ISCMNS-7 at Asti (23-25 Sep 2006)

a Poster
about

"Experimental studies about H/Pd over-loading with thin Pd wires and measurements of Resistance Temperature Coefficient "

by

--- **Prof. Antonio Spallone:**
[Antonio.Spallone@LNF.INFN.IT]
Ricercatore Associato ai Laboratori Nazionali di Frascati dell'Istituto Nazionale di Fisica Nucleare (LNF-INFN) **[WWW.LNF.INFN.IT]**
and
Docente di Matematica e Fisica al Liceo "Edoardo Amaldi" di Roma
[WWW.Liceo-Amaldi.it]

in Collaboration with
F.CELANI[(1)], V.ANDREASSI[(1)], P.MARINI[(2)], V.di STEFANO[(2)]

(1) INFN-LNF, Via E.Fermi 40, 00044 Frascati, (Italy)
(2) EURESYS, Via Lero 30, 00129 Roma, (Italy)

INDEX

- **Introduction** *(D/Pd threshold)*
- **The method** *(H/Pd over-loading)*
- **Electrolysis Protocol** *(OFF/L/H current)*
- **Measurements**:
  - **Loadings** *(H/Pd=1)*
  - **Resistance Temp. coeff.** *(K_θ)*
- **Conclusions**

Introduction

Since March 1989, when M.Fleischmann and S.Pons claimed to produce a enthalpy in excess from an electrolytic cell of D_2O+LiOD (0.1 N) using a Pd cathode loaded with a high concentration of Deuterium, the main critical point was to achieve high D/Pd values (around 1:1). ***Many researchers spent a lot of effort to reach to this goal but the difficulties were greater than expected and the high loading reproducibility very poor.***

Our group for many years has studied the Pd cathode over-loading achieving at D/Pd ratio of about 1 with Pd thick plates using a own high voltage, high frequency, electrolytic pulsed technique. But working at these unstable conditions, the excess heat reproducibility was poor. So we substituted bulk Pd foils (very difficult to over-load in homogeneous way) with long thin wires and instead of high frequency pulse electrolysis (very difficult to study loading parameters, because of electric noise) we used direct current electrolysis.

Rationale

In order to measure H(D)/Pd loading ratio, we use the H(D)-Pd resistance curve, so that, to have accurate measurements we need to solve the following issues:-

- high Pd resistance → long and thin wire;

- low influence of electrolyte on Pd resistance measurement → very diluted solution and distant electrodes;

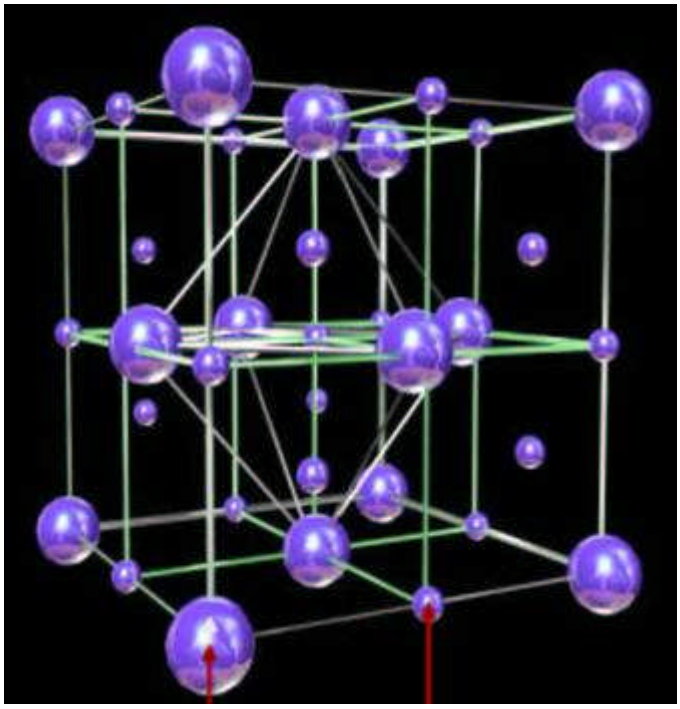
- no uncontrolled metallic deposition on cathode → acidic solution (instead of basic) using very pure water;

- addition of a very low amount of known elements into the solution and production of a quite controlled Pd surface deposition layer.

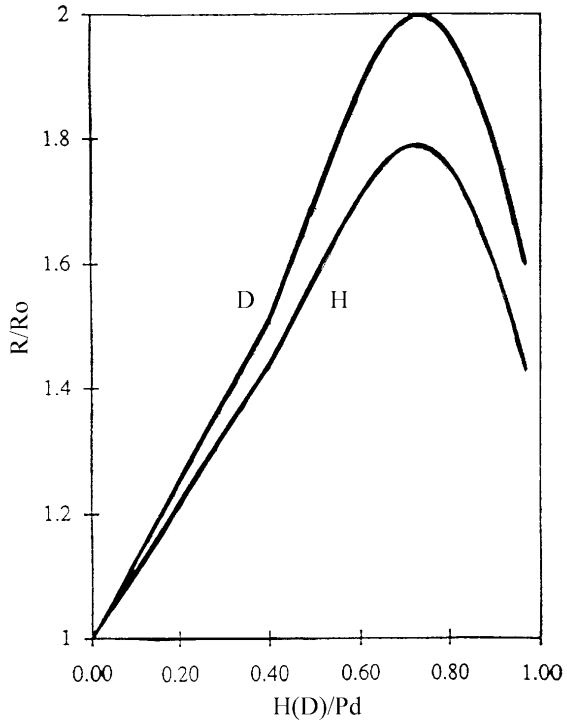
The D/Pd threshold

- **The Pd lattice:**

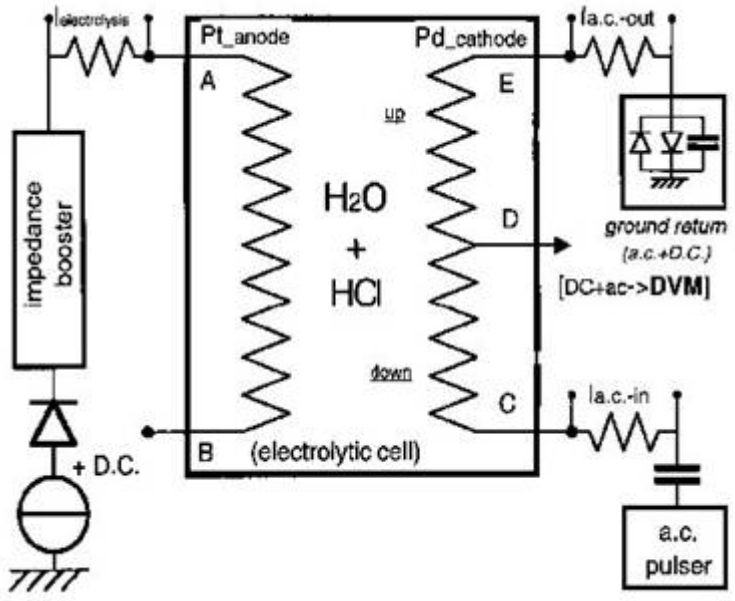
- **The Pd lattice is fcc (face centred cubic)**
- **H or D atoms are formerly located into the lattice centre (α–phase), further interstitial sites of lattice are occupied (α + β phase); finally when the whole of Pd lattice available sites are saturated, we achieve H/Pd or D/Pd=1 (named as γ –phase)**
- **It has been experimentally verified (M. McKubre) that the threshold D/Pd ≥ 0.84 must be overcome to record heat in excess!**



Pd **D**



- **Normalised Palladium resistance versus Hydrogen (Deuterium) molar fraction of Pd. Peak value is: H/Pd=0.75, R/Ro=1.78 (Hydrogen) and D/Pd=0.75, R/Ro=2.0 (Deuterium). Max known loading is H(D)/Pd=0.95 at R/Ro=1.4 (1.6)**



The electrolytic cell is a glass beaker filled by about 400 cm^3 of H_2O+HCl solution (2 cm^3 of HCl at 10 μM/cc) in which are located two parallel (1.5 ÷ 2 cm distant) thin long (19 cm length) wire electrodes (cathode: Pd, 50 um diameter; anode: Pt, 0.5 mm diameter). The cell is located into a thermostatic water bath set at room temperature (22 °C). Cell, bath and room temperature are continuously recorded.

The Loading Tests

- **The Pd wire cathode:**
  - **We tested 50 and 100 μm (10cm long) wires**

- **The electrolyte solution:**
  - ***BASE*: H_2O (400cc) + HCl (or H_2SO4) at *50 μM***
  - ***Loading-supporter*: cation elements addition (Ca, Sr, Li) at *50 μM***
  - ***Loading-catalyzer*: Hg *(50-> 500-> 1000 nM)***

- **The electrolysis Protocol:**
  - **Electrolysis current cycles were performed: *OFF/High=50mA* and/or *Low/High/Low=5mA***
  - **Kation-Hg *deposition* on Pd surface is supposed to be formed *(width 20-> 200 nm)***

Ca

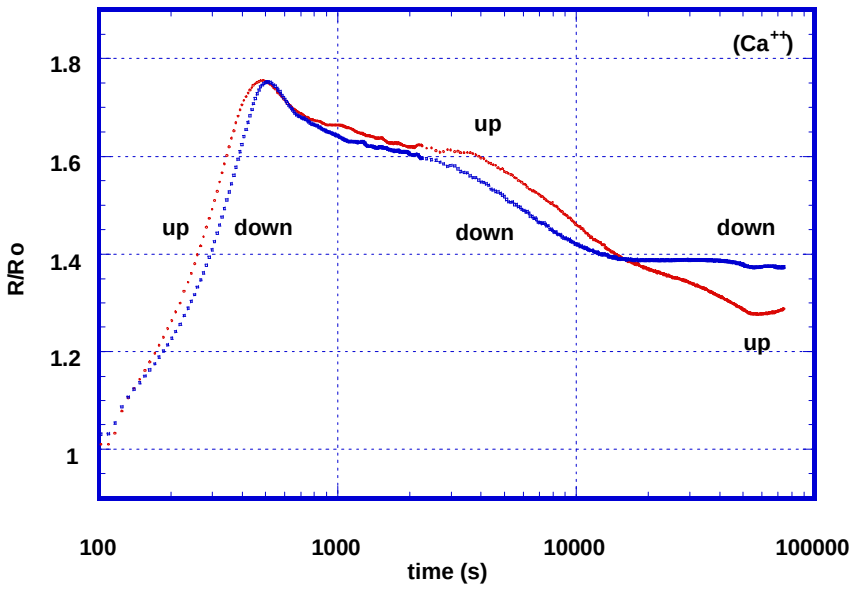


Fig. – *Calcium loading trend.*
Loading trend curve (R/Ro vs log time) occurred when Ca ions ($70*10^{-6}$ M) have been added to the electrolyte; in about 300s resistivity peak was achieved. A shoulder lasting for about a hour after the peak is visible; the highest loading (R/Ro=1.28 for "up" and 1.38 for "down" at 23 °C) reached stable values in about one day.
("up" and "down" labels are corresponding to up (EF) and down (DE) Pd wire segments, see Fig. 4).

Sr

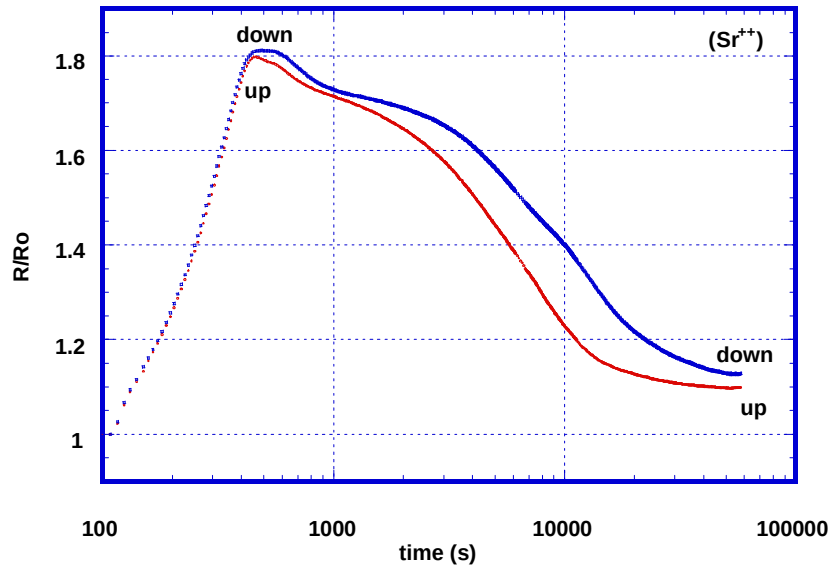


Fig. – *Strontium loading trend.*
Loading trend curve (R/Ro vs log time) occurred when Sr ions ($35*10^{-6}$ M) have been added to the electrolyte; in about 300s resistivity peak was achieved. The shoulder lasts about half hour; loading higher than Ca test (R/Ro=1.13 for "up" and 1.15 for "down" at 27 °C) were reached in less than one day.

