Spallone, A., et al. *An Overview Of Experimental Studies On H/Pd Over-Loading With Thin Pd Wires And Different Electrolytic Solutions*. in *Eleventh International Conference on Condensed Matter Nuclear Science*. 2004. Marseille, France.

An Overview of Experimental Studies on H/Pd Over-loading with Thin Pd Wires and Different Electrolytic Solutions

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ABSTRACT

Hundreds of electrolytic loading tests of thin Pd wires in different experimental conditions have been performed in order to find out the best procedures for stable, high hydrogen overloading into the palladium lattice.

In a very dilute acid solution thin Pd cathodes (50 or 100 μm in diameter) and thick Pt anodes (0.5 mm in diameter) were used in a parallel or coaxial geometry. Normalised resistance (R/Ro) of the Pd cathode was on-line and continuously measured in order to determine the actual H/Pd values.

Different electrolytic solutions have been tested by adding to the acid solution very low amounts of Ca, Sr, Li and Hg ions; high loading H/Pd ratios have been achieved with a satisfactory grade of reproducibility.

Several loading procedures have been performed in a wide range of electrolysis current (from a few mA up to one hundred mA) and at different Hg ion concentrations.

The obtained results allowed for the definition of a loading protocol that ensures very high H/Pd over-loading. Stable $R/Ro \leq 1.2$ values (corresponding to H/Pd ratios ≥ 1) can be currently achieved with an extremely low power electrolytic supply (10 V, 5 mA).

1. INTRODUCTION

During the last six years a lot of effort was spent finding the best hydrogen loading procedures for thin Pd cathodes.

Most researchers agree that in cold fusion experiments, in order to obtain stable and reproducible excess heat, it is necessary to achieve and maintain very high D/Pd (≥ 0.85) loading ratios [1]. The poor results generally achieved by the conventional electrolytic techniques, based on the use of LiOH solutions, especially from the point of view of their reproducibility, induced us to develop a completely different approach. In fact, in our previous papers, we have reported a reproducible procedure to achieve very high loading ratios using palladium thin wires ($H/Pd \approx 1$) [2,3]. This procedure is based on the increasing of the cathodic over-voltage (which is known to be the main controlling parameter of the H(D)-Pd loading) by modifying the nature of the cathode surface (i.e. by inducing the formation of a very thin layer of an alkaline-earth carbonate on its surface).

2. EVALUATION OF THE H/Pd RATIO

In order to estimate the actual H/Pd atomic ratio of the Pd cathode during the electrolytic loading process, we measure the normalised resistance (R/Ro) of the Pd wire; i.e. the ratio between the actual resistance (R, during the loading) and the resistance of the electrode at the beginning of the electrolysis (Ro), when the value H/Pd=0.

The loading ratio was inferred and continuously monitored by means of the well-known relationship [4,5,6] between the resistance and the H (D) content in the Pd matrix (Fig. 1). The actual known values of this relationship terminate at H/Pd=0.9, corresponding to R/Ro=1.40. Beyond this value the correspondence is estimated by a linear extrapolation. Accordingly, we estimate that the ratio H/Pd=1.00 is achieved when R/Ro=1.20.

3. EXPERIMENTAL APPARATUS

A schematic diagram of the experimental set-up is shown in Figure 2. The vessels are typically cylindrical glass beakers of different sizes (from 0.5 up to 5 litres).

The power supply can operate either at constant D.C. current or at constant D.C. voltage. The cathode is grounded. The voltage is applied to the anode through an impedance adapter circuit (impedance booster), in order to avoid current feedback from the A.C. measuring circuit. The latter is composed of a pulse generator (allowing for sinusoidal, square and triangular wave forms; we always used the sinusoidal ones) and a coupling circuit (ground return, for both for the D.C. and A.C. generators).

Temperature sensors (based on Silicon integrated circuits) are located inside the cell (in the solution at three different levels) and outside the cell (two sensors for the thermal bath and one for room temperature) and are monitored on-line.

The Pd cathode, because of its favourable surface/volume ratio, allows for very fast hydrogen absorption and its high resistance (about 8 Ω) improves both the accuracy and the precision of the measurements. Furthermore, the 1/r dependence of the electric field around the wire creates a sharp increase of the pH value in its proximity, promoting the carbonate precipitation in that region. (For more details see Refs 2 and 3.)

