ISCMNS-8 at Catania (13-18 Oct 2007)

a Poster
about

"A Review of Experimental studies about Hydrogen over-loading within Palladium wires (H/Pd ≥ 1) "

by

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Introduction

Since March 1989, when M.Fleishmann and S.Pons claimed to produce a entalpy 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

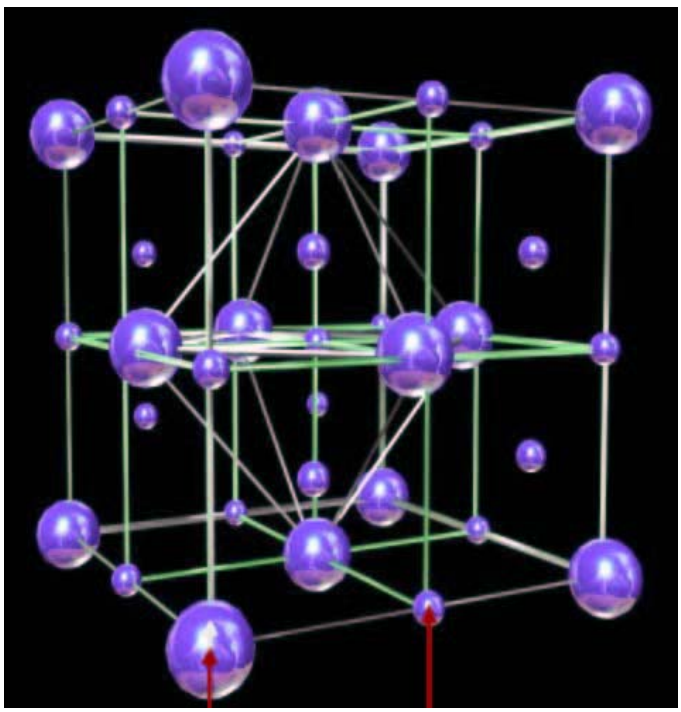
In order to measure H(D)/Pd loading ratio, we use the H(D)-Pd resistance curve, so that, to have accurate measurements we need to solve the following issues:-

A- high Pd resistance → long and thin wire;
B- low influence of electrolyte on Pd resistance measurement → very diluted solution and distant electrodes;
C- no uncontrolled metallic deposition on cathode → acidic solution (instead of basic) using very pure water;
D- addition of a very low amount of known elements into the solution and production of a quite controlled Pd surface deposition layer.