Sr: OFF-deload

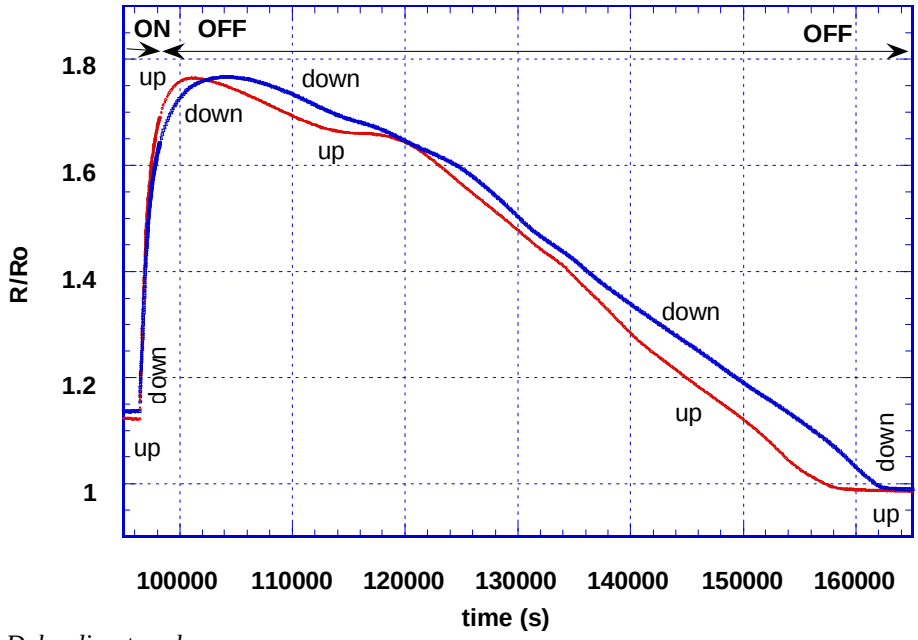


Fig. – *Deloading trend.*
The plot shows Hydrogen deloading versus time. Electrolysis current has been switch off ("OFF" condition) after "ON" condition (R/Ro=1.13 at 23 °C) and in about one hour loading peak was achieved (R/Ro=1.77 at 23 °C). A visible deloading shoulder lasts, about half hour, at R/Ro=1.65; full deloading process requires about 16 hours: both "up" and "down" wire segments return to their initial Ro resistance values.

Sr: OFF/ON cycle

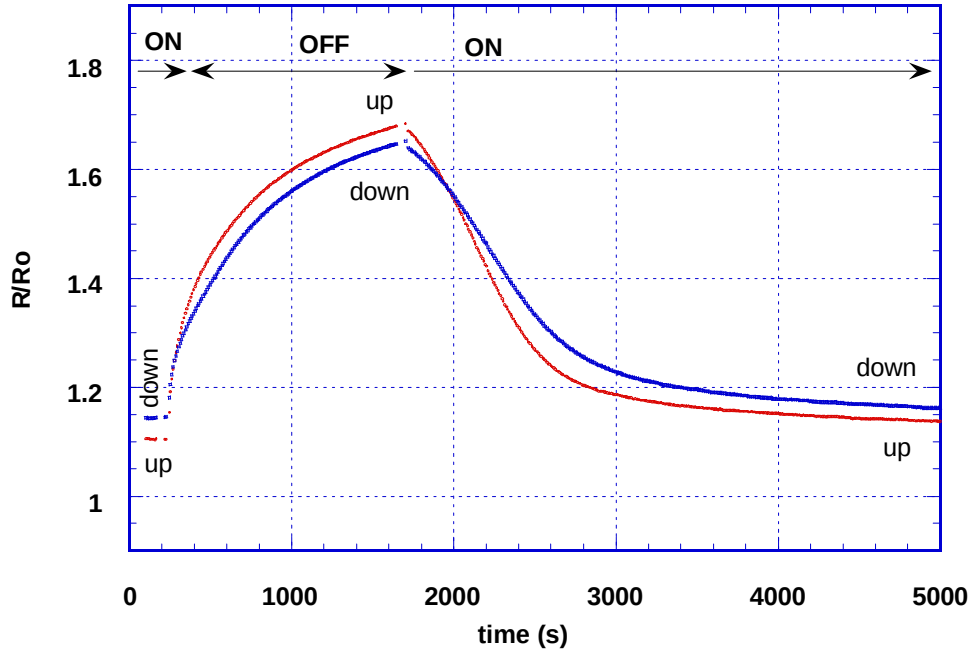
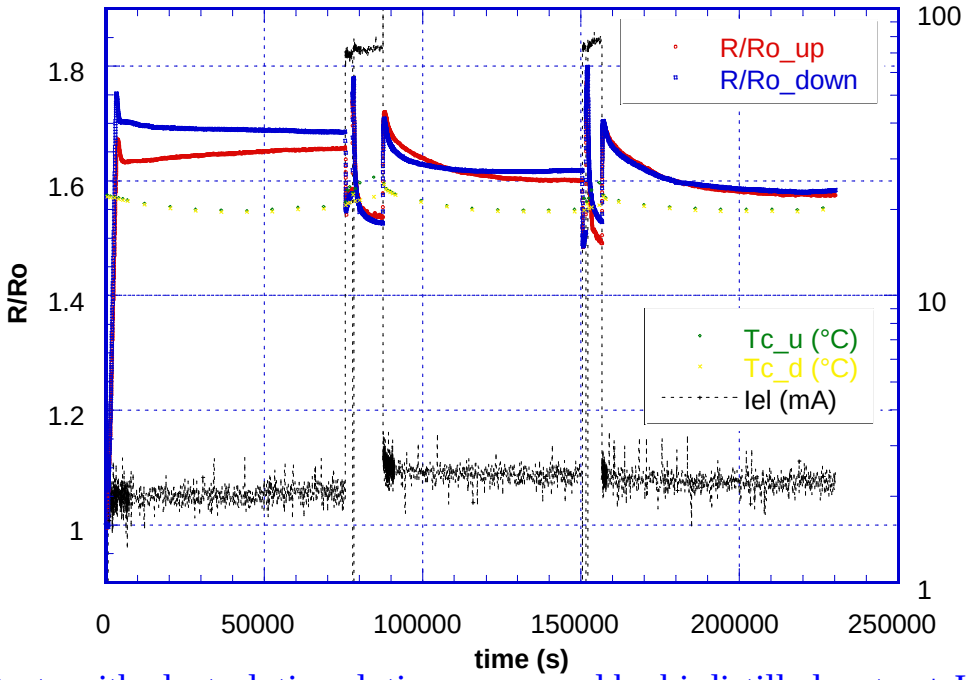


Fig. – *Fast re-loading test.*
Typical test of OFF/ON current cycle: starting from a high loading condition (R/Ro=1.10 at 22 °C), after about half hour of de-loading (near the resistivity peak) because current disconnected ("OFF"), current was switched on ("ON") again. In this condition, reloading is quite fast (less than half hour) and wire reached the previous R/Ro value. Sometimes this procedure, operated cyclically, can be useful to achieve high loading values.

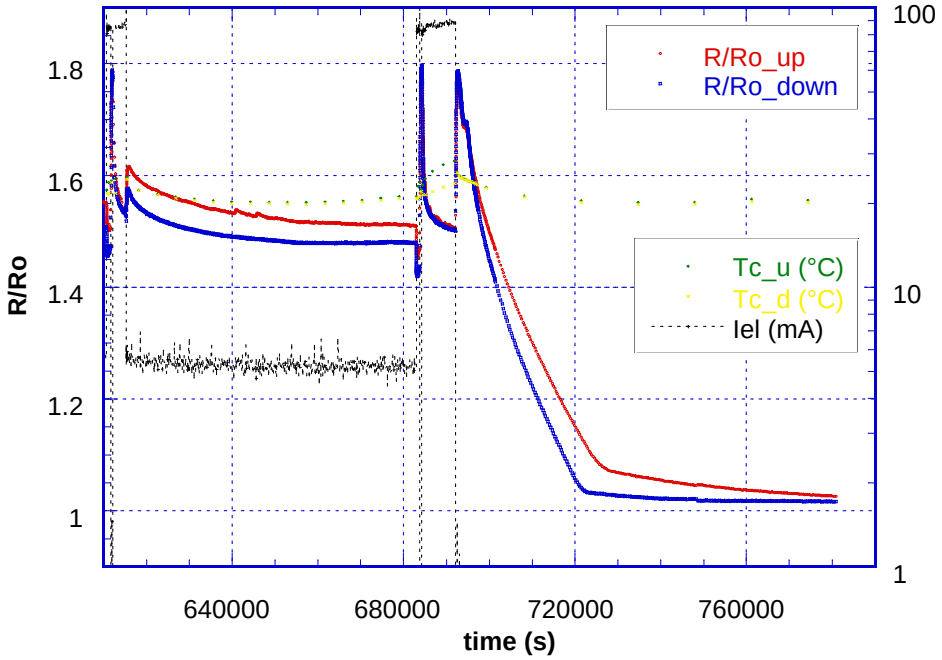
HCl - only

Begin run



Loading tests with electrolytic solution composed by bi-distilled water + HCl:
A) loading protocol: in 2 days best loading at R/Ro=1.6 .

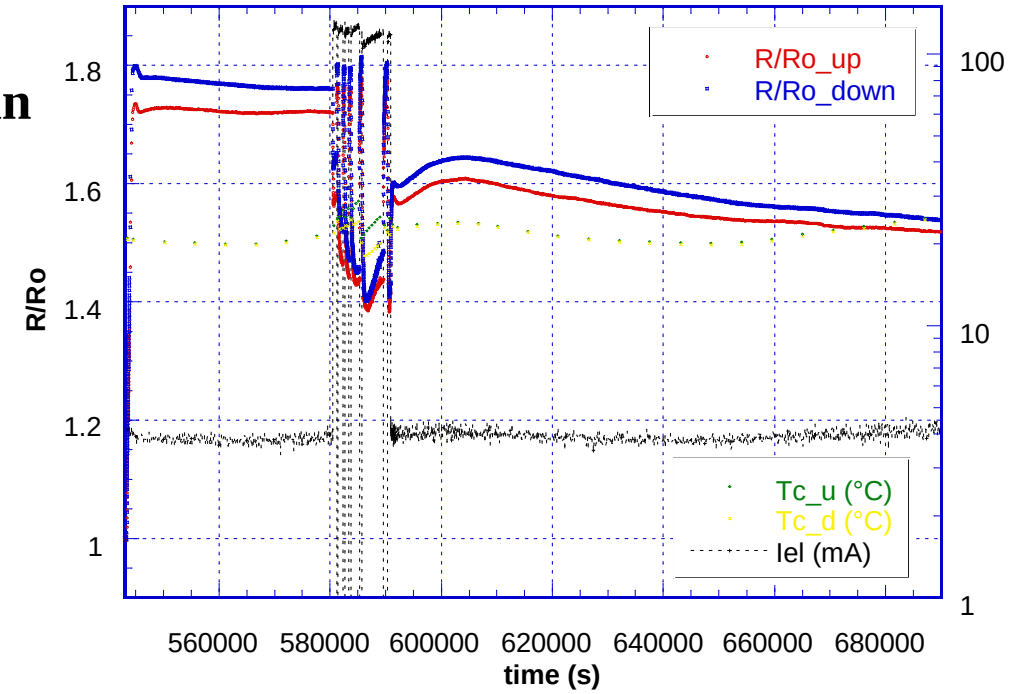
End run



Loading tests with electrolytic solution composed by bi-distilled water + HCl:
B) a further detail of loading protocol (low/high+off/on+low current): a much higher loading improvement (R/Ro= 1.48) occurs at low current (about 5 mA) for long time; at high current (100mA) R/Ro= 1.42 is achieved. Test finished with a long time electrolysis-off operation to verify loading calibration (peak at R/Ro= 1.78, a shoulder at R/Ro=1.70 and return to R/Ro= 1.02 initial condition).

