



LNF-02/014 (P)

2 Luglio 2002

**ELECTROCHEMICAL D LOADING OF PALLADIUM WIRES BY HEAVY
ETHYL-ALCOHOL AND WATER ELECTROLYTE, RELATED TO
RALSTONIA BACTERIA PROBLEMATICS**

F. Celani⁽¹⁾, A. Spallone⁽¹⁾, P. Marini⁽²⁾, V. di Stefano⁽²⁾, M. Nakamura⁽²⁾, A. Mancini⁽³⁾, G. D'Agostaro^(4,1), E. Righi⁽¹⁾, G. Trenta⁽¹⁾, P. Quercia^(5,1), C. Catena^(4,1).

(1) INFN-LNF, Via E. Fermi 40, 00044 Frascati (Roma)–Italy

(2) EURESYS, Via Lero 30, 00129 Roma–Italy

(3) ORIM, SrL, Via Concordia 65, 62100 Piediripa (Mc)–Italy

(4) ENEA-CRCasaccia, Via Anguillarese 301, 00060 Roma–Italy

(5) ASL-RmH, Via E.Fermi1, 00044 Frascati (Roma)–Italy

ABSTRACT

Taking in considerations the several effects of new kinds of bacteria living in heavy water (discovered by us in 1999), from the point of view of Deuterium (D) overloading inside Palladium (Pd), it was developed (since June 2001) a new kind of electrolyte based on mixture of alcohol and water (both heavy) with proper addition of Strontium (Sr) and Mercury (Hg) salts in an acidic environment (DCl, D₂SO₄): all these procedure according to what developed from our group since 1996 for H₂O solutions (without H₂SO₄) and, since 2000, for light water-alcohol (with H₂SO₄). It was found excess heat (by high accuracy flow calorimeter) and excess Tritium (T) production (by low background T measurement instrumentation) only when the loading ratio was quite high and some movements to D inside Pd was performed.

Efforts will be done to increase the absolute values of such experimental results, in the near future.

1. INTRODUCTION

According to our experience, lasting 13 years (since April 1989), the **COLD FUSION** phenomena happens when, and only when, the followings conditions are fulfilled at the **same time**:

a) **Overloading** of deuterium in the Palladium lattice;

b) **Movement** of deuterium into the Palladium without losing of overloading.

The main problem affecting such kind of experiments is the irreproducibility of results. In short, according to the experience get in our experiments, the typical excess power (when it works!!) is of the order of 5—10%. We have got larger value (15-40%) only by using very strong non-equilibrium conditions like the so-called “high peak power, high frequency pulsing” at a repetition rate of 5000-30000Khz with a duty cycle of 1--2%. [Ref.1] Only in one very lucky event (lasting over 12 hours), we got an energy gain of the order of 200% at an input power of about 50—60W [Ref. 2].

We recall that the *practical* limit to “non equilibrium procedure” is the need to adjust continuously and “properly” (even of only few %) the operating power-pulse parameters (frequency, duty-cycle, current and voltage peak) to avoid that the excess heat, for some unknown reasons, decreases spontaneously: the scientist has to “take care” of the electrolytic cell continuously, day and night!!

So, the *practical* solution to the problem seems to be getting and keeping quite large overloading ($D/Pd \gg 0.94$) as long as possible (i.e. without “maintenance”) and “move” the deuterium inside Palladium.

In order to solve such a serious problem our group has performed a systematic campaign of experiments, starting from simpler and more economic Pd-H system, aiming to find out a new protocol, almost “maintenance free”, capable to insure a fast and reproducible loading with thin Pd wires, up to a H/Pd ratio close to one. Later, obviously, the “new” protocol will be transferred to the deuterided electrolytes.

2. EXPERIMENTAL APPROACH

The new protocol, tested successfully also in three different Laboratories (Pirelli-Labs, Milan-Italy; Stanford Research Institute International-USA; our Laboratory, in two completely different arrangements of the electrolytic cells), is based (in an acidic environment, pH about 4.5) on the addition of very small amount (typical concentration some $10^{-5}M$) of alkaline-earth ions.

In this paper we will quote the loading using both the H(D)/Pd value and/or indirect measurement by the value (R/R₀) of the resistance ratio changing (the well known “Baranovsky curve”), as reported also in Ref.1.