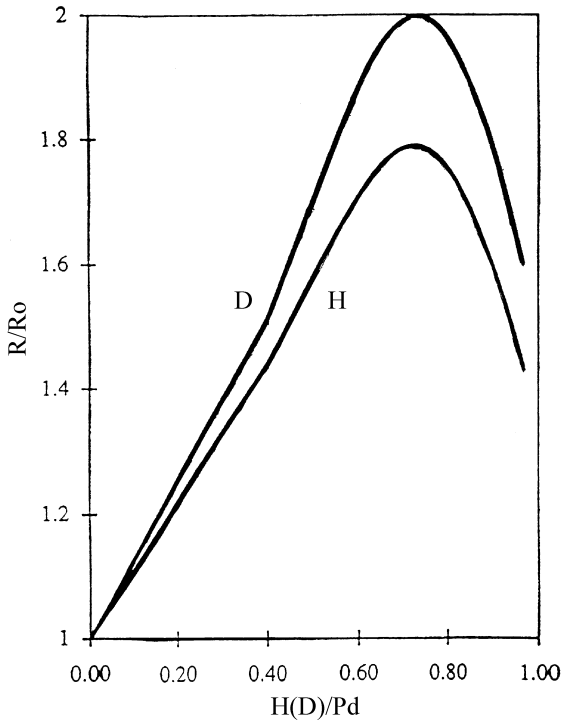
The D/Pd threshold

- **The Pd lattice:**

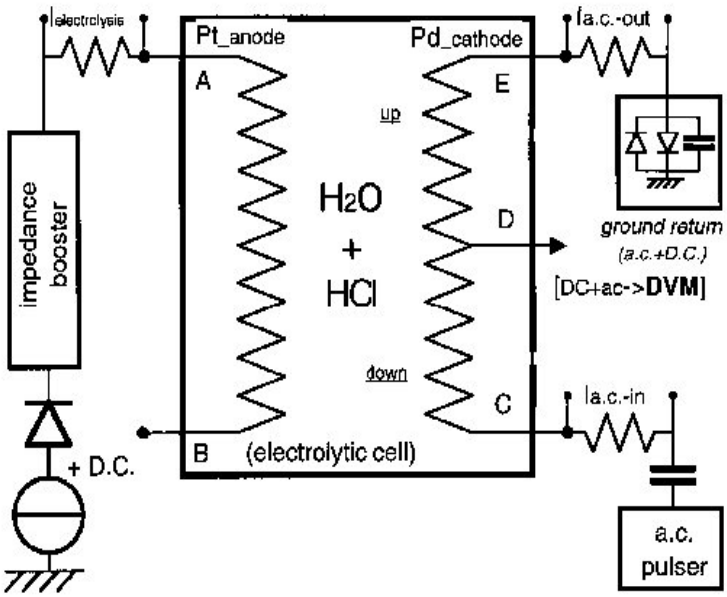
- **The Pd lattice is fcc (face centred cubic)**
- **H or D atoms are formerly located into the lattice centre (α–phase), further interstitial sites of lattice are occupied (α + β phase); finally when the whole of Pd lattice available sites are saturated, we achieve H/Pd or D/Pd=1 (named as γ –phase)**
- **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*: alkaline elements addition (Ca, Sr, Li, K, Na) 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***
- **Alkali-Hg *deposition* on Pd surface is supposed to be formed *(width 20-> 200 nm)***

OLD TESTS:

Ca

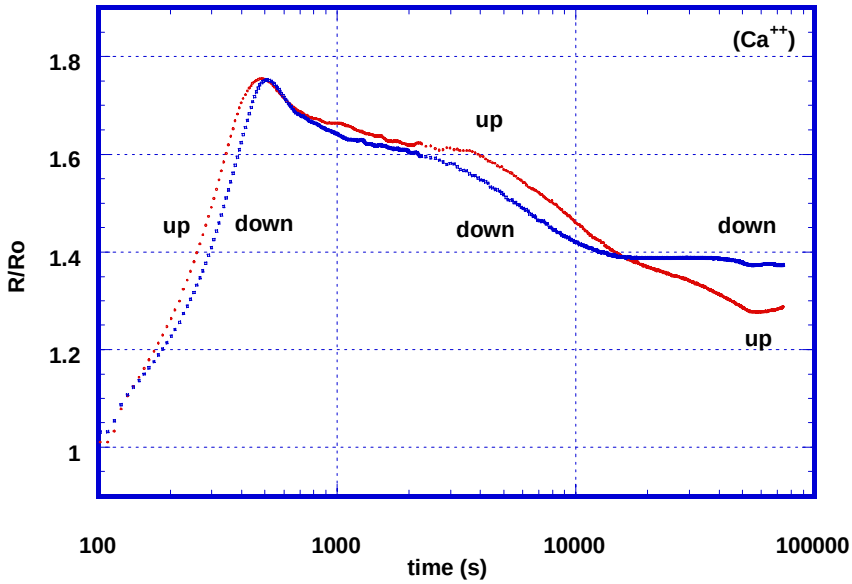


Fig. – *Calcium loading trend.*
Loading trend curve (R/Ro vs log time) occurred when Ca ions ($70*10^{-6}$ M) have been added to the electrolyte; in about 300s resistivity peak was achieved. A shoulder lasting for about a hour after the peak is visible; the highest loading (R/Ro=1.28 for "up" and 1.38 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