Sr - only

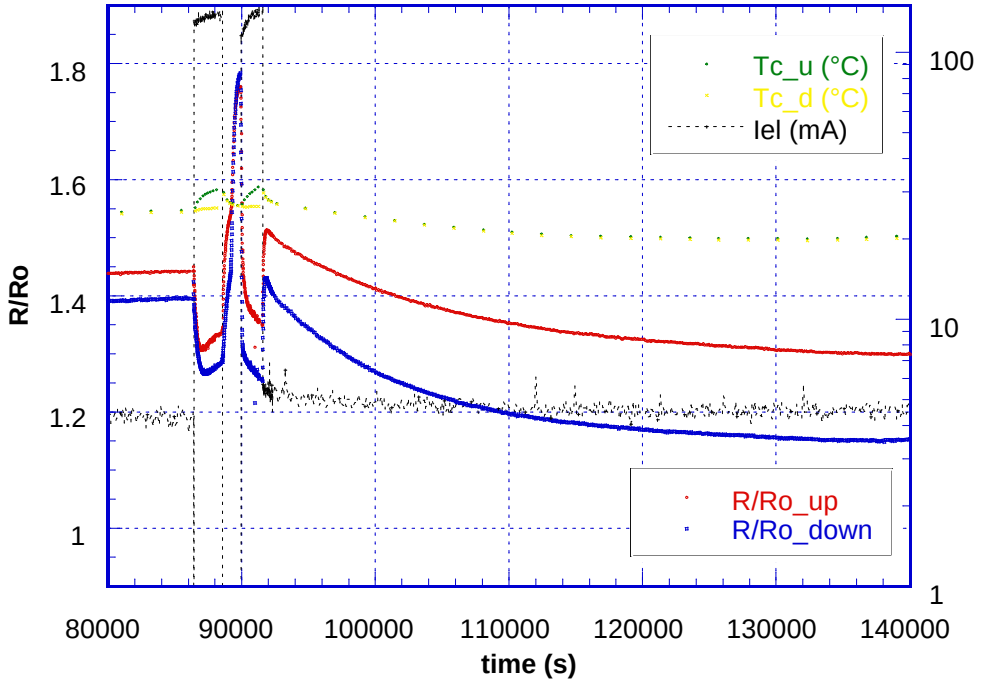
Begin run



Loading tests with electrolytic solution composed by bi-distilled water + HCl +Sr:

The beginning of loading is quite similar to only-HCl loading (R/Ro= 1.7); but, after the several times repetition of off/on current cycles, loading value achieves R/Ro=1.5 at low current (4 mA).

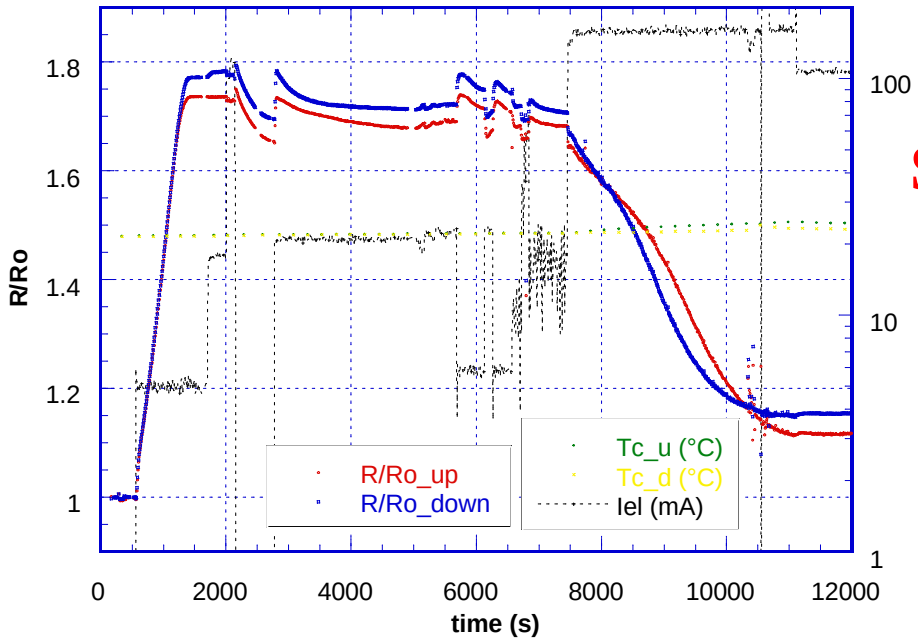
End run



Loading tests with electrolytic solution composed by bi-distilled water + HCl+ Sr:

The final result of this procedure is up to now R/Ro= 1.15 at 5 mA; in this condition loading state is stable in the time. Increasing the current up to 100 mA (high current) a sort of "Tafel effect" increases the loading at R/Ro= 1.08 (not shown in this plot). During the same test, it has been possible to repeat again these values.

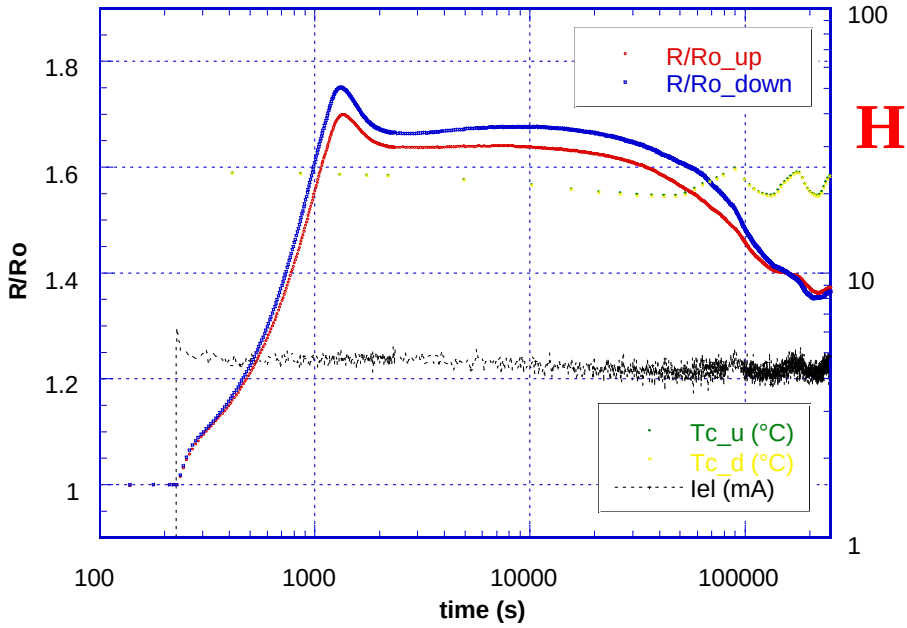
Hg-tests



Sr+Hg

Loading tests with electrolytic solution composed by bi-distilled water + Sr + Hg:

The beginning of loading is operated with $SrSO_4$ and no interesting loading effect has occurred, even ater changing H_2SO_4 solute to HCl and operating low/high current cycles; then adding $HgCl_2$ (10^{-5} Moles) (at time 7500 s) and increasing current to 150 mA, loading increases in 1 hour up to R/Ro= 1.15 and remaining stable (even reducing current to 100 mA).

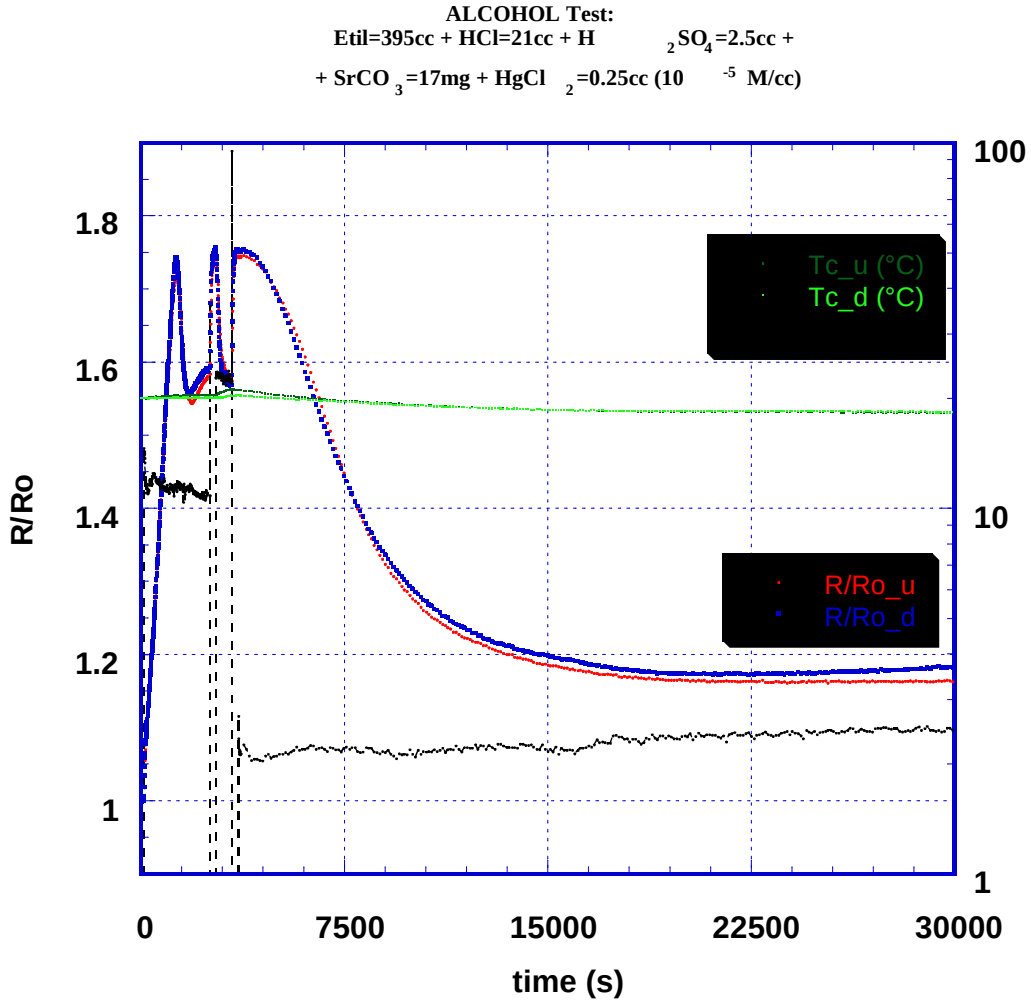


Hg-only

Loading tests with electrolytic solution composed by bi-distilled water + HCl + Hg:

In this test no Sr has been added but only Hg (10^{-7} Moles) and loading effect occurs and in 2 days R/Ro= 1.35 (at 5 mA) has been achieved; further, increasing the current to 75 mA, R/Ro= 1.3 has been achieved (not shown in the plot) and at off-current Pd deloads quickly. Following tests with much more Hg (10^{-5} Moles) have shown no high loading (R/Ro ≅ 1.7) and no deloading occurs when current is off even after many hours.

Ethyl-Alcohol + Hg (+Sr)



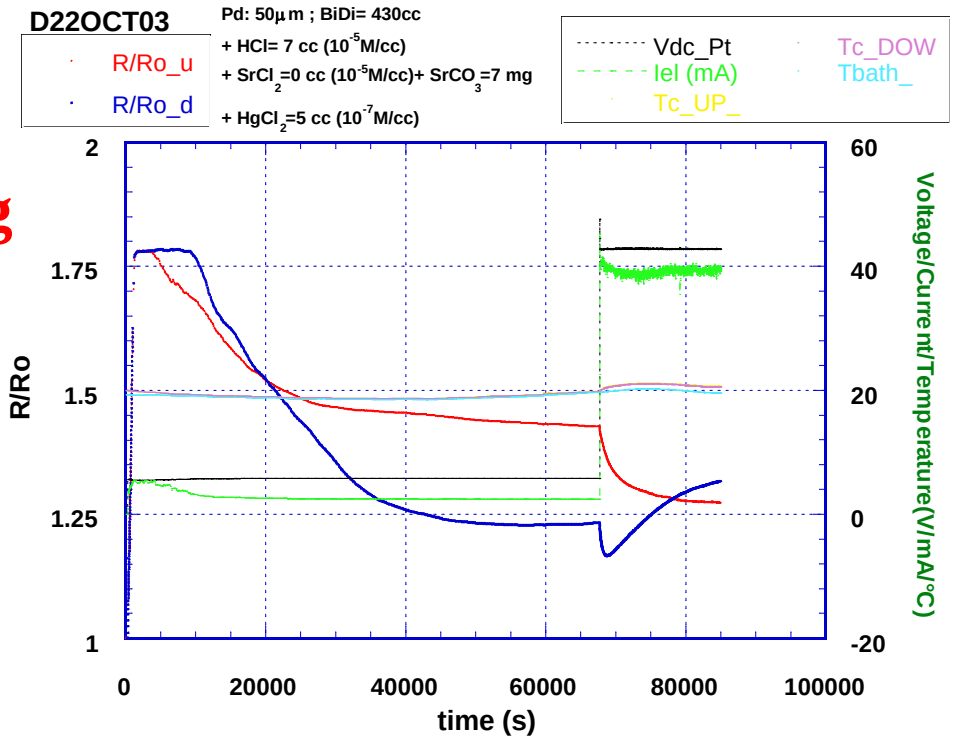
Loading tests with electrolytic solution composed by Alcohol:

After the first loading, a OFF/ON=high current protocol is operated; then a OFF/ON=low current is left for long time. Slowly Pd wire over-charged up to R/Ro= 1.15, at room temperature and 2.5 mA, 11V.

