd ratio.

Less satisfactory results were obtained for Deuterium ($D/Pd \approx 0.85$, no excess heat) because of inorganic and organic contamination normally present in ordinary heavy water. A novel procedure to purify heavy water, developed at INFN–LNF, has permitted to achieve interesting loading, up to $D/Pd \cong 0.97$, for several days and evidence of overheating of Pd wire i.e. “excess heat”.

We have discovered that the obtained poor results with the heavy water are mainly due to the presence of two kinds of new bacteria living in the commercial reactor–grade heavy water we have used for the loading tests. We named such bacteria (*Ralstonia* and *Stenotrophomonas* genera) “*Detusculanense*” specie.

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INTRODUCTION

After ten years of experiences the appearance of excess heat, in the so called “Cold Fusion Phenomena”, according to our opinion it seems to be related to the contemporary occurrence of two different and well defined processes:

- a) *Overloading* of Deuterium in the Palladium lattice and, simultaneously,
- b) *Movement* of Deuterium into the Palladium, without losing of overloading.

The main problem in these kinds of experiments, since 1989, has been the *poor reproducibility* of results.

According to our experience, the typical excess power (during the rare “lucky” conditions we have dealt with) was about $5 \div 10\%$ of the total input power; such an excess power rose, in our “best experiment”, up to a maximum value of 200% for many hours [Ref. 1], corresponding to a remarkably large absolute power value (over 100 Watts). During this “best experiment”, obtained with a long (180cm) and thin (0.1mm) Pd wire, the very large excess power lasted over 12 hours (Fig.1) and we were able to make several different controls (about the reality and the absolute value of excess power). During this phenomenon we switched off electrolysis current for some minutes and the plot clearly shows the wire de-loading; after switched on again, wire re-loaded and gain recovered but the effect extinguished in a few hours.

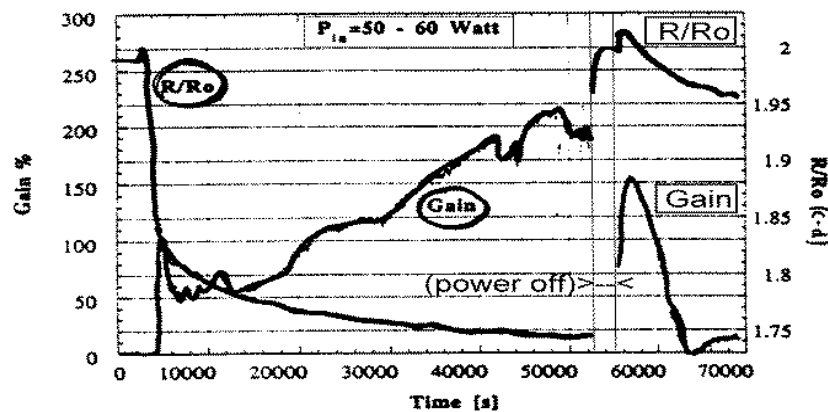


Fig. 1 – Excess heat evidence: Once, a test provided a very large amount of excess power (up to 100 W) correlated to the R/Ro resistivity drop (high D/Pd loading) with a thin long Pd wire; this effect lasted for many hours.

In order to reduce the irreproducible results we decided to develop and test a new electrolytic procedures starting, as a reference, from the simpler Hydrogen/Palladium system.

The main targets, “a really suitable” for new loading technique were the following:

- H/Pd: $> 0.95 \rightarrow R/Ro: < 1.5$;
- Time to get H/Pd > 0.95 : < 50 hours;
- Stability of overloading: > 4 hours;
- Success rate: $> 60\%$.

The maximum loading ratio H/Pd or D/Pd, ever achieved by gas pressure at room temperature, according to the literature, is 0.97 at 50000 atmosphere of pressure (Baranowski data, presented at the Conference of Kawasuci, Japan, Oct.'94). The aim of our new procedure is to approach and even overcome such a value.

It is, in fact, a common experience in Cold Fusion studies that, in order to achieve “anomalous excess heat” it is necessary (but not sufficient) to overcome a certain threshold in the high level region of the D/Pd ratio: M. H. McKubre, at SRI International, performed some systematic studies about this aspect [Ref. 2].