In short, the main results of our interest (i.e. maximise H/Pd and minimise the electrolytic current density) were as following about the five elements (Mg, Ca, Sr, Ba, Ra) studied, or just considered:

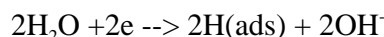
- a) Strontium seems to be the most effective, i.e. $R/R_o=1.3$ with a current density of 20--40 mA/cm^2
- b) Calcium is similar to Sr but gives little bit less value of overloading (R/R_o typically 1.45) even though with very high reproducibility (its concentration value is not so critical);
- c) Barium gives value of R/R_o similar to Sr but with a current density about 4--5 times higher, i.e. input power to the electrolyte about 20 times larger in respect to strontium;
- d) Magnesium give R/R_o of only 1.5, even at large current density;
- e) Radium: practically impossible, for us, to study because its strong radioactivity ($1\text{g} \rightarrow 3.7 \cdot 10^{10} \text{Bq}$).

The use of twice-distilled water was found to be a mandatory requirement: it has been found that the impurities normally yet present in the distilled and/or de-ionised water can negatively affect the loading process.

**** Protocol physics-chemical principles:**

- * Strontium ions (as SrCl_2) are added to the twice-distilled water in such an amount that no precipitation as Strontium carbonate (SrCO_3) can occur in the bulk of the electrolyte with the carbonic ions normally dissolved (as H_2CO_3) in the water;
- * *Strontium carbonate is allowed to precipitate only on the surface of the cathode, because of the local alkalisation produced by the flowing of the electrolytic current:* it is well known that the solubility of carbonates decreases strongly following to increase of the pH.

In the processes at cathode we have:



then, the OH^- ions formed on the cathode promote the precipitation of the SrCO_3 .

The atomic Hydrogen adsorbed on the cathode's surface, can either be absorbed into the Pd bulk:



or bubbled out as H_2 gas



The intrinsically catalytic surface of Pd, used as cathode, promotes generally the *b*) reaction, deleterious to (H,D) overloading purposes.

By using our protocol there is a key advantage: because of the precipitation on the cathode's surface of a thin layer of SrCO_3 , the catalytic properties are consistently reduced. As a consequence, the loading reaction *a*) turns to be predominant, thus allowing a fast achievement of H/Pd ratio $\rightarrow 1$.

** We have found that the addition of very small amount of mercuric ions (as HgCl_2) are also effective because:

- a) increases the over-voltage at Pd surface;
- b) keeps stable the loading level over a long period of time because peculiar ability of Hg to form amalgams at room temperature: it is supposed to act as "anti-cracking agent" against Pd damage due to H,D absorption.

When we tried to apply our protocol for D-Pd loading and H₂O was replaced by D₂O, the results in terms of D/Pd were lower, and/or unstable, than those obtained with light water, as confirmed also at Pirelli Labs [Fig. 1; Ref. 3].

The reasons of such an evident failure are essentially:

- a) The amount of the impurities generally contained in the "as received" heavy water is too large. Foreign inorganic ions, deposited because the Galvani effect on the cathode, were found to hinder the formation of the proper SrCO₃ layer. Twice distillation of D₂O, difficult to be accomplished because of its hygroscopicity (no contact with the atmosphere is required), is a necessary but *not sufficient pre-treatment*.
- b) Heavy water contains bacteria that were identified from us at ENEA-Casaccia [Ref. 4, 5]. These bacteria belong to two new species, which were also found to form *colonies onto cathode surface* because they can "metabolise" even hydrogen gas.
- b1) Therefore, long treatments of the D₂O with KMnO₄ (1g/l; added two times: acid and basic pH) at pH of 1 (by D₂SO₄)→7→13 (by LiOD)→7 under nitrogen at 90°C and at 25°C with vacuum, are previously required for a satisfactory sterilisation [Ref. 6, 7]
- b2) After treatments according to b1), the solution as to be, at least, twice distilled to reduce the amounts of salts added to a value <0.1mg/l: final measurements of the impedance need to give values of the order of 10MΩ/cm.

About those two new bacteria, we experienced that one of this, *Ralstonia* species, "metabolises" several elements including the Hg used in our procedure.