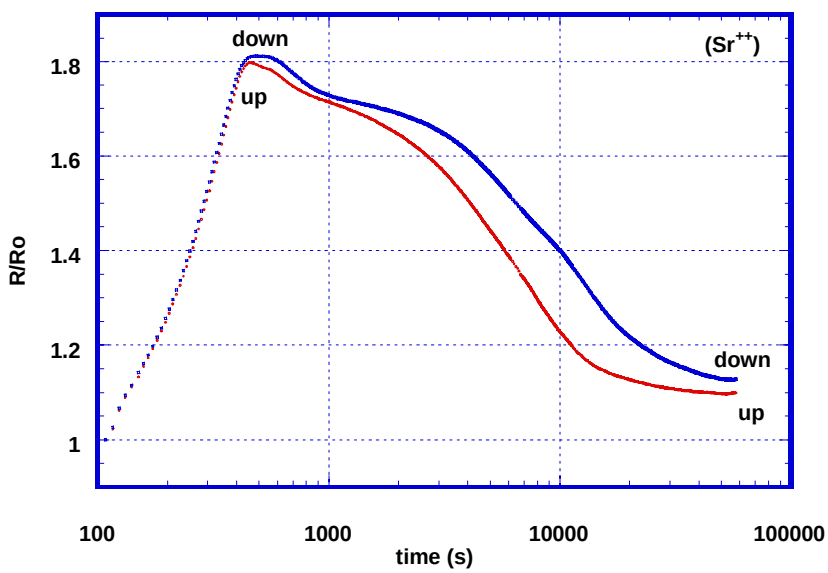


Fig. – *Strontium loading trend.*
Loading trend curve (R/Ro vs log time) occurred when Sr ions ($35*10^{-6}$ M) have been added to the electrolyte; in about 300s resistivity peak was achieved. The shoulder lasts about half hour; loading higher than Ca test (R/Ro=1.13 for "up" and 1.15 for "down" at 27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

Sr: OFF-deload

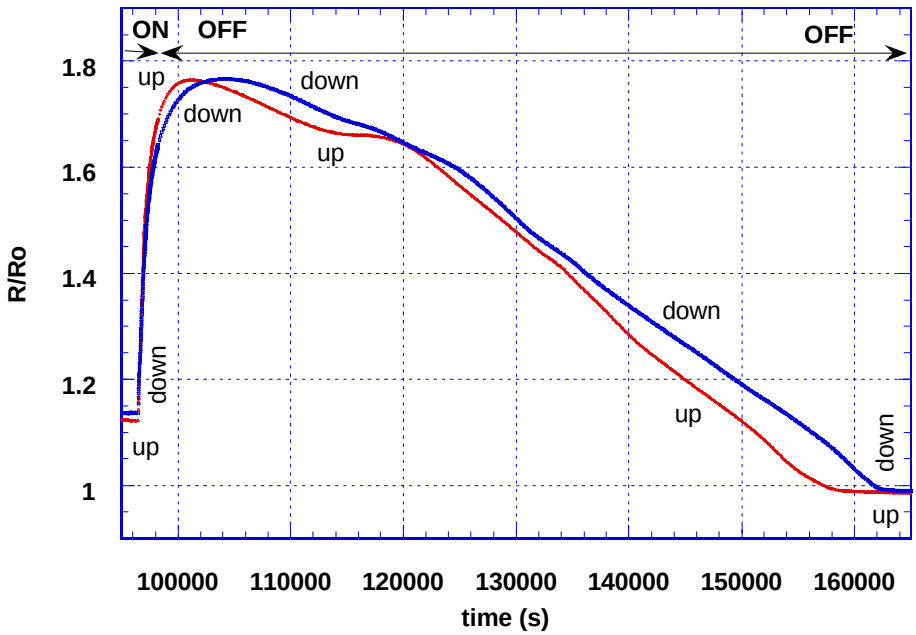


Fig. – *Deloading trend.*
The plot shows Hydrogen deloading versus time. Electrolysis current has been switch off ("OFF" condition) after "ON" condition (R/Ro=1.13 at 23 °C) and in about one hour loading peak was achieved (R/Ro=1.77 at 23 °C). A visible deloading shoulder lasts, about half hour, at R/Ro=1.65;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