— *Typical experimental problems*

During the loading, the Pd volume increases up to 13%, usually in a not homogeneous way. This kind of behaviour is the origin of several drawbacks, capable to seriously affect the loading process:

- a) superficial cracks (paths for H or D de-loading);
- b) dislocations, internal vacancies (production of, high pressure, micro-bubbles of H₂/D₂ inside the defects).

Both the problems are known to be related to the purity and “history” of Pd.

In order to reduce the influence of these hardly controllable parameters, various procedures have been generally adopted. The most common of them can be summarised as following:

- a) large (>500mA/cm²) current density, in order to increase, according to the Tafel law, the cathodic over-voltage;
- b) time pattern of current (like, e.g., the “low-high Takahashi procedure”, developed at Osaka University since 1991 or the “high peak- power pulse method”, developed at INFN-LNF since 1994).

Such procedures in any case do not solve completely the problem of reproducibility.

INFN-LNF PROCEDURE

The loading measurements, expressed as H/Pd or D/Pd, were performed on-line and in-situ, by measuring the variations of Pd resistance [Refs. 3,4], which are known to change, depending on the ratio of H/Pd and D/Pd (Fig. 2) [Refs. 5].

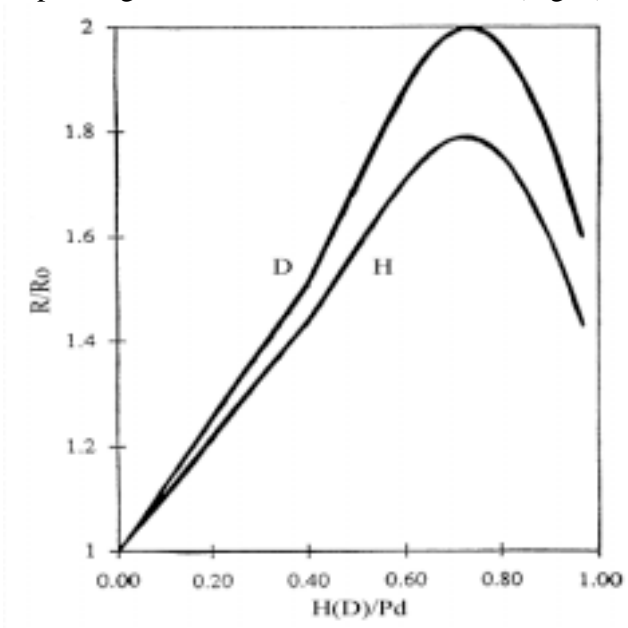


Fig. 2 – Normalised Palladium resistance versus Hydrogen (Deuterium) molar fraction of Pd. Peak value is: H/Pd= 0.75, R/R₀= 1.78 (Hydrogen) and D/Pd= 0.75, R/R₀= 2.0 (Deuterium). Maximum known loading is H(D)/Pd= 0.95 at R/R₀= 1.4 (1.6).

The main characteristic of our method is to induce the precipitation of carbonates, directly on the wire surface, during the electrochemical loading of the Pd wire, as far as to form a semi-permeable, thin and homogeneous barrier, which allows the entrance of Hydrogen or Deuterium into Pd lattice as atomic H or D [Ref. 6]. Such a barrier acts as a poison for the recombination processes: $H+H=H_2$ or $D+D=D_2$.

Such a layer was expected to increase the cathodic over-voltage, through the inhibition of the H-H recombination process.

A peculiar electric circuit has been developed in order to achieve a complete decoupling between electrolysis dc-current (power supply) and Pd wire ac-current (resistance measuring) (Fig.s 3, 4). Furthermore, the cathodic electrolytical current is periodically inverted in such a way that, alternatively, (using a 100 seconds period square wave) the most-cathodic part of the wire is converted into the less-cathodic one and vice-versa: such a procedure (using the “twin relay control” block reported in the plot) is useful for a more homogenous loading.