Sr+Hg

begin

run

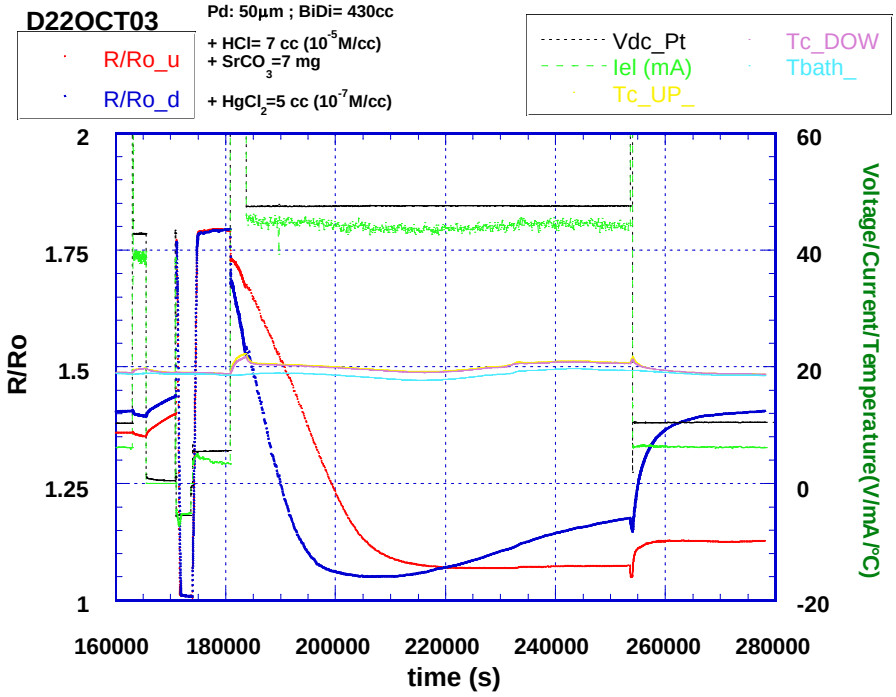


After addition of ***HgCl$_2$=5cc (10^{-7}*** *M/cc), at* ***I=5mA (5V)*** *loading slowly reached R/Ro= 1,43(up) and* ***1.23(down);*** *furthermore at* ***I=40mA****(40V), achieved R/Ro=1.36(u) and* ***1.16(d);*** *(up) loaded upto 1.27 and down deloaded to 1.32; achieving a plateau...*

Sr+Hg

L/H/L

test



After anodic current (-5mA), a similar restarting got a ***good*** *over-loading R/Ro=* ***1,07(up)*** *and* ***1.05(down)*** *with a L/H cycle at* ***I=45mA (45V)*** *! Following cycle H/L shows* ***up*** *reaching a plataeau at R/Ro= 1.10 for long time…*

NEW Li+Hg (test-L/H/L)

(small Hg)

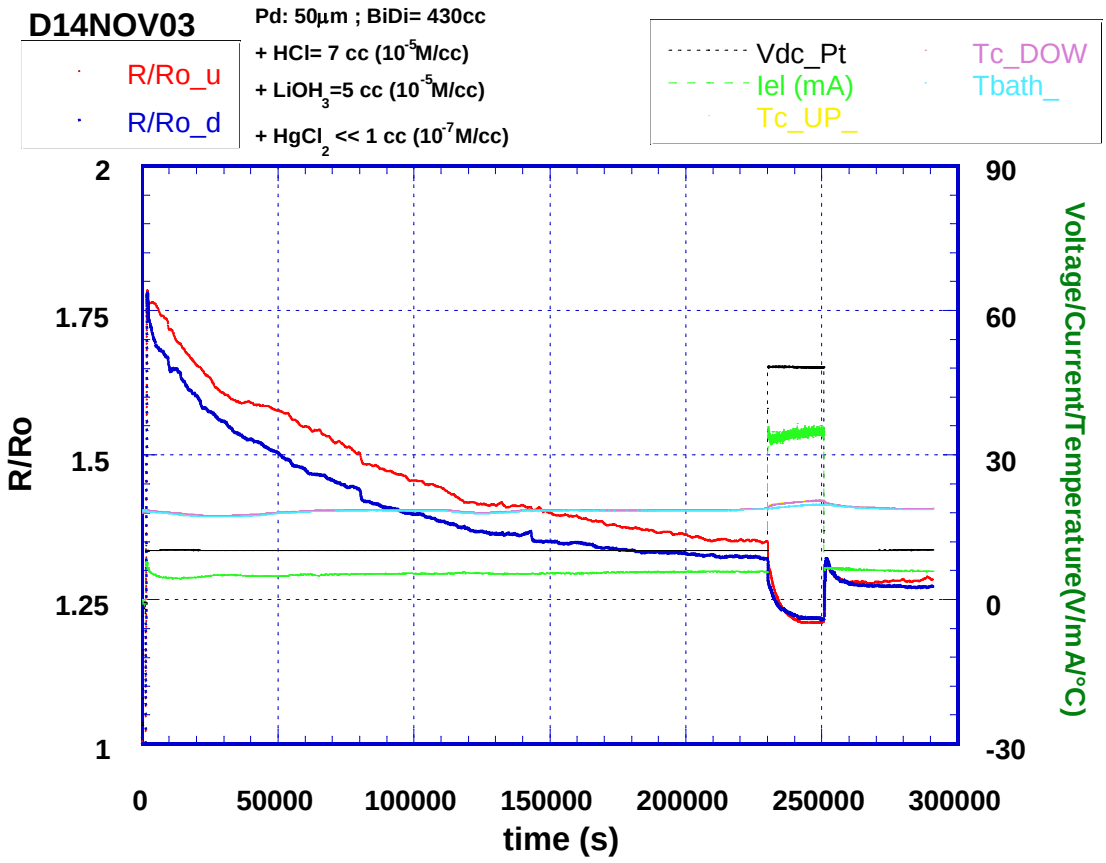


Fig. – Slow high loading at Low-current: [I=5mA, V=10V] (R/Ro=1.33) and then applying a L/High-current cycle: [34mA,48V] (R/Ro=1.21) the loading is increased; a further H/L cycle shows a better value reached at Low-current.

- It seems that Li addition in the electrolytic solution is effective as well as Sr, even with a very small amount of Hg.

NEW Li+Hg (test-L/H/L)

(big Hg)

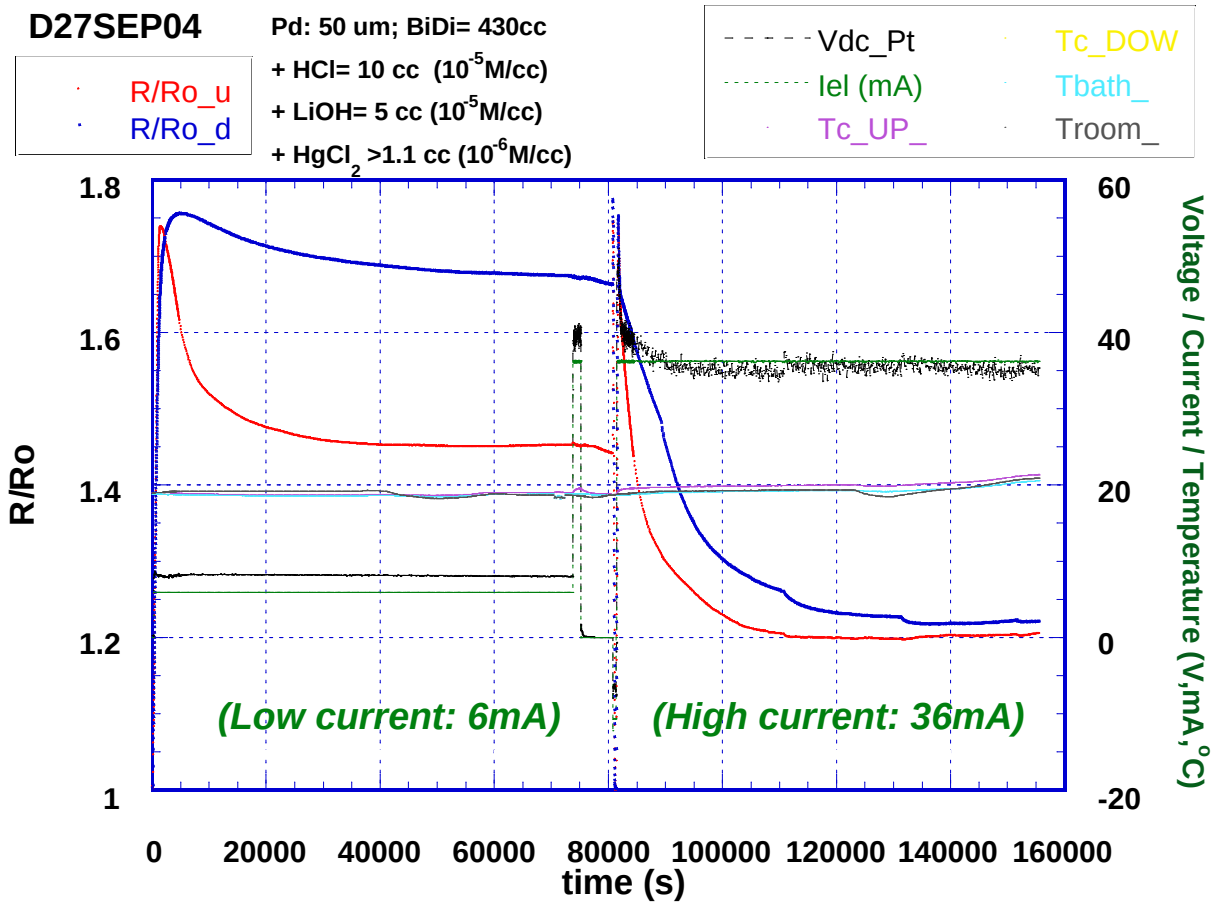


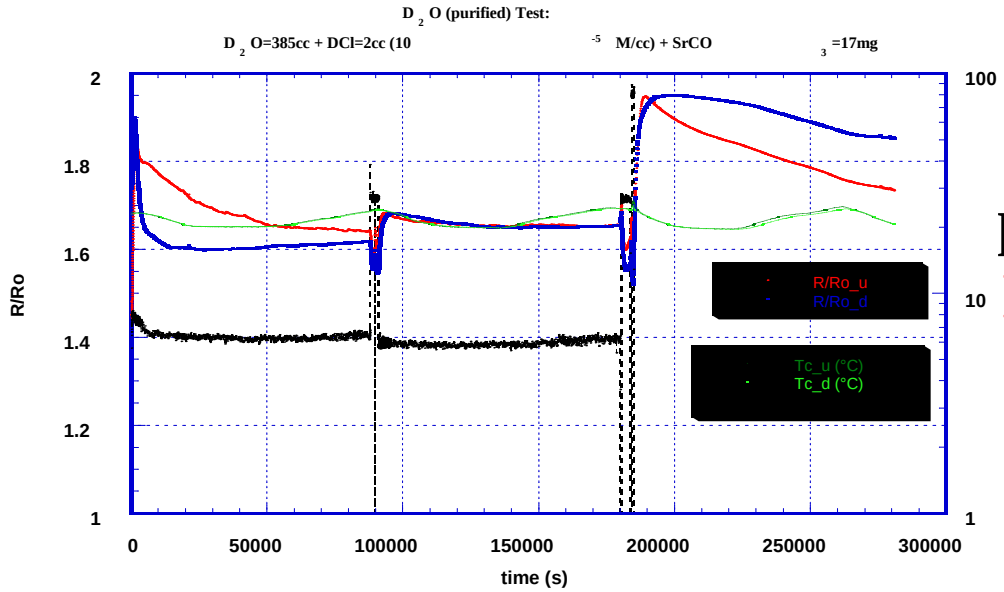
Fig. – Test with high levels of Hg:-

a) Start up and slow loading at Low-current: [I=6mA, V=8V] (R/Ro=1.45); Pd locked by Hg.

b) After anodic current, again start up and slow loading at High-current: [36mA,45V] (R/Ro=1.20); Pd locked.