--- The geometry of the electrolytic cell strongly affects the loading process: the relative position of the electrodes is crucial for a proper set up of the primary electric fields during the electrolysis [7]. Moreover we have to take into account that during the loading the Pd wire's length remarkably increases (5→15%); the wire is consequently forced to bend and the original separation of the electrodes could be significantly changed. We tested two different Pd-Pt electrodes separation values (variable from 1.5 cm up to 7 cm) in two different geometries:

1) A parallel geometry with Pd and Pt wires of the same length at the same separation;
2) A Pd central axial geometry with 4 Pt wires cylindrically located around the cathode at the same separation.

--- The electrodes are about 25 cm long; The Pt wire (sector AB as drawn in Fig. 2) is 1 mm thick; Pd cathodes of two different sizes (50 or 100 μm thickness) are used. A pick-up junction divides the Pd wire into two equally long sections of electric resistance 2 or 8 Ω respectively for the 100 or 50 μm Pd wire diameters. This allows for the measurement of the resistances of the corresponding wire segments (sectors CD and DE are named "up" and "down" in Fig. 2).

--- H_2O, Ethyl Alcohol (C_2H_5OH) or Methyl Alcohol (CH_3OH) was used for the preparation of the electrolyte. In order to reduce the impurities present in commercial heavy water [8, 9] some tests using alcohol based electrolytes were previously performed with D_2O/C_2H_5OD solvents. In the present work the alcohol based electrolytes were also tested for hydrogen loading.

Very low concentrations (less than 1 mMole) of HCl or H_2SO_4 were added to the electrolytes in order to maintain the pH around 4.5 to 5.5; the anode-cathode electrolytic resistance ranged between 1 and 5 KΩ.

--- Small amounts (tenth of μMoles) of different alkaline elements such as Ca, Sr and Li were added to the electrolyte, according to the original procedure previously developed in order to improve the H/Pd loading (motivations and details of this addition are also reported in Ref. 3).

--- Many tests were performed by adding a very small amount of $HgCl_2$ (ranging from 0.1 up to 10 μMoles) to the electrolyte. In some tests very small amounts of Hg (estimated on the order of a tenth of nMole) were actually present in the electrolyte (nominally Hg^{++} free). Because of the de-loading process of the cathode normally effected at the end of a set of experiments, the Hg amalgam previously formed on the Pd surface in the cathodic cycles is stripped away during the final anodic cycle. Some residual traces of Hg normally remains on the Pt surface even after the Hg containing electrolyte has been fully removed. Hg traces on the Pt surface go back into solution as soon as the cathodic cycle of the new set of experiments starts up.

Mercury, as is shown below, plays a fundamental role in the over-loading process.

4. H/Pd LOADING PROCEDURE

In the achievement of very high H/Pd loadings, the role played by the electric parameters (Anode-Cathode voltage and current) is crucial for any given cell geometry and electrolyte. The primary and secondary electric field [7] operating on the Pd cathode may produce an Hg and alkaline element deposit with a particular structure, which seems to be responsible for the Pd-bulk over-loading.

We tried several procedures to produce this particular structure. We changed electrolysis current values not only when the electrolysis started up (Start in Low current: SL or Start in High current; SH) but also during electrolysis. The Pd electrode was loaded, and the loading was steady, after the value of R/Ro was reached 1.8 (Fig. 1).

Low current (Low: L) means just a few milli-Amperes (2→10 mA and 5→15 Volts). High current (High: H) means some tens of milli-Amperes (30→150 mA and 50→200 V) and middle current (M) is in the middle range.

In the following a list of these loading procedures (depending on the Hg deposition onto the Pd) is reported:

- **Start and Load** Start at constant current (Low or High) until the Pd cathode reaches a consistent over-loading (R/Ro<1.3). In general, if the Hg concentration is high, when the current is switched off, a very slow de-loading occurs (although in one test no de-loading was observed for two days) [10]. We call this condition H/Pd-locked.
- **OFF/ON**: The Pd electrode is loaded just over the R/Ro peak, and the current is switched off, allowing the Pd to de-load to the peak. Then the current is switched on again (either at low or at high current). This cycle can be repeated several times until the Pd reaches a high loading. This procedure can be applied when the Hg concentration is very low and the "ON" condition is corresponding to high current during the previous cycles.
- **L/H** Similar to OFF/ON, but the current is not totally switched off. "OFF" corresponds to a low current while "ON" corresponds to a high current.
- **L/H/L** Similar to L/H, but after the Pd achieves a high and steady loading at a high current condition, the current is then set to a low value. At this low current a rapid de-loading occurs, but sometimes the de-loading stops and the Pd reloads slowly up to high values (sometimes higher than the ones obtainable at high current). This procedure is effective when Hg is neither very diluted nor very concentrated.