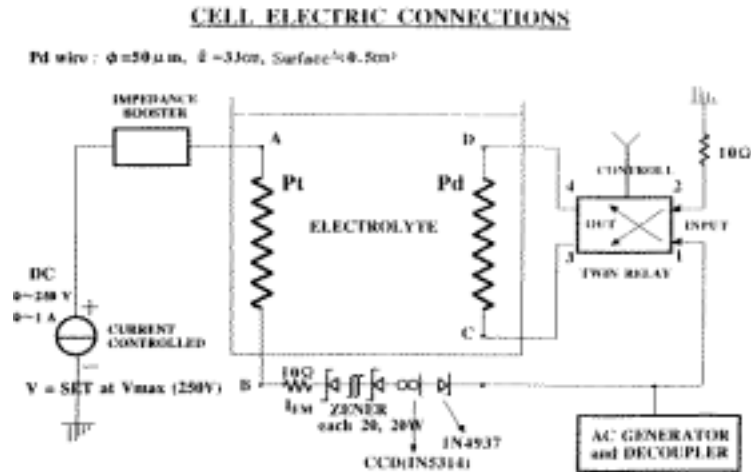


Figure 3 – Apparatus set-up: electrolytic cell, D.C. power supply block and a.c. resistance measurement block; all electric and thermodynamic parameters are acquired by several Digital Voltmeters (DVM) controlled by a computer.

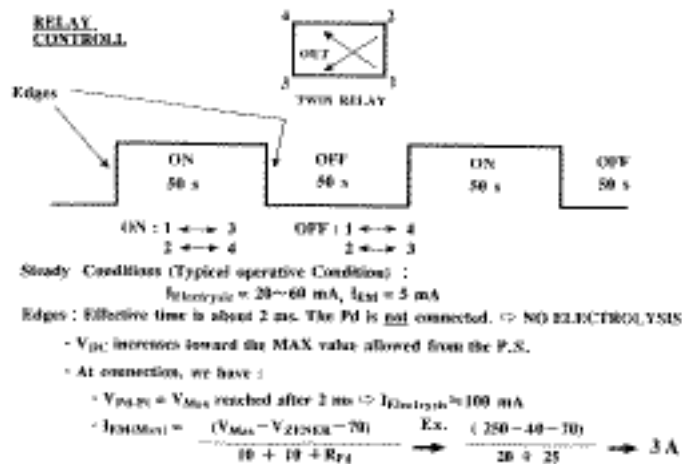


Fig. 4 – Detail of the electrolysis control logic: The “twin relay control” block and diodes chain have been used to improve the loading.

A further important characteristic is the wire's diameter, which is as thin as 50 micrometers in our recent experiments. This allows for the following advantages:

- High current densities can be achieved with low electrolytic currents (and consequently low input power).
- Because of the high value of the wire's resistance the relative error of the loading of the Pd wire is strongly reduced.
- The loading kinetics are increased.
- The dimension of the H/D bubbles released during the electrolysis, for geometrical reasons, cannot exceed the diameter of the wire. Taking into account that the internal pressure of a bubble of gas increases by decreasing its diameter, it is convenient, in order to prevent eventual de-loading, to maintain as low as possible such a diameter.
- Possibility of changing, in large amount, the pH range (9–13) of the solution just around the cathode surface, by changing the electrolysis current density: specific computer simulations were developed for this purpose (Fig.s 5; 6), [Ref. 6].