We just note that, thanks to specific studies, originally needed to understand the behaviour of this bacteria from the point of view of "Cold Fusion" (i.e. effect on the elements added to electrolytic solution on H,D loading), we experimentally proved that they "absorb" almost any kind of heavy metals (Hg, Pb, Cd, Cr, Ni) included the Uranium, up to concentrations as large as several mMoles. The bacteria as been registered on June 2000, at the properly devoted International Scientific Institutions (DDBJ-Japan and NCBI-USA), with the name of *Ralstonia detusculanense*.

We summarise the Technical Specifications of a "good quality", reactor grade, heavy water (as at November 1999):

- | | | |
|----|----------------------------------|------------|
| 1. | D ₂ O Isotopic Purity | > 99.92wt% |
| 2. | KMn O ₄ | = 4mg/kg |
| 3. | Conductivity | <1.5 mS/m |
| 4. | Tritium | <2mCi/kg |
| 5. | Turbidity | < 2 FTU |
| 6. | pH | 6--10 |

Obviously, the addition of KMnO_4 and the “strange” range of values of pH (6—10) are quite clear indications, to expert people, about some bacteria or algae living in it.

3. THE NEW ELECTROLYTIC SOLUTION

Aiming to eliminate wasting time and troublesome pre-treatments, needed to “kill” the bacteria and purify the heavy water from inorganic and organic pollutants, and taking into account that the main controlling parameter of the D-Pd loading seemed to be the ratio between the total amount of the impurities present in the electrolyte and the surface of the cathode, we realised that the problem could be matched from a completely different point of view.

In order to minimise the ratio between the amount of the impurities and the surface of the cathode, two different approaches could be taken into consideration:

- #1) build up a very thin cell, just around the electrodes (Pd surface about 1 cm^2), thus containing a very small amount of electrolyte (i.e. 50cc) and consequently a negligible amount of impurities;
- #2) fill the cell currently used in our experiments, whose volume is about 1000 cc, with a new electrolyte prepared by mixing a majority part of suitable organic solvent (i.e. 950 cc) with a minority part (i.e. 50 cc) of heavy water.

In both cases, with respect to the 1000 cc of D_2O , normally used in our tests, the reduction to 50 cc is equivalent to 20 times reduction of the impurities which could be deposited on the cathode's surface.

The #2 seemed to be extremely more attractive because of its simplicity (no need to build up a new and very delicate cell) and its flexibility (the ratio between the organic solvent and the heavy water can be varied over a large extent).

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 H_2O present as residual impurity (isotopic contamination of H in the D-Pd loading),
- no (or negligible) acid properties (isotopic contamination for partial dissociation and production of H^+ ions),
- boiling point not too far from 100°C (in order to avoid pressurisation operating at $30\text{—}70^\circ\text{C}$).

In relation to the above mentioned requirements, alcohols, ketones, esters seem to be the most promising solvents.

Experimental results

We make some explorative experiments with the previously mentioned solvents and, about them, we found that the ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$), at this moment, is the most “easy” to be used,

taking in consideration also that it is allowable, at a reasonable price (about 1000 US\$/Kg), the “heavy” one (C₂H₅OD).

If the hydro-organic electrolyte could be considered an elegant solution for the problem of the impurities, the proper precipitation of SrCO₃ on the surface of the cathode seemed difficult to be accomplished in the new ambient: how to control the concentration of carbonic ions?

Taking into account that the actual concentration, the “activity”, of the ions in the hydro-organic electrolyte could be remarkably higher than their nominal concentration (referred to both the components of the liquid phase), we realised that Sr ions could be precipitated as SrSO₄ even though the solubility product of this compound ($2.8 \cdot 10^{-7}$ at 25°C) is 175 times higher than that of SrCO₃ ($1.6 \cdot 10^{-9}$ at 25°C).

In this case, the SrSO₄ precipitation in the hydro-organic ambient could be accomplished simply by controlling the amounts of Sr⁺⁺ and SO₄⁼ ions added to the electrolyte.

After several tests we found that a suitable electrolyte could be prepared just by using 1000 cc of ethyl alcohol (95% concentration, i.e. 50cc is water) and by adding to the hydro-alcoholic solution 20mg of SrCl₂, 1-2 cc of H₂SO₄ (0.01M) and 0.5-2 cc of HgCl₂ (0.01M).