5. EXPERIMENTAL TESTS

Table 1 shows only the most revealing tests out of the many hundreds that were performed. In this table all the parameters cited above are listed, that is: cell geometry, Pd sample thickness, electrolyte solution, electric values, and loading procedure. The column "best R/Ro" means the final H/Pd over-loading reached while applying the proper procedure (relative to the "up" and "down" Pd sectors).

The 20 tests in Table 1 are in chronological order (from 1998 till 2004) and some of them have been repeated many times. The "best R/Ro" reproducibility was very poor at the beginning (about 10%) and increased with time reaching reasonably good values (>50%) at present, particularly when the Hg concentration is finely tuned and an optimal "current cycle" procedure is adopted.

Figures 3 and 4 show the values of R/Ro versus time corresponding to the parameters in the first two rows of Table 1. In these figures it can be seen that alkaline elements like Ca and Sr are quite equivalent for the achievement of high loading with a high Hg concentration. A typical Start and Load procedure is also shown. In this case the Pd electrode very often appears to be covered with a very thin Hg film, which is very impervious. This explains the observed very slow de-loading process when the current is switched off (a load and lock condition).

In Figures 5 and 6 a typical OFF/ON operation is shown in connection with runs with Sr and "residual" Hg (data from Table 1, rows 3 and 4). This shows that it is possible to achieve a high and steady loading starting from a low loading (R/Ro=1.8→1.2). Moreover, the de-loading curve (electrolysis OFF for 1 day) shows that the resistance measurements are correct and consistent (peak at R/Ro=1.8 returning to R/Ro=1.0, the starting condition). The de-loading vs. time curve allows the observation of the typical $\beta \rightarrow \alpha+\beta$ **Pd-H** lattice phase transition (occurring at R/Ro≅1.68, H/Pd≅0.6 at room temperature and at a pressure of 1 atmosphere [11]).

Figure 7 (row 7) shows the role played by the Hg addition during the run (at the time of about 75 Ksec). In combination with a Low/High operation; high loading values persist even when the current is decreased.

The effects of the substitution of ethyl alcohol for H_2O (as a base for the electrolyte) are shown in Fig. 8 (row 11). The presence of Sr and Hg in a sulphuric environment is effective for reaching a very high loading, when applying an OFF/High/Low current procedure.

Even with very small Hg additions (down to 0.5 μMoles), it is possible to reach very high loadings (R/Ro=1.05) as shown in Fig. 9 (row 15). In this case just a Start-Low/High current variation is sufficient to trigger the loading process.

By exchanging Sr with Li similar high loading effects are obtained (rows 16 through 19) but additions of fair amounts of Hg (1 μMole), cause the role played by the electrolytic current to become crucial, as shown in Fig. 10 (row 20). In this plot, the first run is performed at Low current (5 mA) resulting in a poor loading. On the contrary, the subsequent run, which was started with a Medium range current of 36 mA (after a de-loading at R/Ro=1, with –5 mA anodic current) a steady high loading (R/Ro=1.2) was obtained within a few hours.

Several tests with methyl alcohol have also been performed showing loadings around R/Ro=1.3.

We never measured “anomalous” temperature variations inside the cell even when very high loadings were achieved.