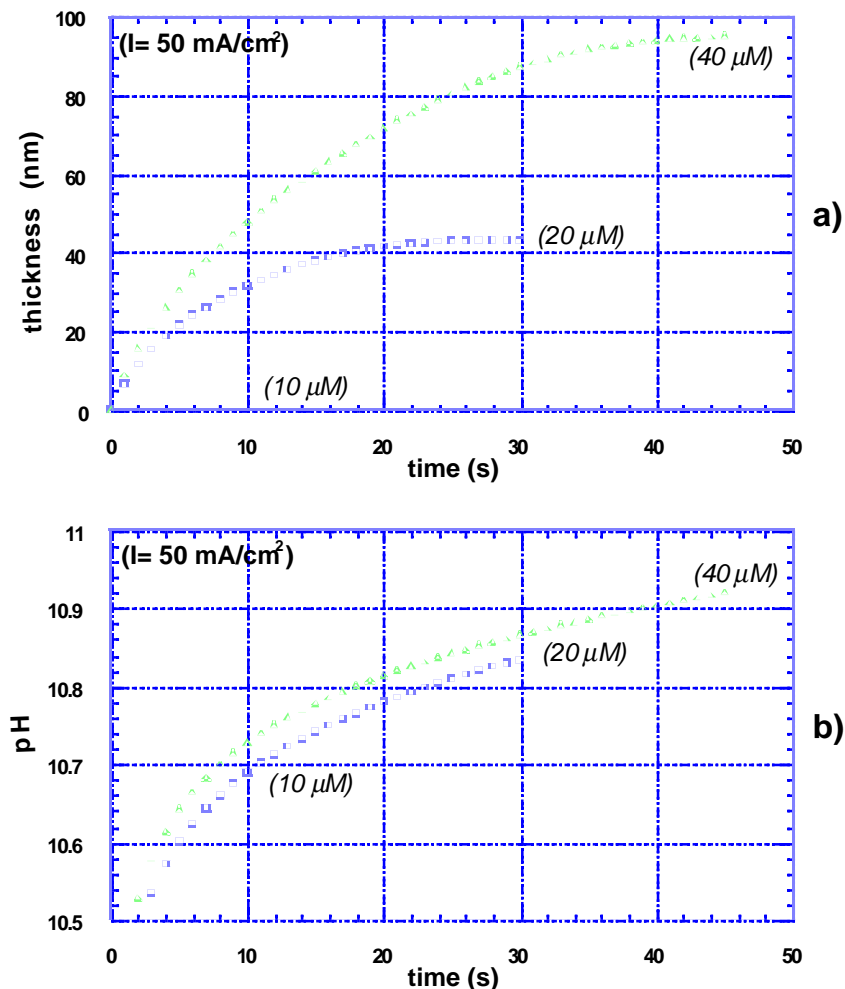


Figure 5 – Computer simulation at constant current density of 50 mA/cm^2 , wire diameter $50 \text{ }\mu\text{m}$. a) SrCO₃ deposition thickness, versus time, at 10, 20, 40 μM of Sr²⁺ ions concentrations; b) pH variation versus time at 10, 20, 40 μM of Sr²⁺ ions concentrations.

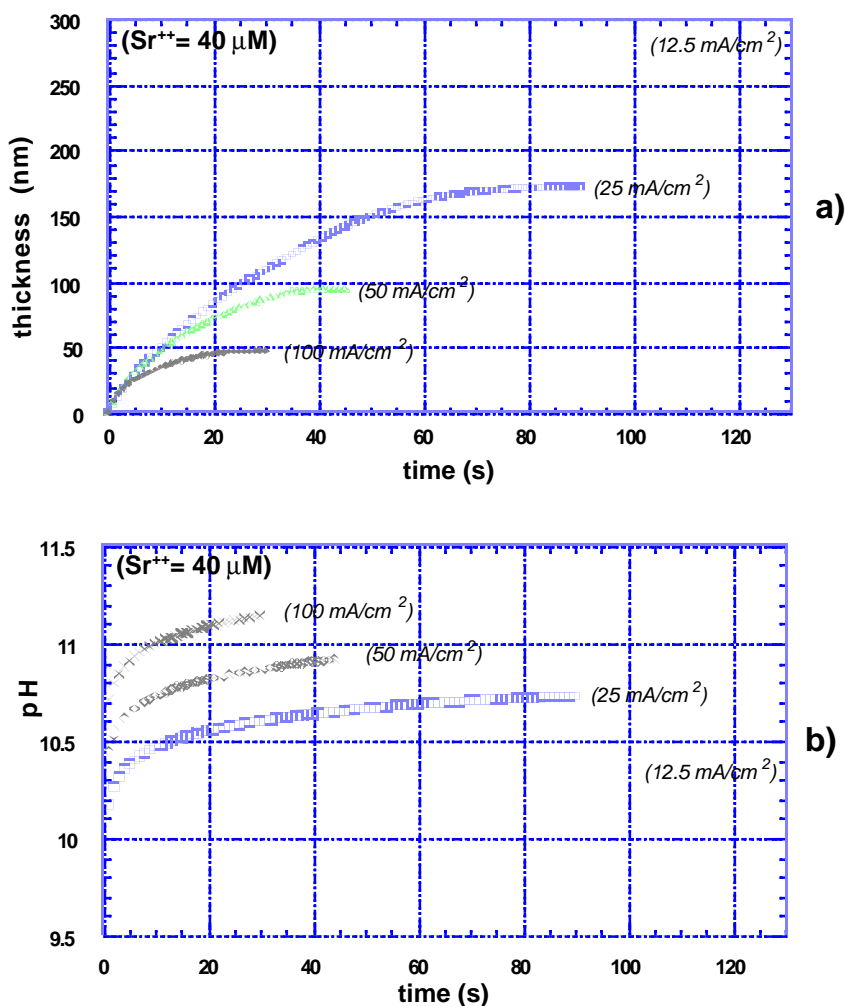


Figure 6 – Computer simulation at constant concentration of $40 \mu\text{M}$ Sr^{++} ion concentration, Pd wire diameter $50 \mu\text{m}$. a) SrCO_3 deposition thickness versus time at 12.5, 25, 50, 100 mA/cm^2 ; b) pH variation versus time at 12.5, 25, 50, 100 mA/cm^2 current density. A comparison with other fits indicates that the slope of the curve becomes more flat when the loading (at low current) is very high.