The electrolysis was started with the following conditions:

Anode: Pt (wire, length 30cm, diameter 200μm); Cathode: Pd (wire, total length 30cm with 2 portions of 15cm, diameter 50μm); electrodes parallel (inter-distance 4cm); Current: 5mA; Voltage: 20-50V; T=20°C.

We notify that, according to our procedure, before starting the loading experiment, a series of anodic electrolysis with respect to Pd ($J=2\text{mA}/\text{cm}^2$ for some minutes) are carried out after addition of each component of the electrolyte in order to verify the expected values of the conductivity of the electrolyte.

The loading rate of the cathode, after 1 day of “conditioning”, was surprisingly high: in less than 20 minutes a H/PD ratio very close (or even over, no reliable data allowable from literature) to one ($R/R_o = 1.20$!!!) is currently achieved.

We would like to inform that, changing (about 30-50%) the amounts of Sr salt and H₂SO₄, it is possible to get R/R_o close to 1.25 without waiting the 1 day of conditioning. This kind of procedure needed more experiments to be fully reproducible.

Our results, with light alcohol and water, have been completely reproduced, and even improved, ($R/R_o=1.1$!!!) at Pirelli Labs, Italy (**Fig. 2**).

The experiments with heavy alcohol started at July 2001 and only from march 2002 we were able to test the cell in a new, specially developed, calorimetric system (flow calorimeter with a resolution of 0.05W from 24 to 30°C).

The calorimeter is build using only glass, PTFE, PFA because corrosion, contamination, decomposition problems related to the combined effect of acids and organic solvents under electrolysis. The calorimeter is still now under improvement to reduce the corrosion and decomposition effects growing after about 2 days of operations.

Anyway, we were able to get, only after 30 minutes from starting of electrolysis, a quite interesting value of loading ($R/R_o < 1.67$) with associated excess heat (about 150mW with an input power of about 400mW, **Fig. 3**). Moreover, this experiment give clear evidence of *anomalous Tritium production*, see the proper paper of same authors at this Conference.

4. CONCLUSIONS

It was shown, experimentally, that the anomalous effects (thermal and nuclear ashes) in Cold Fusion experiments are due to combined conditions of large loading and “movement” of Deuterium (inside Palladium lattice) or flowing through its surface, properly treated with “multiple coatings” of suitable elements (Sr, Ca, Ba, Hg), like a semiconductor diode structure: it seems not too far, according to us, the time when it will be possible to “use”, in the everyday life, the practical effects of such kind of discovery.

ACKNOWLEDGEMENTS

We would like to notify that Dr. Naoto Asami and Prof Kazuaki Matsui, now at Institute of Applied Energy of Tokyo (Japan), were the first people that realised about NON-inorganic pollution of heavy water during Cold Fusion experiments (NHE Project, 1999, Sapporo, Japan). Their observations were for us starting points for further analysis.

We are deeply indebted, because very fine work about replications, and (*several times*) *their original and wonderful improvements*, of our experimental procedure, made at Pirelli Labs (Milan, Italy) from Dr. Flavio Fontana, Dr. Daniele Garbelli, Dr. Donato Azzarone and Dr. Luca Gamberale. Their SEM analysis, and physical discussions of results obtained, on our electrodes (before and after electrolysis), helped us to quickly improve the new protocol.

We are indebted to Prof. Piergiorgio Sona at CESI (Milan, Italy) because very long, stimulating discussions and “warnings” about our, unusual, experimental set-up and electrolytes.

We deeply thank Prof. Akito Takahashi, (Osaka University, Japan), because useful suggestion and criticism related to the experimental set-up and excess heat measurements.

We recognise, and thank, the skilful work performed from our technician Vincenzo Andreassi at INFN-LNF during the project and construction of new PTFE, PFA flow calorimeter.