	Pd Φ (μm)	Electrolysis Solution (HCl in μM)	Alkaline Element (in μM)	$HgCl_2$ (in μM)	Power Supply (V;mA)	*LOAD* procedure	“best” *R/Ro* (u;d)	*Remark (set-up)*
1	50	H_2O=2400cc +HCl= 140	$CaCl_2$= 70	Hg ≈ 10	(60;20)	Start and Load	(1.28;1.35)	K-A=7 cm geo. parallel
2	50	H_2O=2400cc +HCl= 140	$SrCl_2$= 35	Hg ≈ 10	(40;20)	Start and Load	(1.15;1.18) *(load+lock)*	idem
3	50	H_2O=2400cc +HCl= 210	$SrCl_2$= 180	very low (<< 0.1)	(150;90)	OFF/ON	(1.16;1.20)	K-A=6 cm geo. parallel
4	50	H_2O=2400cc +HCl= 210	$SrCl_2$= 180	very low (<< 0.1)	(150;65)	OFF/ON *(+ deload)*	(1.10;1.11)	idem
5	50	H_2O=2400cc +HCl= 500	$SrCl_2$= 20	very low (<< 0.1)	(100;77)	OFF/ON	(1.20;1.25)	idem
6	50	H_2O=2400cc +HCl= 250	$SrCl_2$= 160	very low (<< 0.1)	(150;70)	OFF/ON	(1.25;1.30)	idem
7	50	H_2O=5000cc +HCl= 250	$SrSO_4$= 60	Hg=10cc	(90;105) →(40;50)	LOW/HIGH /LOW	(1.12;1.15)	K-A=1.5cm geom. axial
8	50	H_2O=1200cc +HCl= 20	$SrCl_2$= 30	very low (<< 0.1)	(140;133)	OFF/ON	(1.15;1.15)	idem
9	50	H_2O=1200cc +HCl= 20	$SrCl_2$= 30	very low (<< 0.1)	(6.5;4.4)	HIGH/LOW	(1.28;1.28)	idem
10	100	Ethyl=395cc +H_2O=20cc H_2SO_4= 25 +HCl= 210	$SrCO_3$ =17mg *(powder)*	Hg= 5	(11;2)	Start and Load	(1.25;1.30)	idem
11	100	Ethyl=395cc H_*SO_4= 25 +HCl= 210	$SrCO_3$ =17mg *(powder)*	Hg= 2.5	(11;2.5)	Start OFF/H/L	(1.15;1.15)	idem
12	100	Ethyl=395cc +H_2O=20cc H_2SO_4= 10 +HCl= 200	$SrCO_3$ =30mg *(powder)*	Hg= 8	(12;3.7) → (12;1)	Start and Load	(1.34;1.34)	idem
13	100	H_2O=400cc +HCl=200	$SrCO_3$ =85mg *(powder)*	Hg= 5	(45;60)	Start in L /M/H	(1.30;1.35)	idem
14	100	H_2O=400cc +HCl=200	$SrCl_2(6H_2O)$= 53mg	Hg= 2.5	(6;7)	Start and Load	(1.33;1.36)	idem
15	50	H_2O=420cc +HCl= 70	$SrCO_3$ = 7mg *(powder)*	Hg= 0.5	(10;6) → (50;45)	Start in L /H	(1.07;1.05)	idem
16	50	H_2O=420cc +HCl= 70	$SrCO_3$ = 7mg *(powder)*	Hg= 0.5	(10;6)	H/L	(1.31;1.26)	idem
17	50	H_2O=420cc +HCl= 70	LiOH= 50	Hg = 0 → 0.2	(10;6) → (48;34)	L/H/L	(1.25;1.25) *(1.21 in H)*	idem
18	50	H_2O=420cc +HCl= 70	LiOH= 50	Hg= 0.3	(10;5) → (48;34)	L/H/L	(1.33;1.31) *(1.19 in H)*	idem
19	50	H_2O=420cc +HCl= 70	LiOH= 50	Hg= 0.1	(10;6) → (49;53)	L/H/L	(1.30;1.30) *(1.22 in H)*	idem
20	50	H_2O=420cc +HCl= 100	LiOH= 50	Hg= 1	(10;5) → (42;36)→	Start in L→ Start in H→	→(1.5;1.5) →(1.2;1.2)	idem

Table 1 – The most relevant tests (out of many hundreds) showing high over-loadings performed with different solutions, different added elements and different loading procedures (tests performed at room temperature, 22 ±5°C).

6. DISCUSSION

Taking into account also previous studies (particularly the ones performed during the last two years), we can confirm that our procedure for the Pd-H overloading up to 1:1 loading ratio is effective using both aqueous and alcoholic solutions. This method is based on a proper deposition of a alkaline and mercury containing thin film onto the Pd cathode surface (independent of the wire section). Particular current cycles can improve the loading.