Other important characteristics of our method regarding both the electrolyte composition and the procedure for the acquirement of the proper coating on the cathodic surface, can be shortly summarized:

- It is possible to obtain an electrolytic environment (around the cathode) where, depending on the electrolyte composition and the current density, it is possible to control the solubility of alkaline earth carbonates. It is well known in fact that, depending on the electrolytic current, the pH around the cathode rises up, allowing carbonates precipitation: their solubility is actually pH controlled.
- It is possible to control the thickness of the deposit, in a feed-back way, changing the amount of acid and therefore the pH of the solution or by properly changing the values of the current density.

Finally, it has been shown that H and D are present in the Pd lattice as protons and deuterons; it is therefore possible to promote their movement by applying an electric field along the wire. It is known that the electro-migration effect is controlled by the drop of voltage along the wire and such a drop is easy to be obtained with a thin wire.

As far as the cracks problem is concerned, since 1998 we have found out that the addition of very small amount of mercury ions ($\text{HgCl}_2 \approx 10^{-6}\text{M}$) to the electrolyte is very effective. Mercury, galvanically deposits on the cathode surface, because of the formation of amalgams with Pd, is capable to strongly reduce the harmful effects of cracks [Ref. 7].

The differences between the old procedure, based on the use of LiOD as electrolyte, and the new one fully developed since April 1998 (explorative, wide-range, experiments started from 1994), is summarised in Table I.

Table I – Comparison between the old procedure and the new INFN – LNF protocol.

	Old procedure (conventional)	INFN protocol
Cathode	Rods, plates	Thin wires 50 – 100 microns
pH	Strongly alkaline (13 – 14)	Slightly acid (4.5 – 5.5)
Electrolyte	LiOH, LiOD	CaCl_2 – SrCl_2
Concentration	0.1 – 1 M	10^{-5} – 10^{-4} M
Voltage	< 30V	50 – 250V

— Critical points

The *purity* of the *water* is one of the most important and *critical* points of our procedure.

We want to stress that the composition of our electrolytic solution is close to a pure water (only extremely low amount of electrolytes are added); a typical composition in our experiments (Pd wire, 30cm of length and 50 μm of diameter) is the following:

- $\text{H}_2\text{O} = 1200\text{cc}$ (66.6 mole);
- $\text{HCl} = 2 \cdot 10^{-5}$ moles;
- $\text{SrCl}_2 = 2 \cdot 10^{-5}$ moles (1 mol of Sr=88g, then *only 1.8 mg of Sr*);
- HgCl_2 (Anti Cracking Agent) = 10^{-6} moles

The impurities normally dissolve in the light or the heavy water, can be divided in three groups:

- a) Inorganic substances (solid, liquid, gaseous, light water contamination into heavy water);
- b) Organic substances (generally expressed as total carbon);
- c) Bacteria.

The typical amount of impurities in both waters are the following:

H₂O:

- 1) Inorganic substances
 - a) Deionised, $\approx 10\text{mg/l} \Rightarrow$ not good;
 - b) Bidistilled, $\approx 0.3\text{mg/l} \Rightarrow$ good;
- 2) Organic substance $\approx 0.2 \text{ mg/l}$;

- 3) Livings = 0 (if properly saved, after high temperature distillation with acidified KMnO_4 , in sterilized vessels).

D₂O:

- 1) 10–20 mg/l inorganic substance (distillation is strongly required);
- 2) about 10 mg/l organic substance [Ref. 8];
- 3) Livings: 60–700 bacteria/ml, depending on production batches, was measured at ENEA–Casaccia Laboratories (Rome, Italy).

According to our investigations, we found that some of the bacteria, normally present in the heavy water, could be quite deleterious to our loading protocol:

- a) they are able to change the solution pH because of the acidic properties of some products of their metabolism;
- b) they tend to organize colonies on the surface of the cathode, in that competing with the appropriate carbonates coating;
- c) they prevent the proper galvanic deposition of the anti-cracking agent on the cathode.