→ ***It is quite evident that with high levels of Hg it is important to use high current before Hg fully covers the Pd-cathode.***

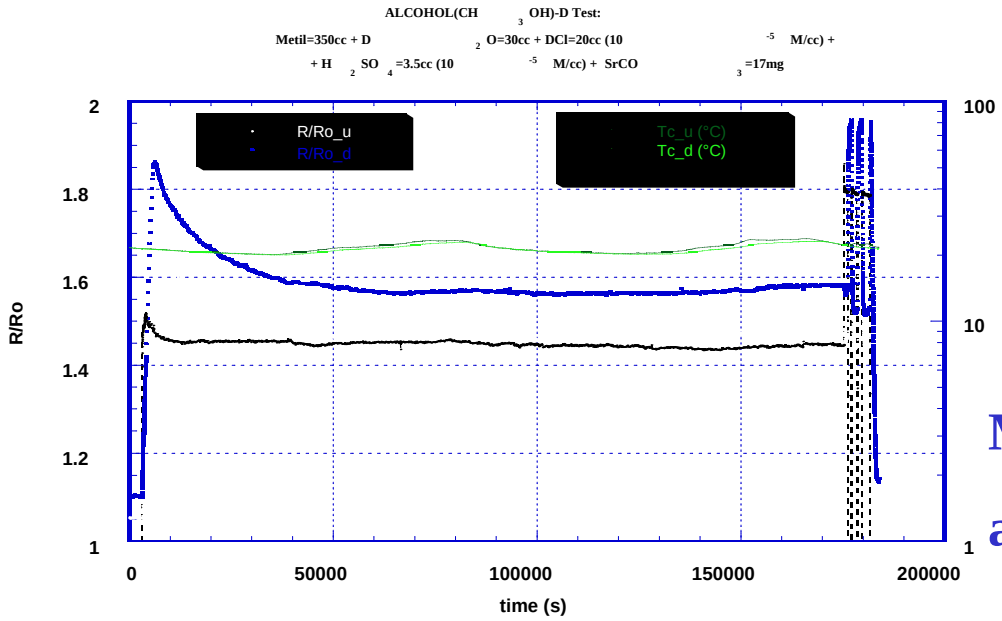
D_2O tests with Sr-only



pure D_2O

Loading tests with electrolytic solution composed by purified D_2O + Sr:

After a loading, R/Ro= 1.6 (I= 6mA, V= 11V); OFF/ON current cycles are operated. Finally Pd wire slowly discharges in OFF current condition



D_2O in Methyl alcohol

Loading tests with electrolytic solution composed by Methyl-Alcohol in D_2O:

After a long term OFF-deloading, a new loading is operated reaching a value of R/Ro= 1.6 (I= 8mA, V= 11V);

D_2O tests with Li+Hg

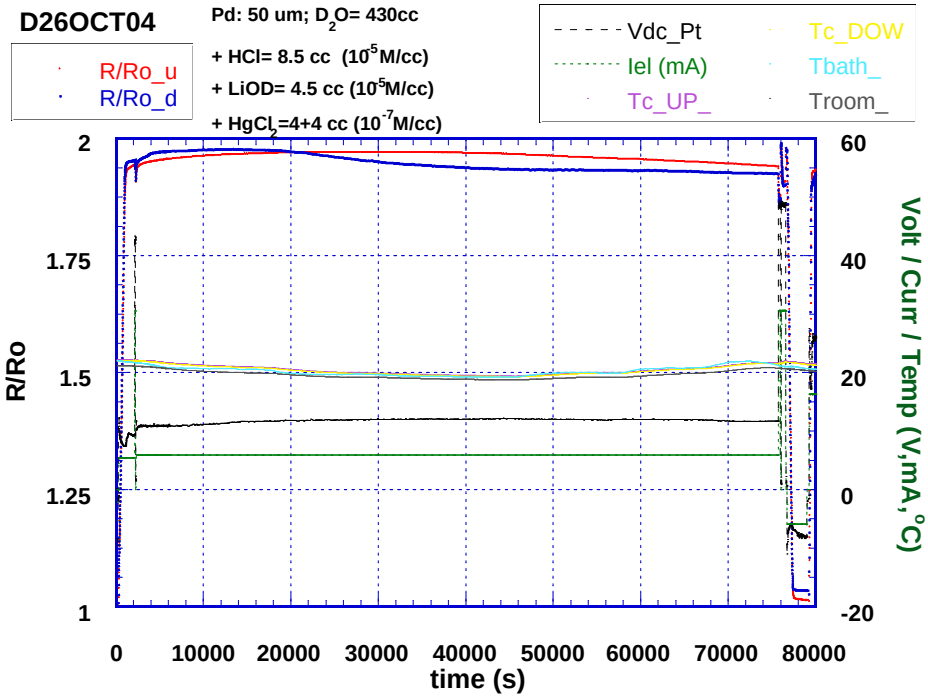


Fig.: - Loading tests with electrolytic solution: **D_2O + Li + Hg=4cc** (10^{-7}/M/cc):

No enough loading: R/Ro= 1.90 (I= 6mA, V= 12V); L/H current cycles are operated with no loading increasing.

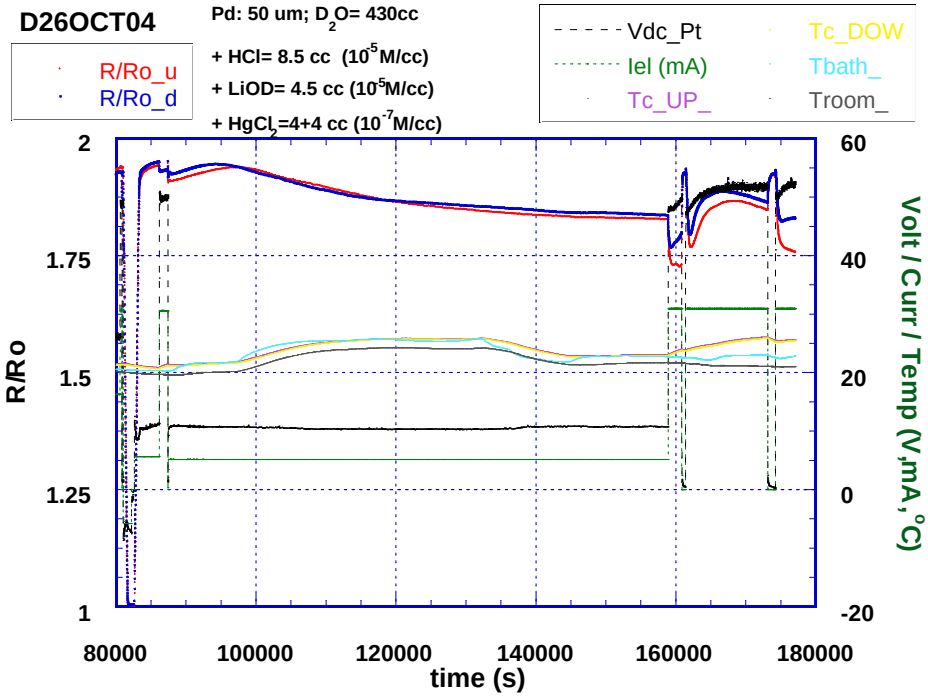
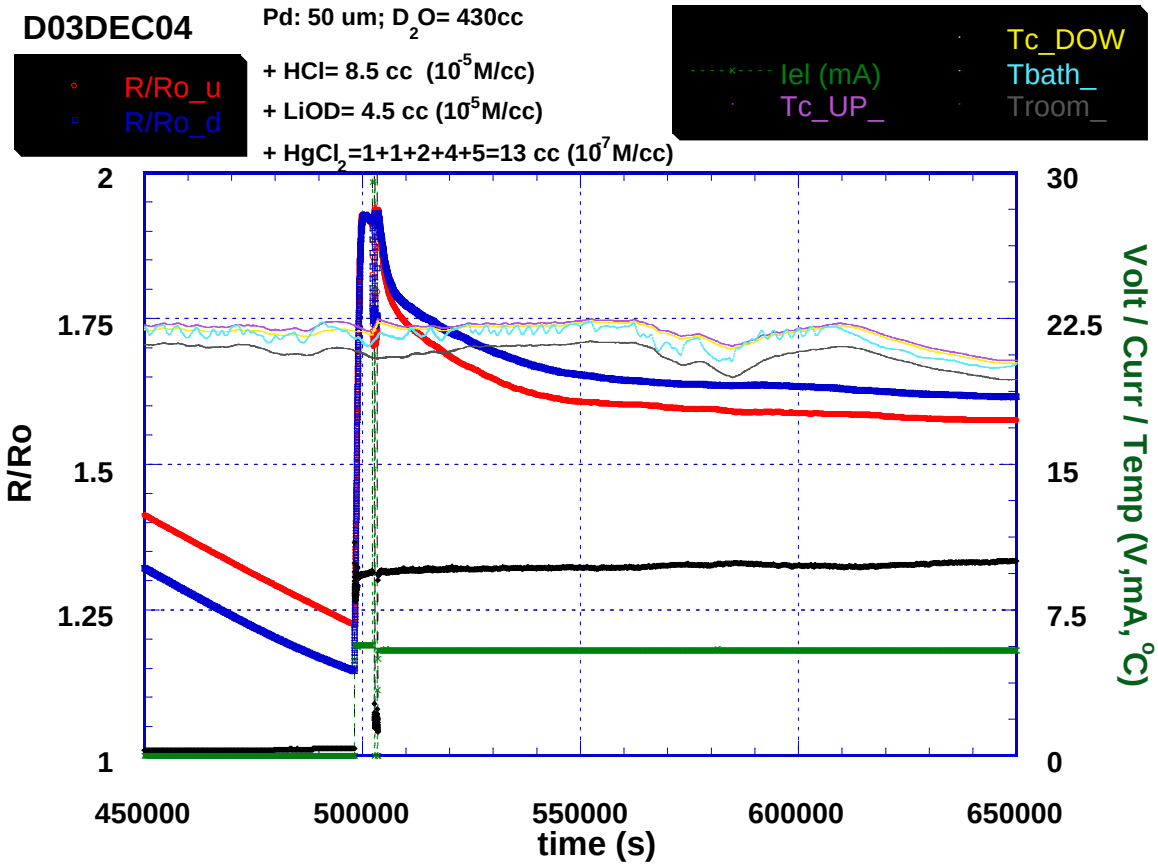
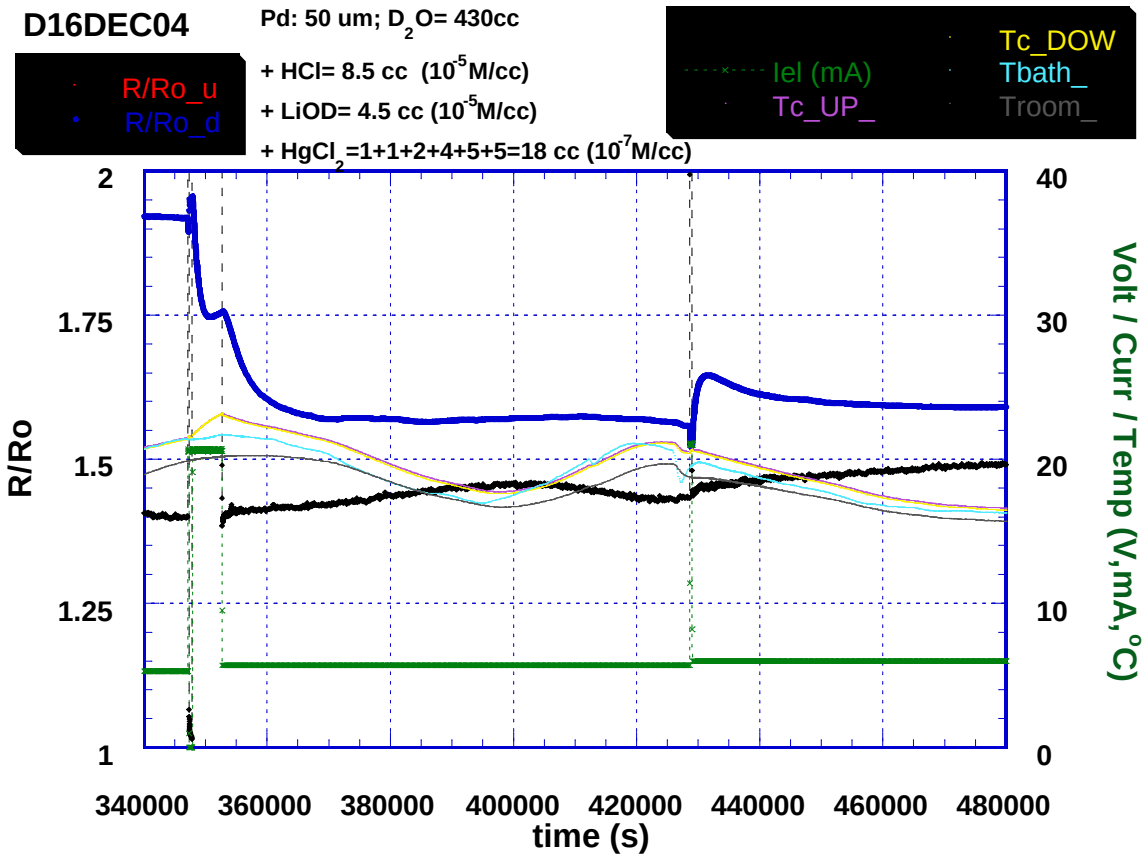