The complexity of these tests and the large spread of the process parameters distribution, can be tracked down to a peculiar deposition layer (ranging from 20 to 200 nm) onto the Pd cathode. We conjecture the formation of a nano-structure on the surface that can give rise to relevant electrochemical potentials and locally high current densities [12].

During the performance of a test consisting of a dozen of high current loadings (120 V; 60 mA) at high Hg concentration (about 10 μMoles) it was observed that after each loading/de-loading cycle the Ro value increased some percent. At the end of the test we measured the Pd wire thickness and found a decrease in diameter from the original 50 to 46 μm. These values are consistent with the increase of Ro with respect to the one at the beginning of the test. It is reasonable to assume that the alkaline, Hg and Pd layer formed during the loading (cathodic) cycle resulted in the removal of about a 200 nm Pd layer during each de-loading (anodic) cycle.

A further structural analysis of this deposition is required to confirm the rightness of our conjecture.

It was shown [9] that the achievement of high loadings with D_2O instead of H_2O is much more difficult. Nevertheless we think that our method could be transferred to heavy water solutions. New tests are in progress showing encouraging preliminary results ($R/Ro \cong 1.55$ at a low current regime of 5 mA). The obstacles limiting the over-loading of Pd-D systems are mainly due to impurities present in the commercial D_2O.

ACKNOWLEDGEMENTS

We are indebted to Eng. Alfredo Mancini for his valuable support.

We are grateful to Dr. Daniele Garbelli and Dr Luca Gamberale for their important help and we want to thank Dr Mike McKubre for his useful suggestions.

Regarding the last tests, it has been crucial the expertness of Mr Vincenzo Andreassi, our skilled technician.

REFERENCES

[1] M.C.H. McKubre et al. *Frontiers of Cold Fusion* (Proc. ICCF3, 1992, Nagoya, Japan), 5(1993)

[2] 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", SIF - Conf. Proc. Vol. 70 pg 181-190, Lerici (La Spezia), Italy 21-26 May 2000; Edited by F. Scaramuzzi, Compositori–Bologna, Italy (2000).

[3] A. Spallone, F. Celani, P. Marini and V. di Stefano.
"NEW ELECTROLYTIC PROCEDURE FOR THE OBTAINMENT OF VERY HIGH H/Pd LOADING RATIOS. PRELIMINARY ATTEMPTS FOR ITS APPLICATION TO THE D-Pd SYSTEM."
Proceedings of the "8th International Conference on Cold Fusion", SIF - Conf. Proc. Vol. 70 pg 191-198, Lerici (La Spezia), Italy 21-26 May 2000; Edited by F. Scaramuzzi, Compositori–Bologna, Italy (2000).

[4] B. Baranowski and R. Wisniewski (1969), *Phys. Stat. Sol.* **35**, 539

[5] J.C. Barton, F.A. Lewis and I. Woodward (1963), *Trans. Faraday Soc.* **59**, 1201

[6] M. McKubre et al. *Conf. Proc. ICCF1* (Salt Lake City, Utah) March 28-31 1990, p.20-31

[7] Patrizio GALLONE, **"Principi dei processi elettrochimici"**, Tamburini Editore Milano, 1970, pp.197—199, (IN ITALIAN).

[8] F.Celani, A.Spallone et al.
"ELECTROCHEMICAL D LOADING OF PALLADIUM WIRES BY HEAVY ETHYL-ALCOHOL AND WATER ELECTROLYTE, RELATED TO *RALSTONIA* BACTERIA PROBLEMATICS."
Proceedings of the 9th International Conference on Cold Fusion, "Condensed Matter Nuclear Science" pg 29-35, Beijing (China), 19-24 May 2002; Edited by Xing Z. Li.

[9] A. Spallone, F. Celani, P. Marini and V. di Stefano.

"EXPERIMENTAL STUDIES TO ACHIEVE H/Pd LOADING RATIO CLOSE TO 1 IN THIN WIRES, USING DIFFERENT ELECTROLYTIC SOLUTIONS."
Proceedings of the 9th International Conference on Cold Fusion, "Condensed Matter Nuclear Science" pg 319-322, Beijing (China), 19-24 May 2002; Edited by Xing Z. Li.