PROCEDURES FOR D₂O PURIFICATION

Several operations have to be performed in order to purify (#1) and to maintain purity (#2, #3) the working heavy water (1 litre):

- 1) Bacteria “depletion” by the following multi– steps procedure:
 - a) addition 1 g of KMnO_4 + 1 cc of H_2SO_4 (96%) (\Rightarrow pH= 1.3); keep at 80 °C for 1 hour;
 - b) several vacuum distillations (by Rotavapor) at 30 °C, until pH 5.5 ÷ 6 has been reached;
 - c) addition of LiOD up to obtain pH=13; keep at 80 °C for 30 minutes;
 - d) several vacuum distillation at 30 °C until a.c. resistivity > 400 Kohm·cm and pH =7 ÷ 8;
- 2) Addition of colloidal silica (particles diameter 12 nm) + glutaraldehyde as bactericide (from KEMPRO Italiana), to reduce the growing speed of bacteria after purification;
- 3) Addition of HgCl_2 (10^{-6} M) only when D/Pd > 0.90.

IDENTIFICATION AND CHARACTERIZATION OF BACTERIA

The bacteria existing in the heavy water have been characterized by means of the following techniques:

- phenotypic characterization;
- cellular lipid and fatty acid analyses;
- phylogenetic analysis of 16S rDNA nucleotide sequences, adopting the most advanced procedures and reagents recently developed by Perkin Elmer Biosystems.

Two genera of bacteria, both Gram–negative, have been identified and both have been registered as *new species* at the GenBank of the “National Center for Biotechnology Information – National Institutes of Health” (Bethesda, MD, USA) and DNA Data Bank of Japan “Center for Information Biology, National Institute of Genetics” (Mishima, Shizuoka, Japan).

The bacteria belong to genera: *Ralstonia* and *Stenotrophomonas*. The name given to both new species is: *Detusculanense*.

- The biological analyses have shown why such bacteria were so deleterious to our protocol:
- they are able to “metabolise” alkaline earth ions (in particular Sr^{++} up to a concentration as large as $2 \cdot 10^{-2}$ M), preventing in this way the precipitation on the cathode surface of the carbonate coating;
 - they are able, furthermore, to “metabolise” even the very poisonous HgCl_2 up to a concentration of 10^{-4} M, so inhibiting its anti – cracking action.

RESULTS

As reported in detail in our another paper (see, A. Spallone et al.) at the same Conference, we can claim that the prefixed target has been completely achieved for H loading ($\text{H/Pd} > 0.98$). The loading stability lasts for days [Ref. 9].

In these experiments some measurements of the thermal resistivity coefficient (α_T) of the hydrogen loaded Pd wire have been carried out at H/Pd ratios higher than 0.8. It is known that such a coefficient monotonically decreases, by increasing the H/Pd value (from $\alpha_T = 4.1 \cdot 10^{-3} \text{ K}^{-1}$ when H/Pd = 0, to $\alpha_T = 2.0 \cdot 10^{-3} \text{ K}^{-1}$ when H/Pd = 0.7) [Ref. 10].

We have found that at higher H/Pd values, the thermal coefficient shows an abrupt increase. When

the loading ratio is as high as $R/R_0 \cong 1.15$ at room temperature, we measured for the thermal resistivity coefficient the value: $\alpha_T = 5.5 \cdot 10^{-3} \pm 1.5 \cdot 10^{-3} \text{ K}^{-1}$.

This value is remarkably higher than that of the pure (H de-loaded) Pd wire. The evidence of such an abrupt change in slope of the thermal coefficient resistivity, at very high values of the H/Pd ratio, strongly suggests that a new phase in the Pd–H system has been able to nucleate.

About D loading, we found strong differences when the heavy water was used “as received” and when it was been previously purified according to the above mentioned procedure.

In the first case loadings exceeding $\text{D/Pd} = 0.92$ (Fig. 7) can be hardly achieved. No thermal anomalies were ever observed.