REFERENCES

- [1] Francesco CELANI, Antonio Spallone et al.
“Deuterium overloading of palladium wires by means of high power μ s pulsed electrolysis and electromigration: suggestions of a “phase transition” and related excess heat”
Physics Letters A 214 (1996) 1—13
- [2] F. Celani, A. Spallone et al.
“New Kinds of Electrolytic Regimes and Geometrical Configurations to Obtain Anomalous Results in Pd(M)-D Systems” pg. 93--104
ICCF-6 October 13-18, 1996 Japan. PROGRESS IN NEW HYDROGEN ENERGY, Vol.1, pg. 93—104
Published by NEDO and IAE (Tokyo, Japan), December 11, 1996. Edited by Makoto OKAMOTO
- [3] D.Azzarone, F. Fontana, D. Garbelli.
“HYDROGEN/DEUTERIUM LOADING IN THIN PALLADIUM WIRES”

- Proceedings of the “8th International Conference on Cold Fusion”, Lerici, Italy 21-26 May 2000; - Conf. Proc. Vol. 70 pg 199-204 Edited by F. Scaramuzzi; Compositori– SIF, Bologna, 2000; Italy. ISBN 88-7794-256-8
- [4]D’Agostaro, G.A.F., Celani, F.J.V.A., (.....) and Nakamura, M.
National Centre Biology Information: LOCUS: AF280433; 1537 bp DNA linear BCT 19-JAN-2002
DEFINITION: *Ralstonia detusculanense*; ORGANISM: Ralstonia detusculanense
Bacteria; Proteobacteria; beta subdivision; Ralstonia group; Ralstonia.
Submitted 20-JUN-2000
<http://www.ncbi.nlm.nih.gov>
- [5] D’Agostaro, G.A.F., Celani, F.J.V.A., (....) and Nakamura, M.
National Centre Biology Information: LOCUS: AF280434; 535 bp DNA linear BCT 19-JAN-2002
DEFINITION: *Stenotrophomonas detusculanens*; ORGANISM: Stenotrophomonas detusculanense
Bacteria; Proteobacteria; gamma subdivision; Xanthomonas group; Stenotrophomonas.
Submitted (20-JUN-2000)
<http://www.ncbi.nlm.nih.gov>
- [6] F.Celani, A.Spallone et al.
“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.”
Proceedings of the “8th International Conference on Cold Fusion”, Lerici, Italy 21-26 May 2000; - Conf. Proc. Vol. 70 pg 181-190 Edited by F. Scaramuzzi; Compositori– SIF, Bologna, 2000; Italy. ISBN 88-7794-256-8
- [7] F.Celani, A. Spallone et al.
“Electrochemical H-D loading of Palladium wires by hydro-alcoholic electrolytes related to the new discovered *Ralstonia* bacteria into heavy water”.
JCF3-5 3rd Meeting of Japan CF_Research Society, October 25-26, 2001; Yokohama National University.
<http://fomcane.nucl.eng.osaka-u.ac.jp/jcf/>

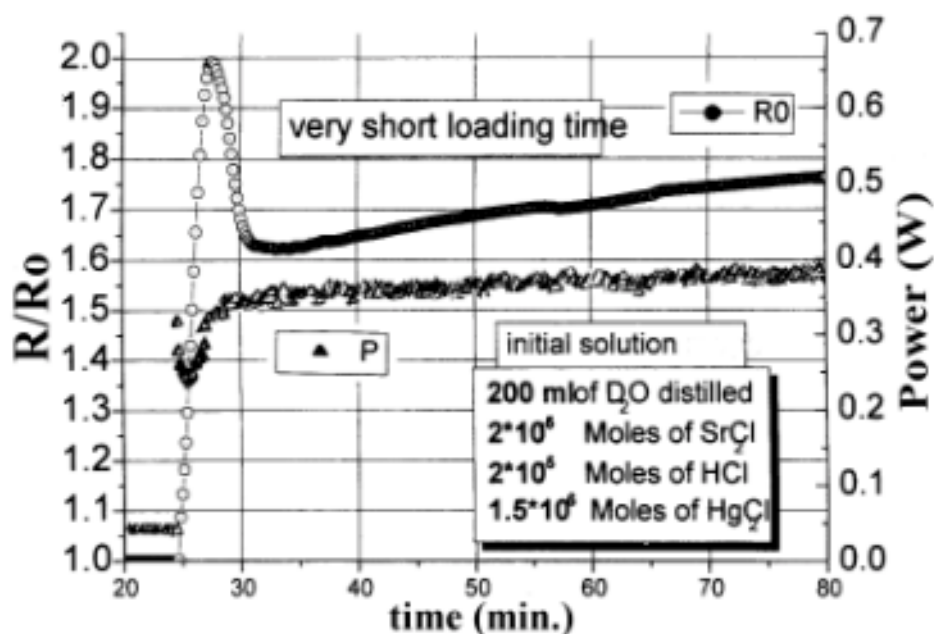


Fig. 1 – Experiment. performed at Pirelli Labs. Very fast overloading ($R/R_0 = 1.62$) using $SrCl_2$, $HgCl_2$, HCl ($pH=4.5$) with D_2O . The overloading is not stable over time.