[**10**] A. Spallone, F. Celani, P. Marini and V. di Stefano.
"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"*, Conf. Proc. 22-24 Oct. 1999, Asti, Italy --- Published by INFN: *LNF-00/018 (P), 27 Giugno 2000.*

[**11**] F.Celani, A.Spallone, P.Tripodi et al.
"THE EFFECT OF GAMMA-BETA PHASE ON H(D)/PD OVERLOADING."
Proceedings of the "Seventh Intern. Conf. on Cold Fusion", Vol. 1 pg. 62-67; Apr. 19-24, 1998 - Vancouver BC, Canada.

[**12**] Y. Arata.
"THE FORMATION OF ''SOLID DEUTERIUM'' SOLIDIFIED INSIDE CRYSTAL LATTICE AND INTENSE SOLID-STATE NUCLEAR FUSION (''COLD FUSION'')" .
Il Nuovo Saggiatore (Bollettino SIF) Vol.20, No.5-6, pg.56-61 (2004)

FIGURES

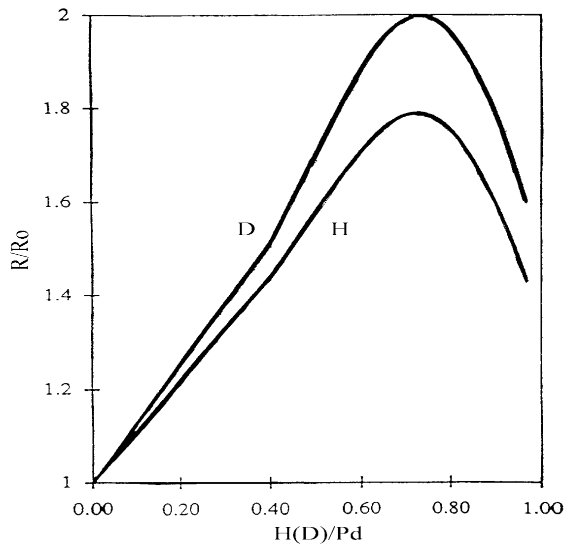

Fig. 1 – Normalized Resistance R/Ro vs H(D)/Pd.

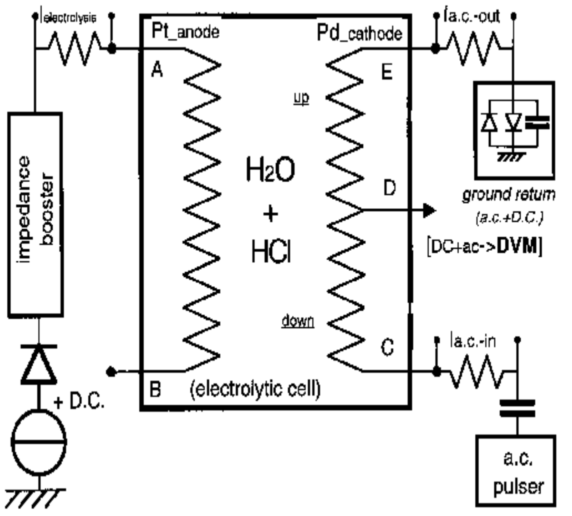

Fig. 2 – Electrolytic cell: a schematic view.

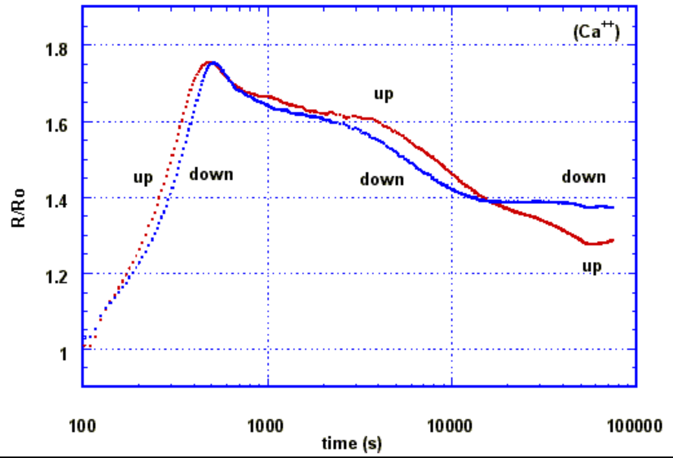

Fig. 3 – Test "Start and Load" with **Ca** ions and high **Hg** concentration (Tab.1,1).