Fig.: - Loading tests with electrolytic solution: **D_2O + Li + Hg=8cc** (10^{-7}/M/cc):

A better loading: R/Ro= 1.83 (I= 6mA, V= 12V); L/H:32mA current cycles are operated showing a loading increasing up to R/Ro= 1.73


D03DEC04
Pd: 50 um; D2O= 430cc
+ HCl= 8.5 cc (10-5M/cc)
+ LiOD= 4.5 cc (10-5M/cc)
+ HgCl2=1+1+2+4+5=13 cc (10-7M/cc)
R/Ro_u
R/Ro_d
Iel (mA)
Tc_UP_
Tc_DOW
Tbath_
Troom_
R/Ro
Volt / Curr / Temp (V,mA,°C)
time (s)
2
1.75
1.5
1.25
1
30
22.5
15
7.5
0
450000
500000
550000
600000
650000


D16DEC04
Pd: 50 um; D2O= 430cc
+ HCl= 8.5 cc (10-5M/cc)
+ LiOD= 4.5 cc (10-5M/cc)
+ HgCl2=1+1+2+4+5+5=18 cc (10-7M/cc)
R/Ro_u
R/Ro_d
Iel (mA)
Tc_UP_
Tc_DOW
Tbath_
Troom_
R/Ro
Volt / Curr / Temp (V,mA,°C)
time (s)
2
1.75
1.5
1.25
1
40
30
20
10
0
340000
360000
380000
400000
420000
440000
460000
480000

Remarks:

We tested different electrolytic solutions for H(D)/Pd overloading (related to a very thin Pd-cathode structure...); we can state:

1) **H/Pd = 1 (R/Ro=1.15) achieved using H_2O or Alcohols (+Sr, +Hg) (at very low electrolysis power ≅50 mW;**

2) **H/Pd (with H_2O) procedure is reproduced (by SRI-Group: McKubre/Tripodi and Pirelli-Group: Fontana/Garbelli);**

3) **D/Pd=1 is much harder to reach because impurities contamination in ordinary D_2O (at the best, D/Pd =0.95 with R/Ro= 1.55): Deuterated Alcohol seems promising.**

H/Pd CONCLUSIONS

- **To achieve a H/Pd over-loading:**

1. **Cations elements addition to acid solution (Li, Sr, Ca and maybe others…)**
2. **Very low Hg ions concentration (and low power supply electrolysis of tenth of mW)**
3. ***A proper metallic structure deposited onto Pd surface (by special electrolysis current protocol)***

- **and many tests to optimize the effect…**

Dependence of Resistance by Temperature

It is known that the electric resistance of a metal or an alloy is approximately linearly dependent on the temperature; we used the following formula:

$$R(\vartheta) = R_0(1 + k_\theta \cdot \vartheta)$$

where the symbols:

R	**(Ω)**	**is the electric resistance of Pd wire or Pd-H alloy**
Ro	**(Ω)**	**is the wire resistance at 0° Celsius temperature**
θ	**(°C)**	**is the temperature in Celsius centigrade scale**
K_θ	**($°C^{-1}$)**	**is the thermal coefficient of resistance**

It is also known that the thermal coefficient K_θ depends on the H/Pd ratio, in fact, during the H loading of Pd, the wire resistance increases up to a peak value and the thermal coefficient decrease down to a minimum value, as shown by the known Baranowsky curve.

We report measurements of R/Ro and K_θ beyond the peak showing that the resistance decreases while the thermal coefficient increases as rapidly as H/Pd ratio increases.

Resistance Temperature coefficient: k_θ

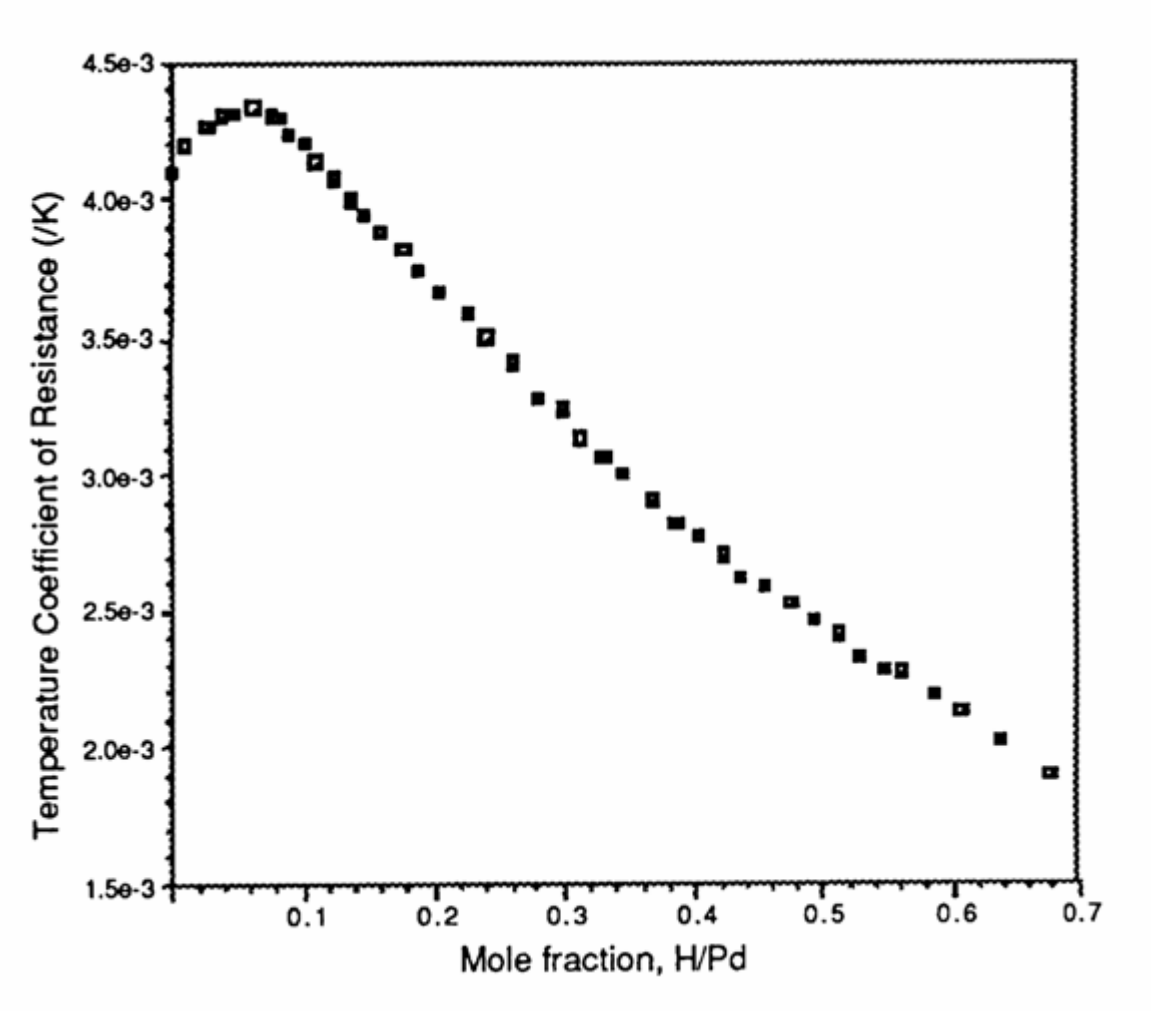
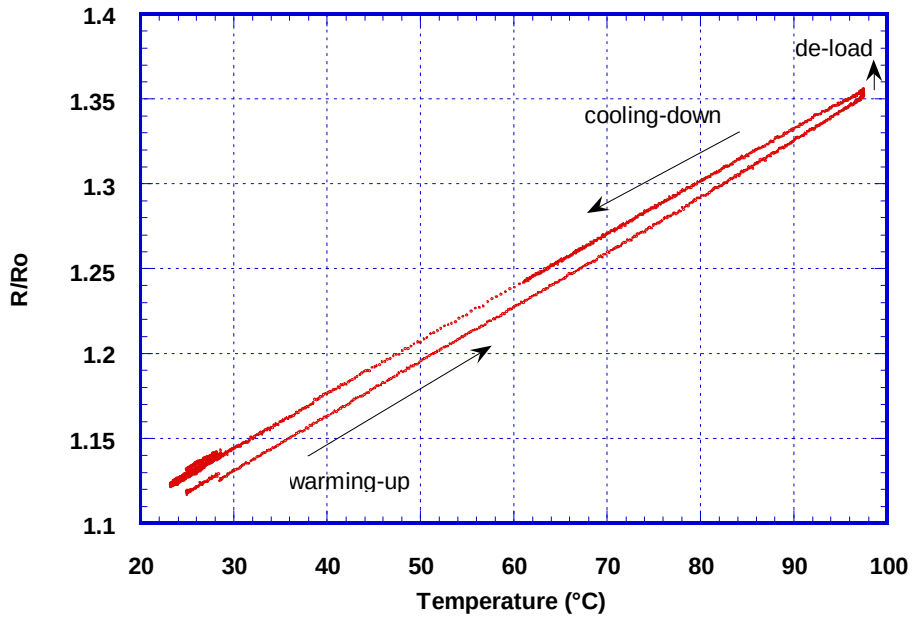


Fig. - ***H/Pd resistance temperature coefficient.***

According to the literature (Baranowsky et al.) this coefficient almost linearly decreases from $4.1 \cdot 10^{-3}$ K^{-1} (end of α phase) to $1.8 \cdot 10^{-3}$ K^{-1} (end of $\alpha+\beta$ phase) because H loading. At H/Pd >0.70 no data are allowable.

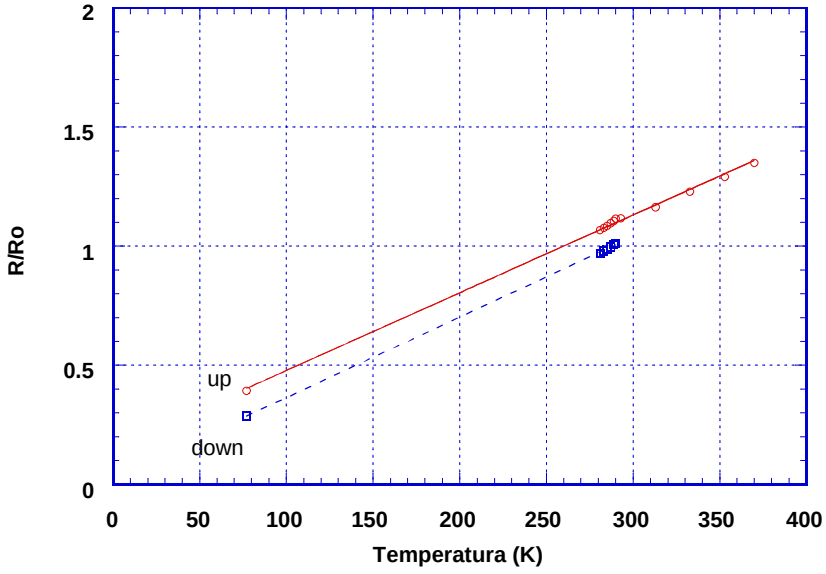
k_θ tests



(100°C)

Fig. – *Hg coated wire, high temperature measurements.*

After achieving R/Ro=1.1, the Pd surface has been coated with Hg (by $HgCl_2$ electrolysis) and a cycle of "high temperature test" was performed.Only a weak de-loading occurred at 100 °C (2 hours at ebullition state). In this experiment the temperature coefficient ($\alpha_{T\,w}$) was estimated to be $3.2 \cdot 10^{-3}\ °C^{-1}$.