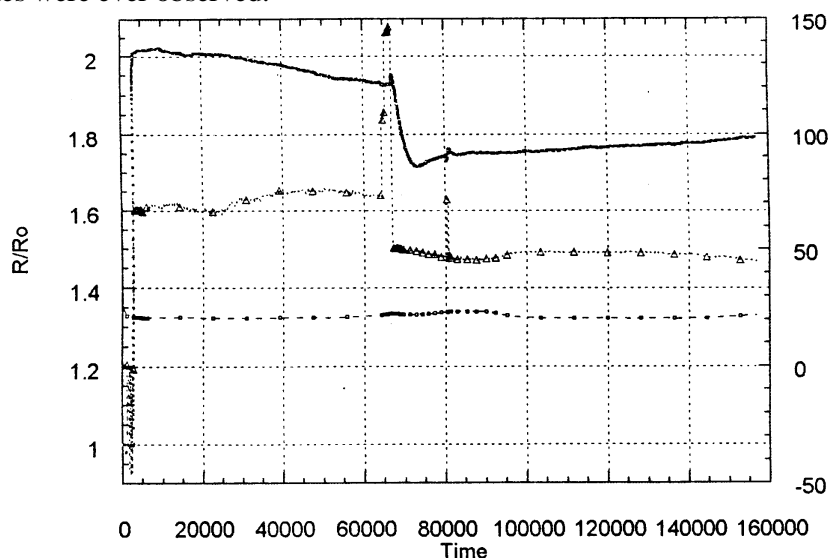


Figure 7 – Commercial reactor–grade D_2O test: $\text{D/Pd} = 0.92$ is achieved after Hg addition. The loading goes to decrease in the time; no thermal anomalies have been observed.

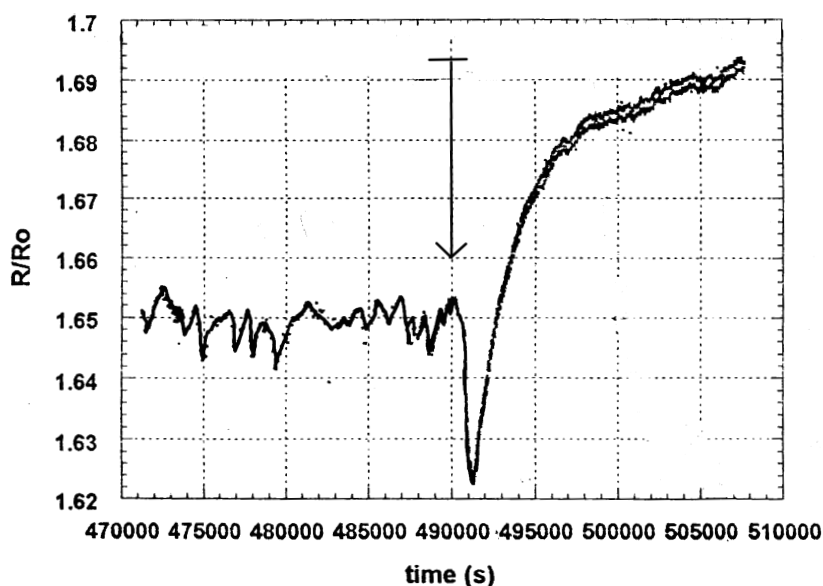


Figure 8 – LNF-purified D₂O test: After LNF-purification procedure, a high loading (D/Pd= 0.97) have been achieved, lasting several days; an anomalous loading effect occurs after decreasing electrolysis current: it can be explained with a higher temperature of wire occurred during the loading.

In the second one (Fig. 8) loading values in the range D/Pd 0.97 ÷ 0.98 have been obtained for several days. When we reduced the electrolysis current from 40 to 25 mA (high→low current) an anomalous effect occurred: instead of obtaining a de-loading of the wire (as expected by Tafel effect) we recorded an apparent increase of loading for some minutes, followed by the usual, slow de-loading. A possible explanation could be that the wire was actually and continuously emitting excess heat; when the current was reduced, the excess heat progressively had been vanishing, reducing at the same time the actual wire's temperature. So, what could appear a further loading is simply a drop down of the wire resistance due to a drop down of the wire temperature. In absence of a flow calorimeter, we were able to evaluate a rough and conservative estimation of excess heat: 0.5 W respect to 2.0W of input.

CONCLUSIONS

In conclusion the following statements can be proposed:

1. The problem to get H/Pd > 0.97 in a reproducible way has been solved by the use of SrCl₂-HCl-CO₂ and small amounts of HgCl₂ as electrolytes (the Pd wire surface is coated with thin layers of SrCO₃ and amalgam of Hg). Our results have been successfully reproduced by Pirelli (Milan, Italy) and SRII (Stanford, USA);
2. The same procedure, using D₂O, was less efficient because of bacteria contamination;
3. Properly purified D₂O and a new circuitry allowed us to get large loading (D/Pd > 0.97); strong indications of anomalous "excess heat" (about 0.5 W over 2 W of input power) in a reproducible way (3 times) were observed;
4. Further work on D₂O "purification" is needed; "sterile" electrolysis seems to be necessary.