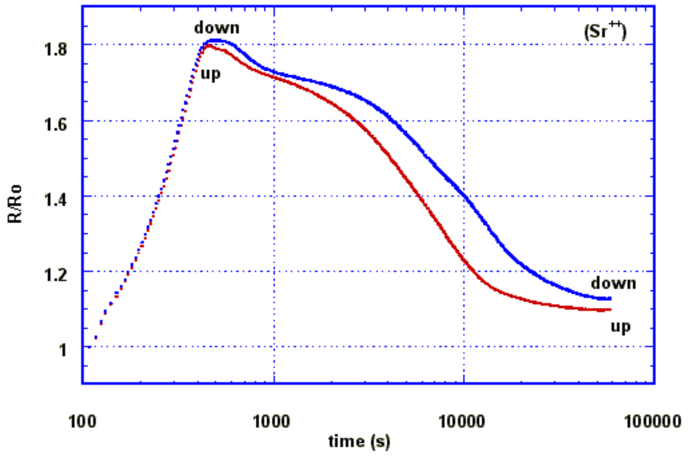

Fig. 4 – Test "Start and Load" with **Sr** + **Hg** (10μM), ending with a H/Pd "lock" (Tab.1,2).

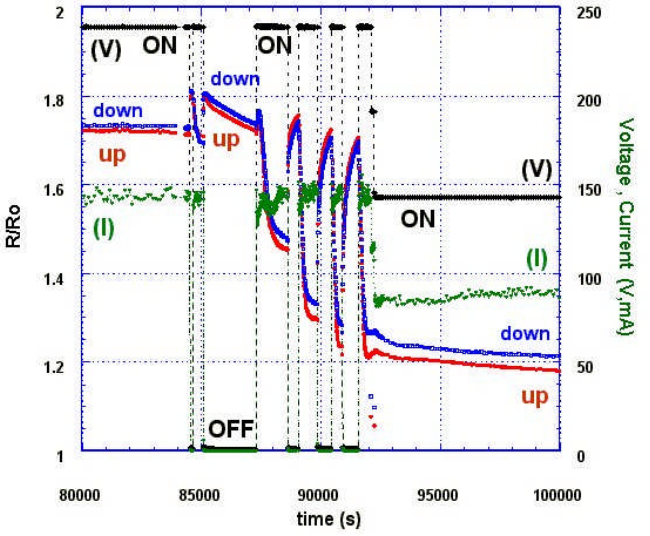

Fig. 5– Test of OFF/ON procedure with **Sr** (+ **Hg** very low concentration) (Tab.1,3).

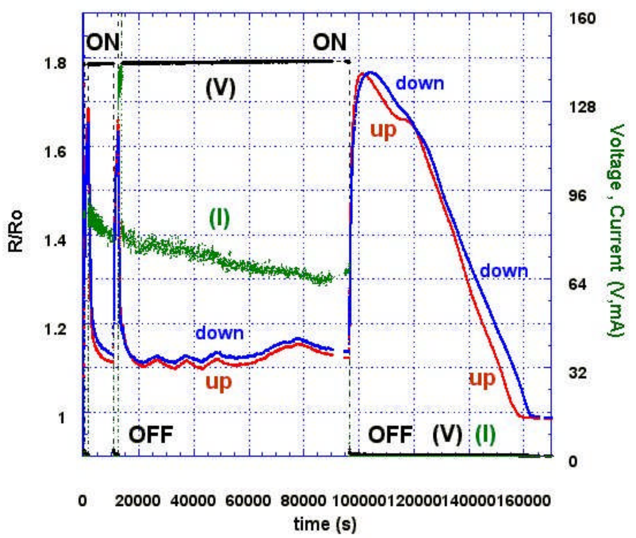

Fig. 6 – Test OFF/ON with **Sr** (+ very low **Hg**) and de-loading run in OFF (Tab.1,4).

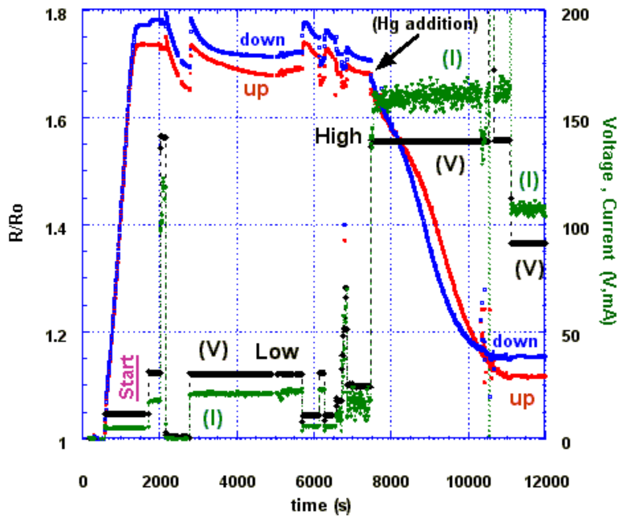

Fig. 7– Test with **Sr** and **Hg** addition during the run with a L/H operation (Tab.1,7).