(77 K)

Fig. – *Hg coated wire, test at very low temperatures.*

After achieving R/Ro=1.1, the Pd surface was coated with Hg and a cycle of low temperature test (up to liquid nitrogen) was performed. For sector "up" both high and low temperatures data are available: they are roughly on the same line. In the range 77÷300 K the temperature coefficient, α_T, was estimated to be $3.3 \div 3.4 \cdot 10^{-3}\ °C^{-1}$.

MAXIMUM overload at R/Ro= 1.12 ; K_θ=13±1

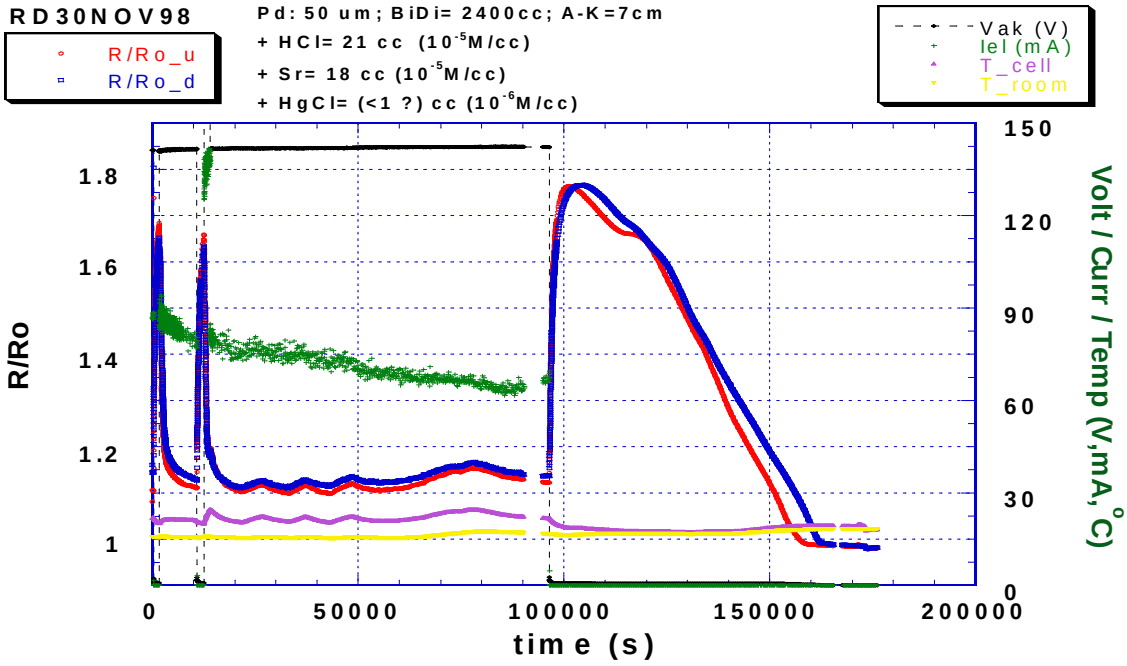


Fig.: - H/Pd Loading tests:
After "current cycles" R/Ro reaches 1.12, staying stable along time for 1 day within temperature fluctuations. A long time off-current complete deloading is shown at the end of test.

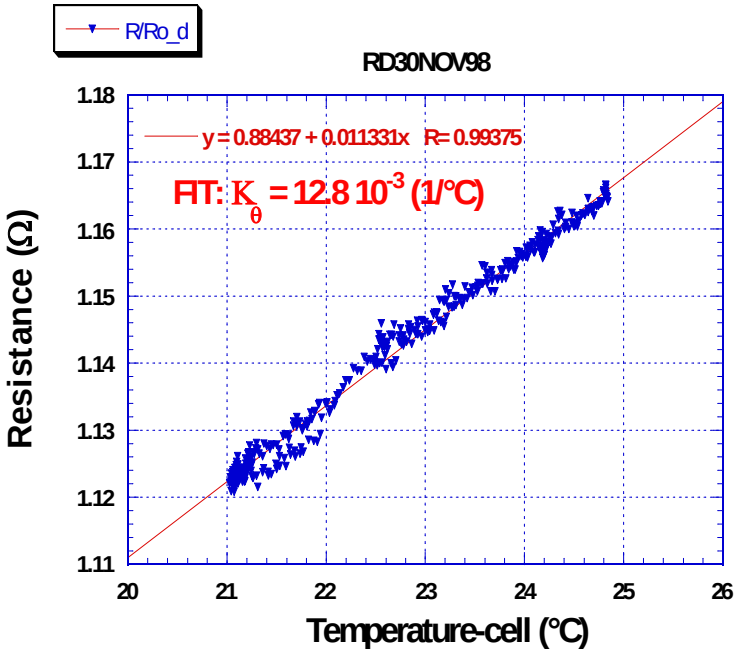


Fig.: - Thermal Coefficient data fit with the linear approach:
Fit is operated during a several cell temperature cycles; a good linear trend is shown.

Overload at R/Ro= 1.2 ; K_θ=10±1

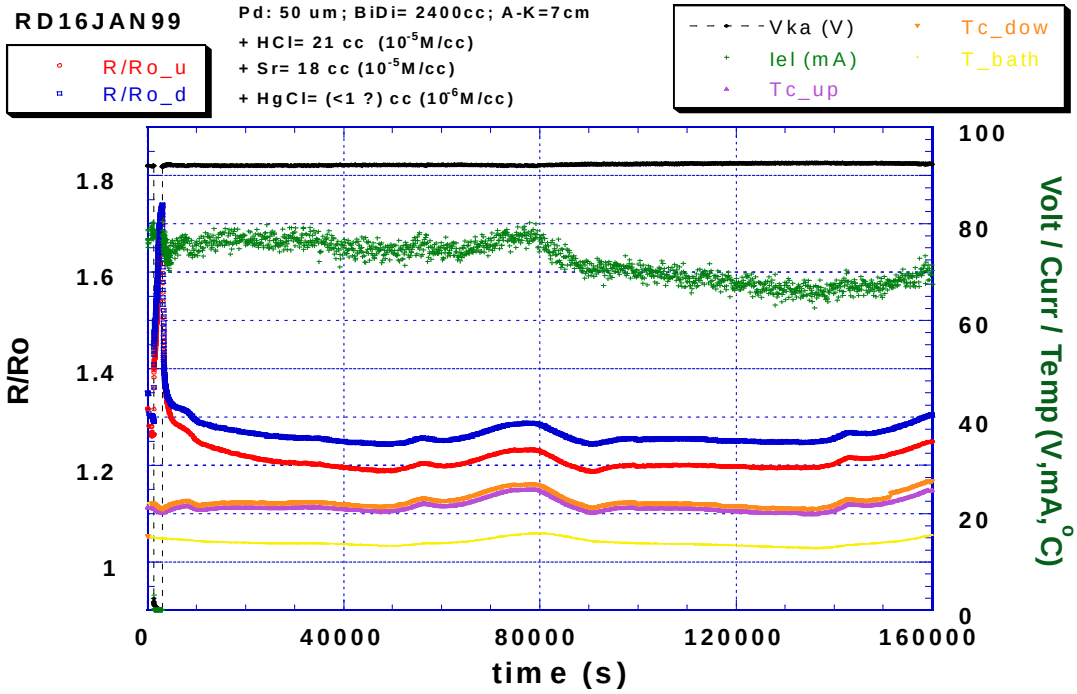
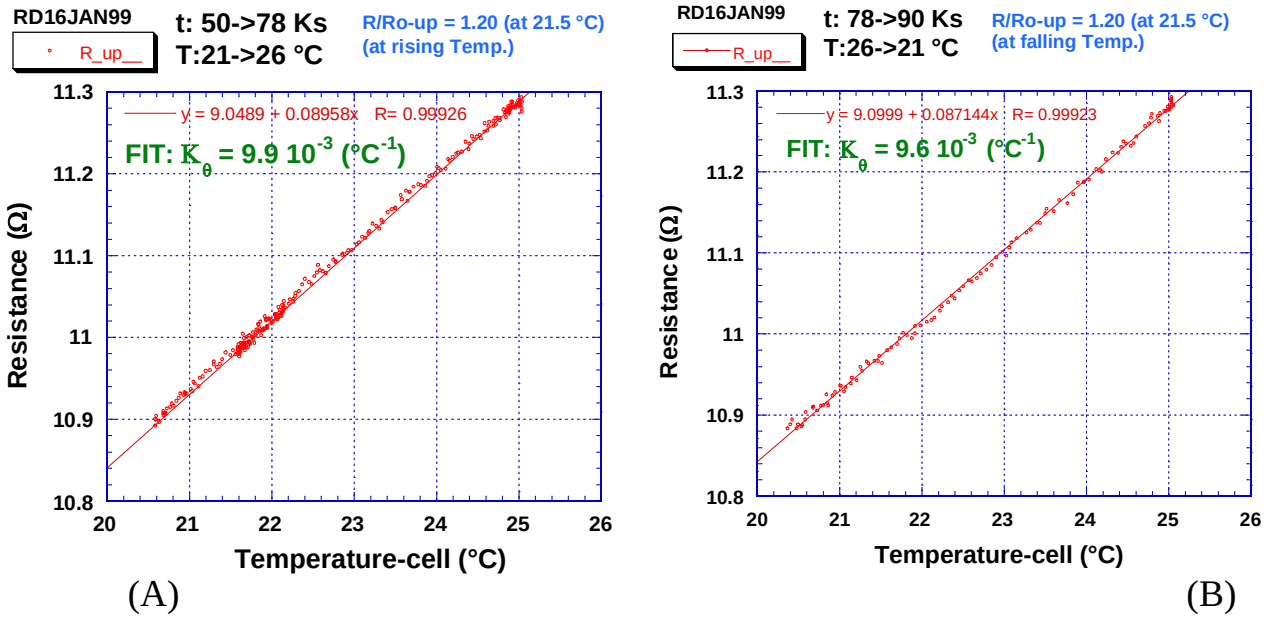


Fig.: - H/Pd Loading test:
After "current cycles" R/Ro reaches 1.12, staying stable for about 2 days within temperature fluctuations (from 50->90 Ks time we have a complete temp. Cycle)



(A) (B)

Fig. - Thermal Coefficient data fit:
A) Fit is operated at the rising cell temperature for several hours (day-time);
B) Fit is operated at the falling cell temperature (night-time) returning to the initial value.

Loading peak R/Ro= 1.75 ; K_θ=2.8

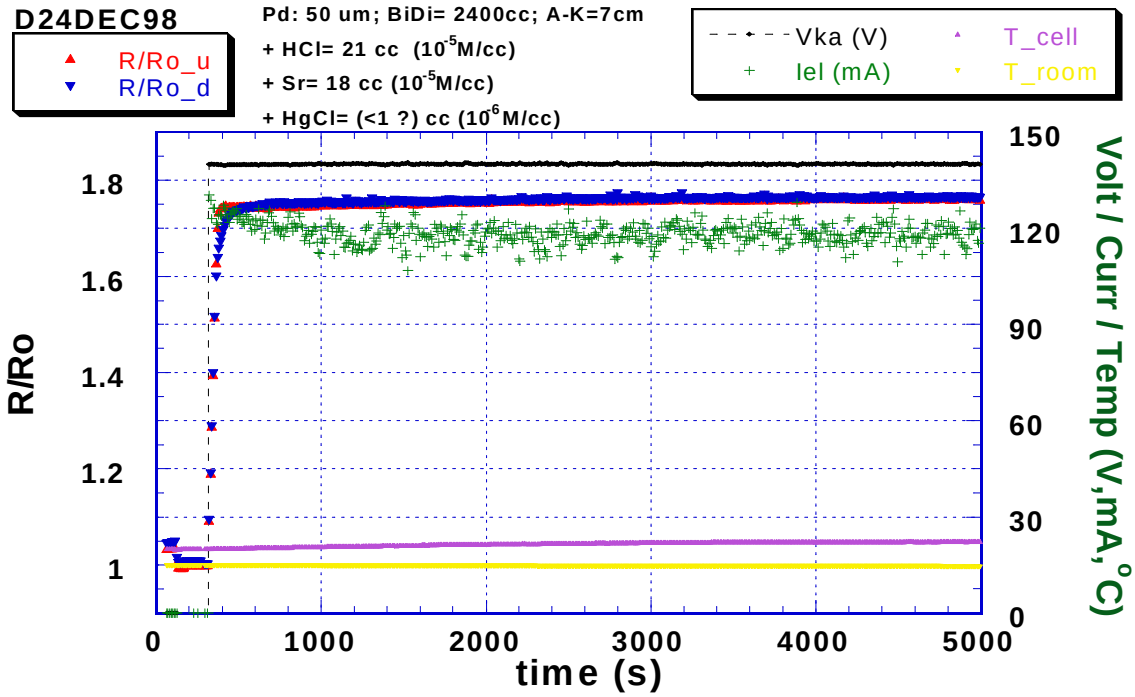


Fig.: - H/Pd Loading test up to the peak:
After a fast loading "start up" (in a few minutes), R/Ro remains at the peak value for about 2 days; day/night temperature cycles are recorded by following wire resistance variation.