The identified bacteria seem to be able to metabolise dangerous heavy metals (Cd, Cr, Pb, Hg). Studies are in progress and they will be published in a future paper.

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We would like to thank (we will be always in debt with him) Prof. **Giuliano Preparata** (Milan University, Italy), who was the first person (since 1994), to introduce us to some specific properties of thin Pd wires from the point of view of H/D overloading.

We are very sad: He passed away on April 24, 2000 (just one month before the beginning of this Conference). For most of the authors of the present paper Giuliano was not only a Scientist involved in the same field of Research but, overall, a personal, old, friend.

We thank Prof. Jean Paul Vigier (Paris University, France), both for some useful criticism and several suggestions about the comparison of numerical simulation with experimental data.

Dr. Naoto Asami, Dr. Kazuaki Matsui and their colleagues at NHE (presently at IAE Tokyo, Japan) gives us several suggestions and experimental data (obtained in their Laboratories) about purity of H₂O and D₂O: they clarified to us something problematic on their purification.

Prof. Piergiorgio Sona (ENEL Ricerca, Milan, Italy) spent a lot of time on discussions with us about catalytic proprieties of surfaces and methods to modify them.

Prof. Edmund Storms (ENECO, USA) gave us some useful suggestions regarding the more useful acid (between HCl and H₂SO₄) capable to insure the constant of pH during the electrolysis.

Mr Francesco Todarello (KEMPRO Italiana, Ariccia, Italy) provided us information about methods used in the distillation of light water (industrial grade) to reduce the problem of bacteria growing. He developed new types of colloidal silica for our specific purposes.

We are deeply indebted with Prof. Lino Daddi (Accademia Militare Navale, Livorno, Italy) who gave us several information about the proper procedures for the purification of the light water in comparison with the heavy water.

References

- [1] F.Celani et al., *Progress in New Hydrogen Energy – Vol. 1* (Proc. ICCF6, Oct. 13–18, 1996, Sapporo, Japan), 93–104 (1996).
- [2] M.C.H. McKubre et al. *Frontiers of Cold Fusion* (Proc. ICCF3, 1992, Nagoya, Japan), 5(1993).
- [3] B. Baranowsky and R. Wisniewsky (1969), *Phys. Stat. Sol.* **35**, 539.
- [4] J.C. Barton, F.A. Lewis and I. Woodward (1963), *Trans. Faraday Soc.* **59**, 1201.
- [5] M. McKubre et al. *Conf. Proc. ICCF1* (Salt Lake City, Utah) March 28–31 1990, p.20–31
- [6] F. Celani et al. “High Hydrogen loading of thin Palladium wires through alkaline–earth carbonates precipitation on the cathodic surface. Evidence of a new phase in the Pd–H system.” *Published by INFN–LNF–00/006 (P)*, 6 Marzo 2000 – (To be published by *Physics Letter A*).
- [7] F. Celani et al. “A study on the electrochemistry parameters to achieve reproducible high H/Pd values in relation to ‘anomalous’ excess heat; proteobacteria contamination problematics.” Presented at the “*IV Workshop on Anomalies in Hydrogen/Deuterium Loaded Metals*”, 22–24 Oct. 1999, Asti, Italy. Publishing by SIF, ed. Compositori, Bologna (Italy) as Conference Proceedings.

- [8] Naoto Asami, Institute of Applied Energy, Tokyo (Japan), May 1999; (*private communication*).
- [9] A. Spallone et al. “A reproducible method to achieve very high (over 1:1) H/Pd loading ratio using thin wires in acidic solution with addition of very low concentration impurities.” Presented at the “*IV Workshop on Anomalies in Hydrogen/Deuterium Loaded Metals*”, 22–24 Oct. 1999, Asti, Italy. INFN– LNF– Report 00/018 (P), 27 *Giugno 2000*. Publishing by SIF, ed. Compositori, Bologna (Italy) as Conference Proceedings.
- [10] B. Baranowski, Filipek et al. (1990), *J. Less Common Metals* , **158**, 347b.