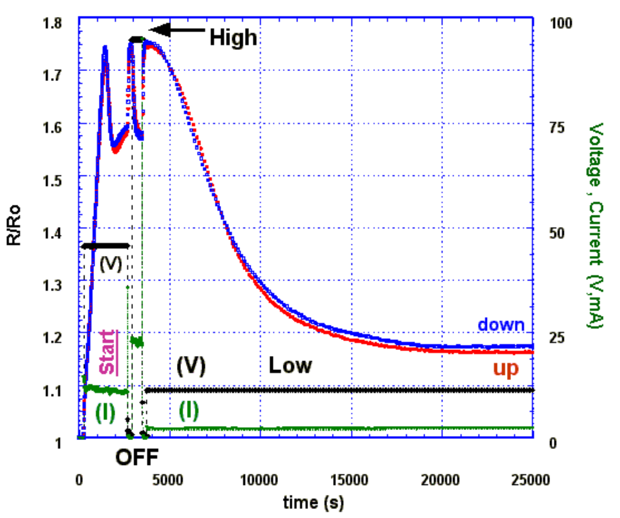

Fig. 8 – Test with **Sr**+**Hg** in an **Ethylic** solution; Start-OFF/H/L procedure (Tab.1,11).

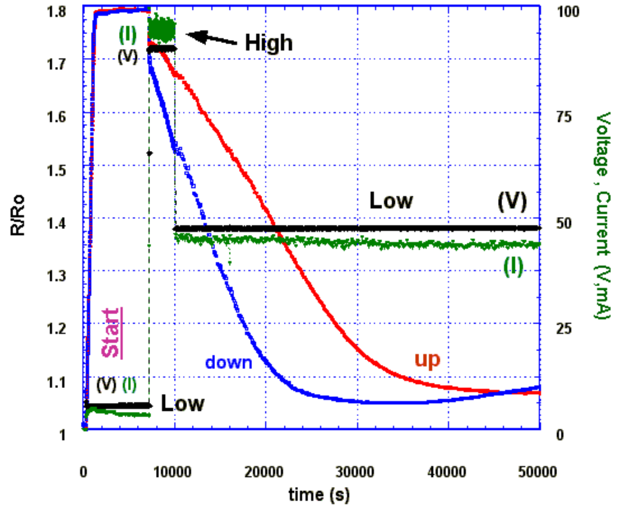

Fig. 9 – Test with **Sr** + **Hg** (0.5μM); Start-L/H/M procedure (Tab.1,15).

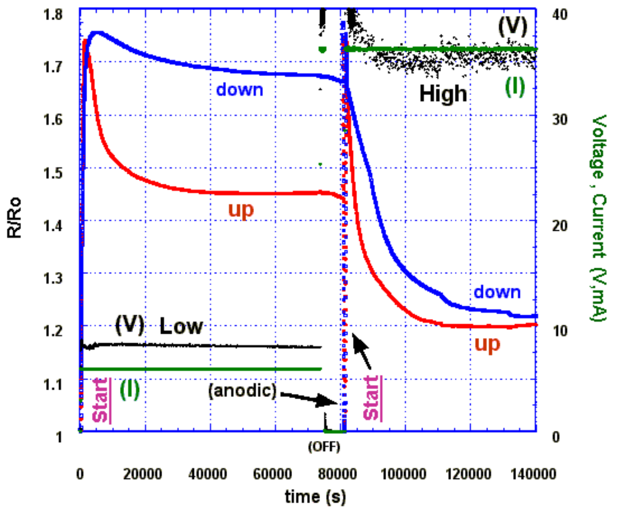

Fig. 10 –Test with **Li**+**Hg** (1μM); Start-L and Start-H procedures comparison (Tab.1,20).