Sr: OFF/ON cycle

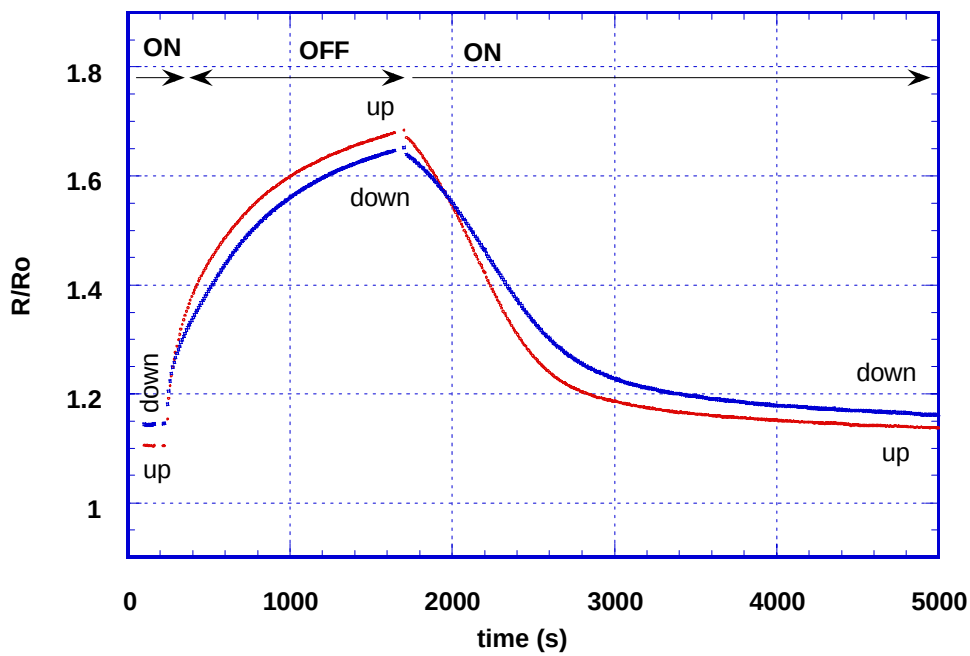
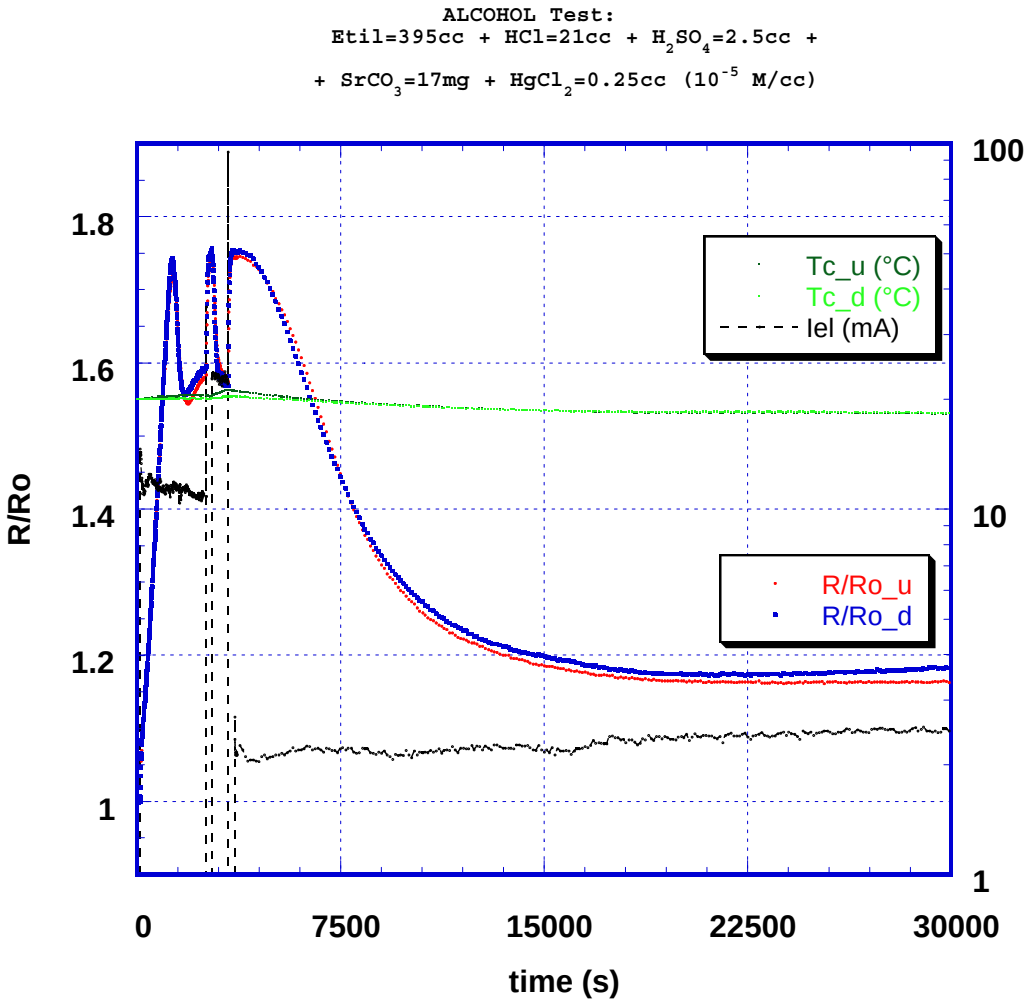