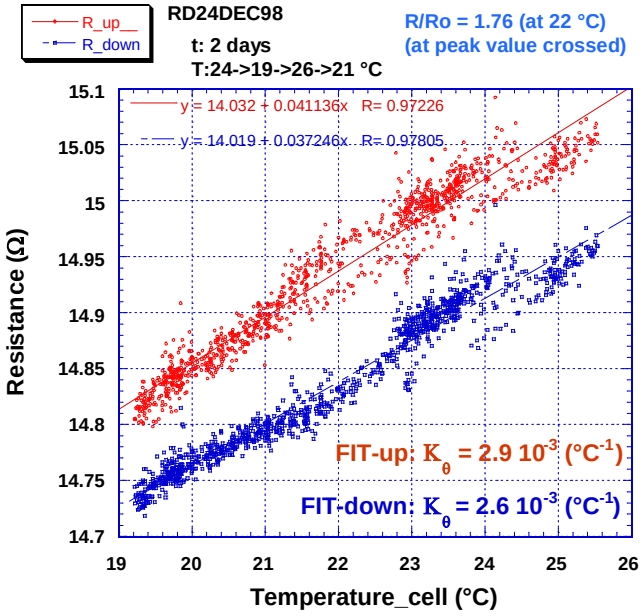


Fig. - Thermal Coefficient data fits for up/down wire sectors:
Fits are operated at the rising/falling cell temperature for 2 days (day-night thermal cycles).

Non-Loaded Pd; R/Ro= 1.0 ; K_θ=4.1

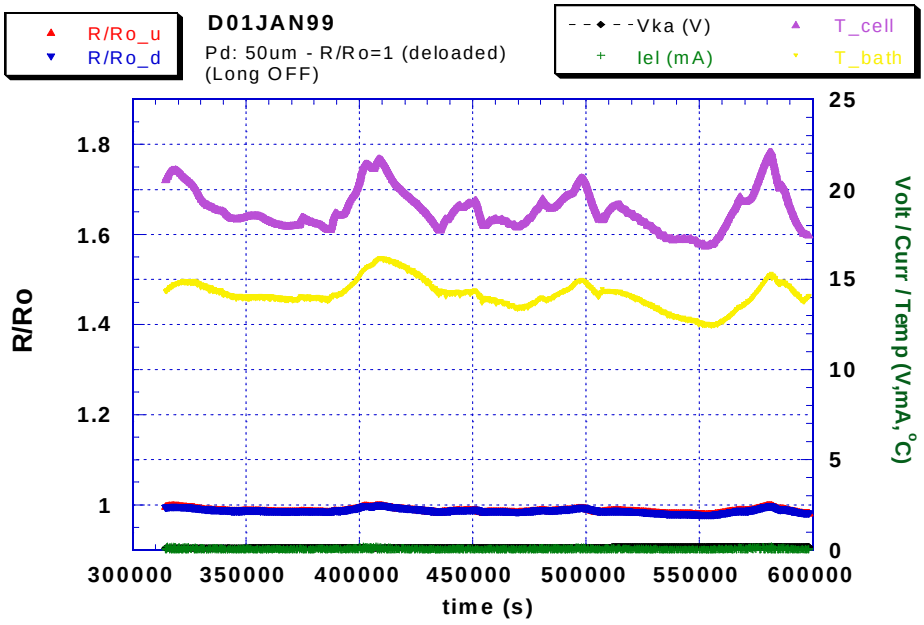


Fig.: - H/Pd=0 Loading test:
Unloaded Pd (no charging up) for about 3 days; day/night temperature cycles are recorded by following wire Resistance variation around R/Ro=1.

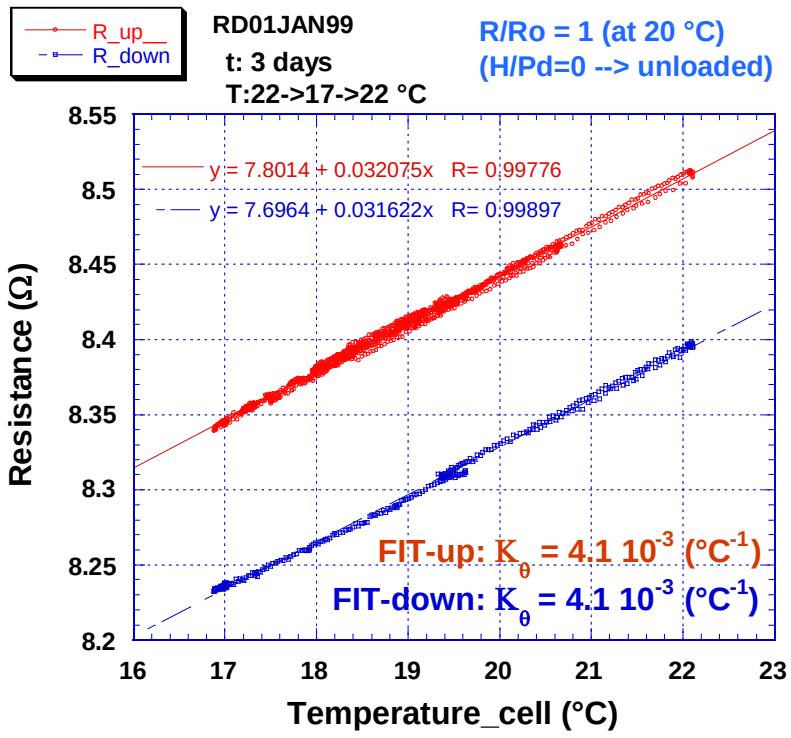


Fig. - Thermal Coefficient data fits for up/down wire sectors:
Fits are operated at the rising/falling cell temperature for 3 days (day-night thermal cycles). This is in agreement to the thermal coeficient value of pure Pd reported in literature.

K_θ RESULTS:

H/Pd	(up) R/Ro ± 0.1	(up) K_θ (10^{-3}/m°C)	(down) R/Ro ± 0.1	(down) K_θ (10^{-3}/m°C)	Temp (°C)	Remarks (date run)
0.00	1.0	4.1 ± 0.1	1.0	4.1 ± 0.1	20	*(01-JAN-99) Pd fully deloaded*
0.81	1.75	2.8 ± 0.3	1.75	2.6 ± 0.3	20	*(24-DEC-99) R/Ro ≈ peak*
0.89÷0.91	1.58	7.2 ± 1	1.61	6.7 ± 0.5	20	*(26-MAY-99)*
0.93	1.52	≈ 7 ± 1.5	1.52	≈ 7 ± 1.5	20	*(13-NOV-98)*
0.95÷0.96	1.44	≅ 8.3 ± 1	1.46	≅ 8.4 ± 1	20	*(11-NOV-98)*
1.02÷1.03	1.19	9.9 ± 0.5	1.24	9.6 ± 0.5	20	*(16-JAN-99)*
1.03÷1.04	1.18	10.7 ± 0.5	1.21	10.6 ± 0.5	20	*(16-NOV-98)*
1.05÷1.06	1.10	≅ 13 ± 1.5	1.13	12.8 ± 0.5	20	*(30-NOV-98) Maximum Load*

Tab.: - K_θ results from tests:

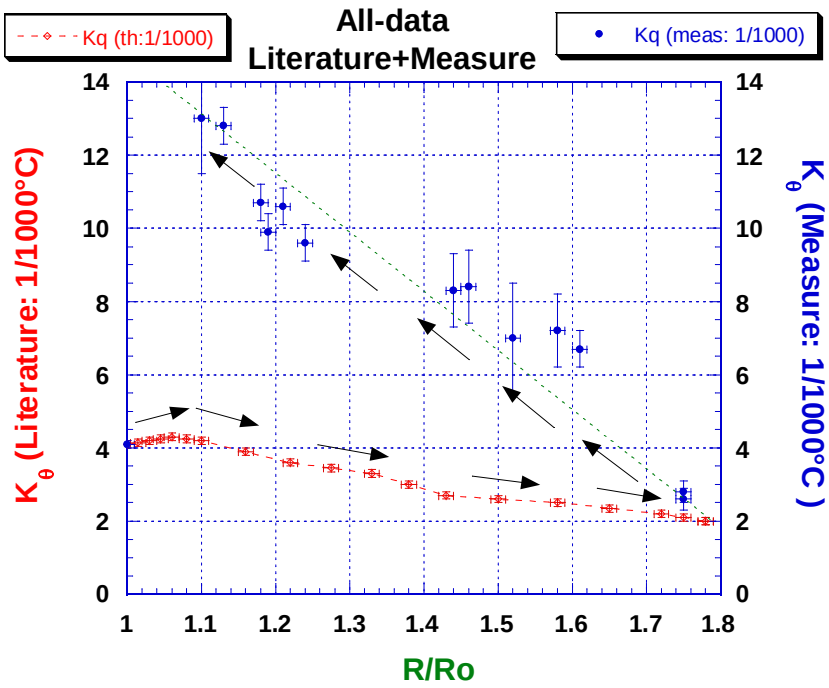
In this table we report several tests performed at stable loading conditions:

a) The first value is in agreement with expected value (K_θ = 4.1).

b) At the R/Ro peak value the thermal coefficient is a little higher (30%) than that one reported in literature (K_θ = 2.0).

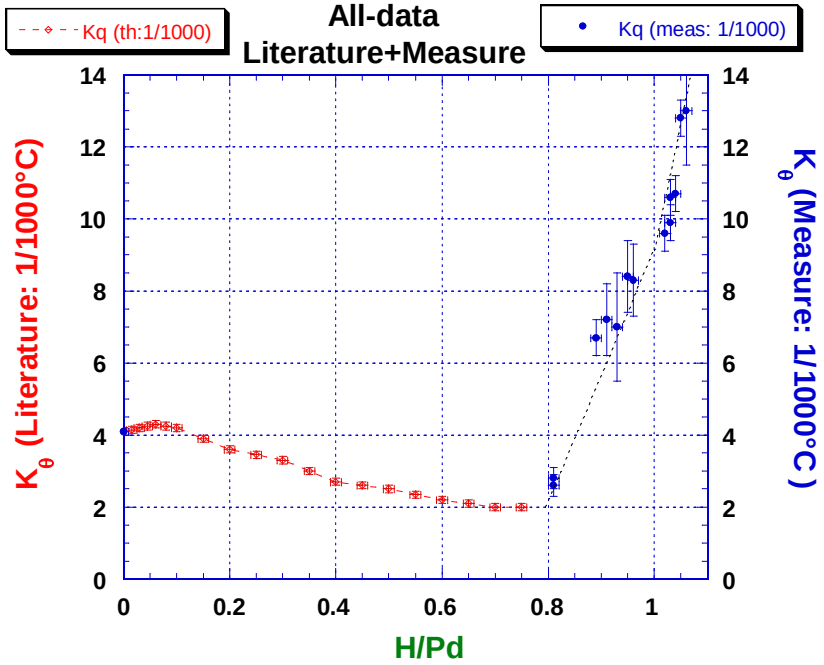
c) All values, beyond the R/Ro peak, show a rapidly increase of thermal coefficient.

K_θ PLOTS



- **Fig.: K_θ vs R/Ro:**

  Known literature data (red points below the R/Ro peak) are shown. New additional experimental data (blue points beyond the R/Ro peak) are reported, showing the progressive increase of $\mathbf{K_\theta}$ as the H/Pd value grows up (overloading).*; the arrows show the trend of K_θ as the loading ratio grows up.*



- **Fig.: K_θ vs H/Pd:**

  Known literature data (red points) are shown. New additional experimental data (blue points) are reported showing a $\mathbf{K_\theta}$ increasing at higher H/Pd values (overloading).

K_θ CONCLUSIONs

--- H/Pd over-loading → K_θ increase!

1) Phase α (from literature):

During H/Pd loading from 0 to 0.06, K_θ increases from 4.1 to 4.4 mK^{-1} showing the α-phase growth.

2) Phase α+β (from literature):

During H/Pd loading from 0.06 to 0.75 (R/Ro peak), K_θ decreases from 4.4 to 1.8 mK^{-1} showing the α+β phase growth.

3) Phase β or β+γ (experimental data):

During H/Pd loading from 0.75 to 1.10, K_θ rapidly increases from 2 up to 13 mK^{-1}indicating a possible β+γ phase growth.

→ ***QUESTION*:**

- **Is this a confirmation of the existance of a new phase (γ) ?…**