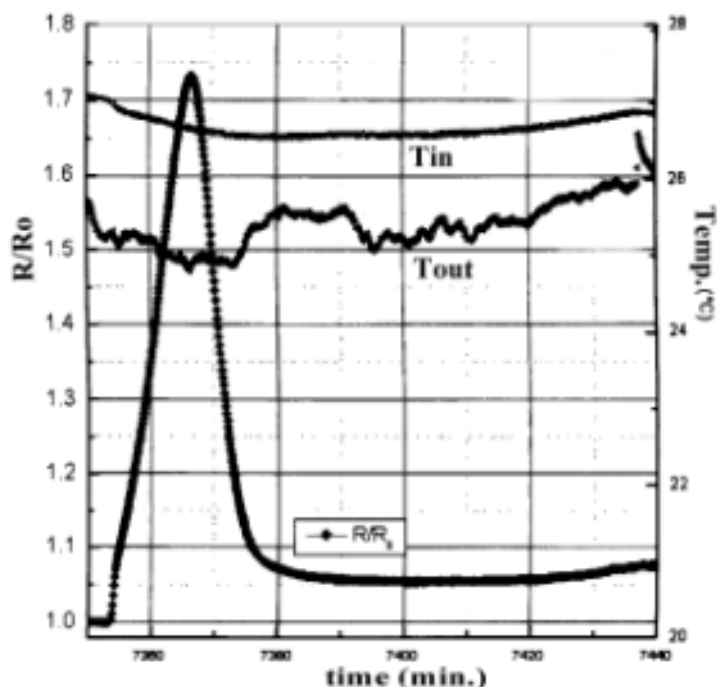


Fig. 2 – Experiment performed at Pirelli Labs. Replication, and large improvements, of INFN-LNF results about light ethyl alcohol-water solution. The R/R_0 value reached (1.05) is quite impressive. The slope of curve, in the right side, between 1.7 and 1.2 is higher than the left side.

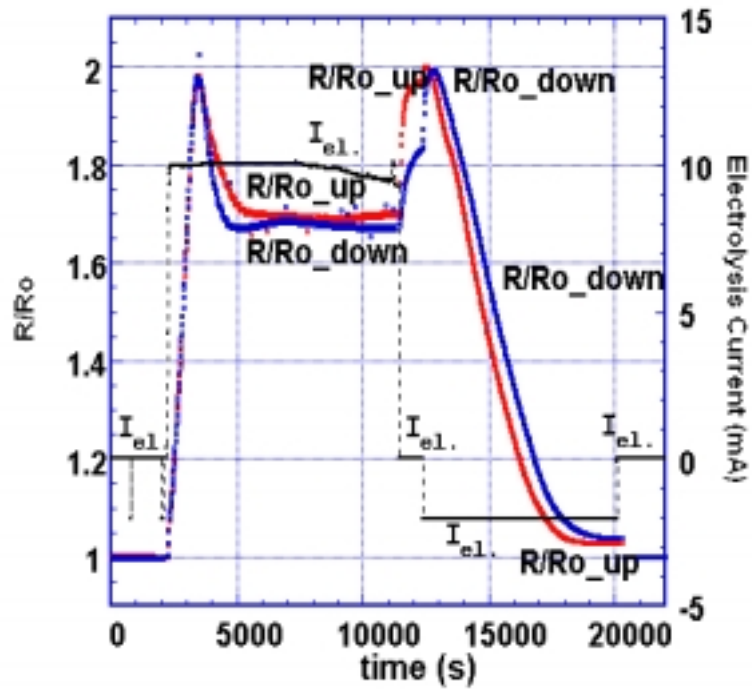


Fig. 3 – Experiment performed at INFN-LNF. Heavy ethyl alcohol and water. The overloading was enough good ($R/R_o=1.67$) and overall stable (over 3 hours) until we decided to stop the electrolysis (at time 11500 sec., I electrolysis from 10mA to 0 and later, time 12500, anodic stripping at 2 mA) in order to control the correct working of the experiment.