Fig. – *Fast re-loading test.*
Typical test of OFF/ON current cycle: starting from a high loading condition (R/Ro=1.10 at 22 °C), after about half hour of de-loading (near the resistivity peak) because current disconnected ("OFF"), current was switched on ("ON") again. In this condition, reloading is 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.

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.

NEW TESTS:

- Experimental tests about Pd-H loading with alkaline elements

(producing Pd-surface deposition):

electrolite ***(NO-Hg)***	**CO_3**	**SO_4**
H_2O + HCl (50 µmol) *Loading at R/Ro-peak: (R/Ro=1.75, H/Pd=0.67)*	----	---
+ Na	Concentration: 20 mg Procedure: L/H current Result: **R/Ro=1.6**, H/Pd=0.9	----
+ Li	Concentration: 200 µmol Procedure: Low current Result: **R/Ro=1.52**, H/Pd=0.92	Concentration: 30 µmol Procedure: L/H current Result: **R/Ro=1.40,** H/Pd=0.94
+ K	Concentration: 25 mg Procedure: Low current Result: **R/Ro=1.50**, H/Pd=0.92	Concentration: 10 mg Procedure: L/H/L Result: **R/Ro=1.43**, H/Pd=0.94
+ Sr	Concentration: powder (saturation) Procedure: L/H/L current Result: **R/Ro=1.30**, H/Pd=0.96	Concentration: powder (saturation) Procedure: L/H current Result: **R/Ro=1.20**, H/Pd=0.97
+ Ca	Concentration: 70 µmol Procedure: Middle current Result: **R/Ro=1.30**, H/Pd=0.96	----

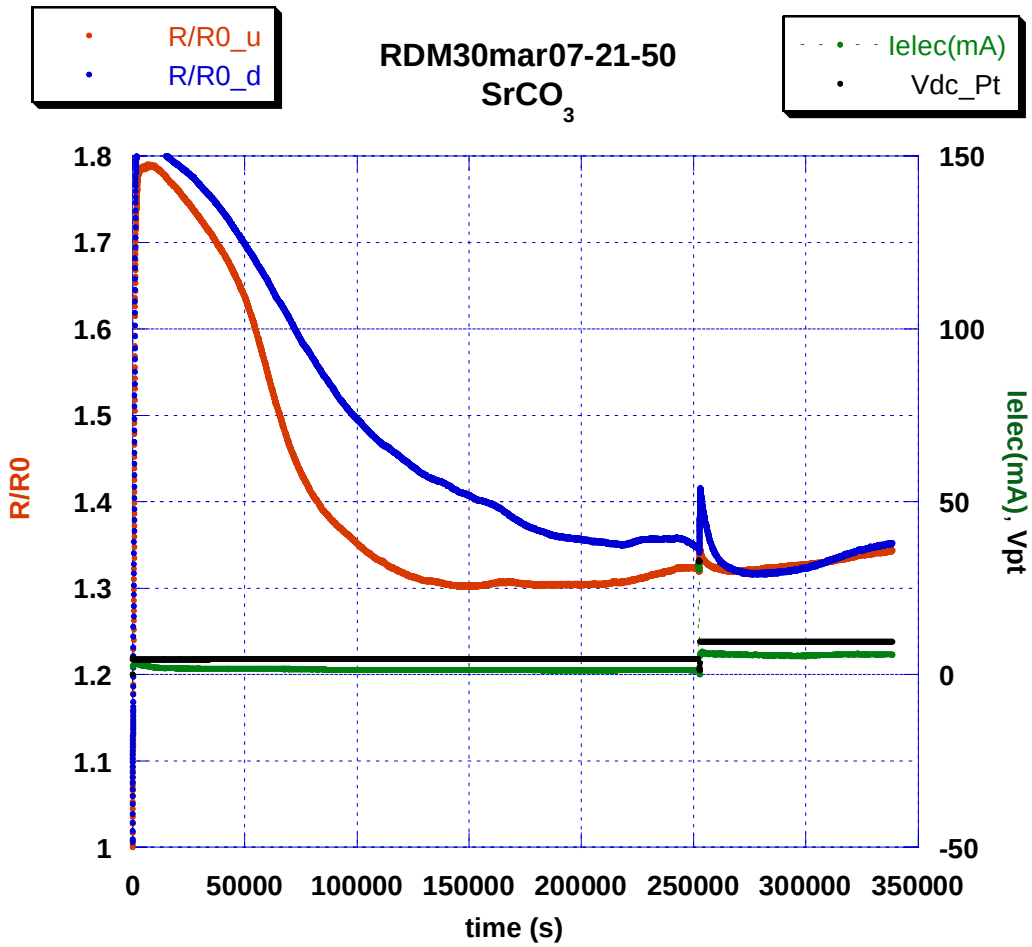


Fig. – *Sr-carbonate loading trend.*
Loading trend curve (R/Ro vs time) occurred when Sr-carbonate ions were deposed onto Pd-surface.

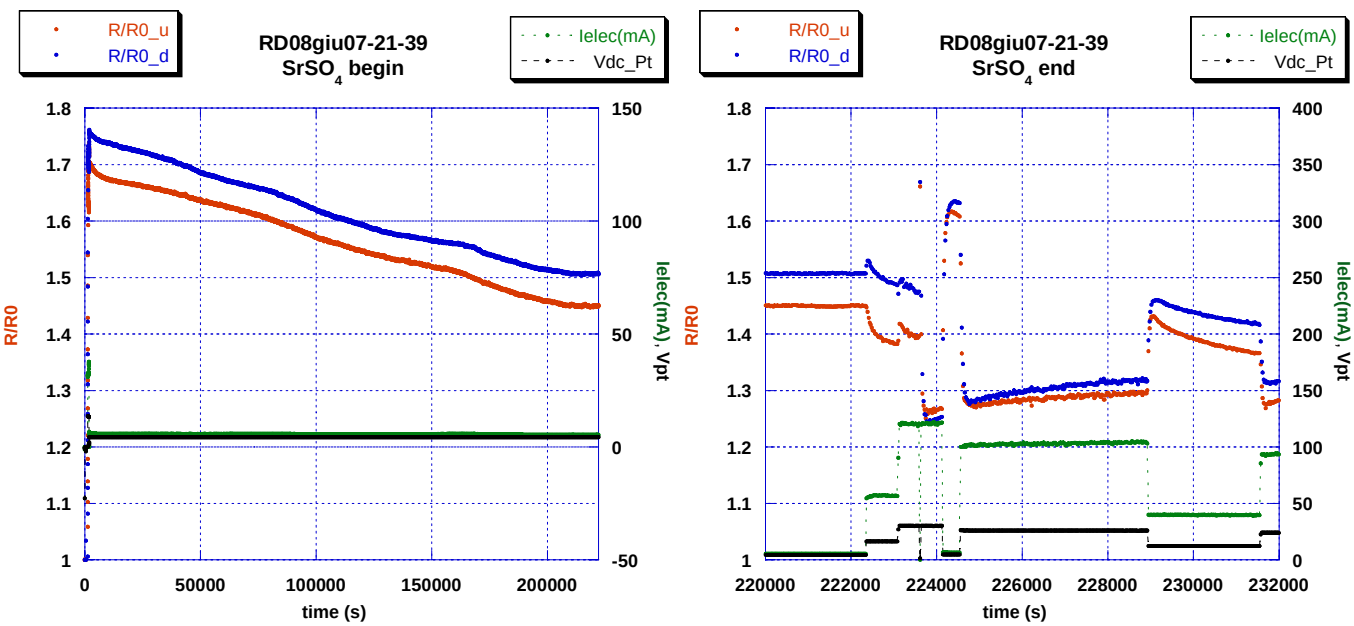


Fig. – *Sr-sulfate loading trend.*
Loading trend curve (R/Ro vs time) occurred when Sr-sulfate ions were deposed onto Pd-surface.
A) Initial loading at low current; B) Details of L/H/OFF/H procedure.

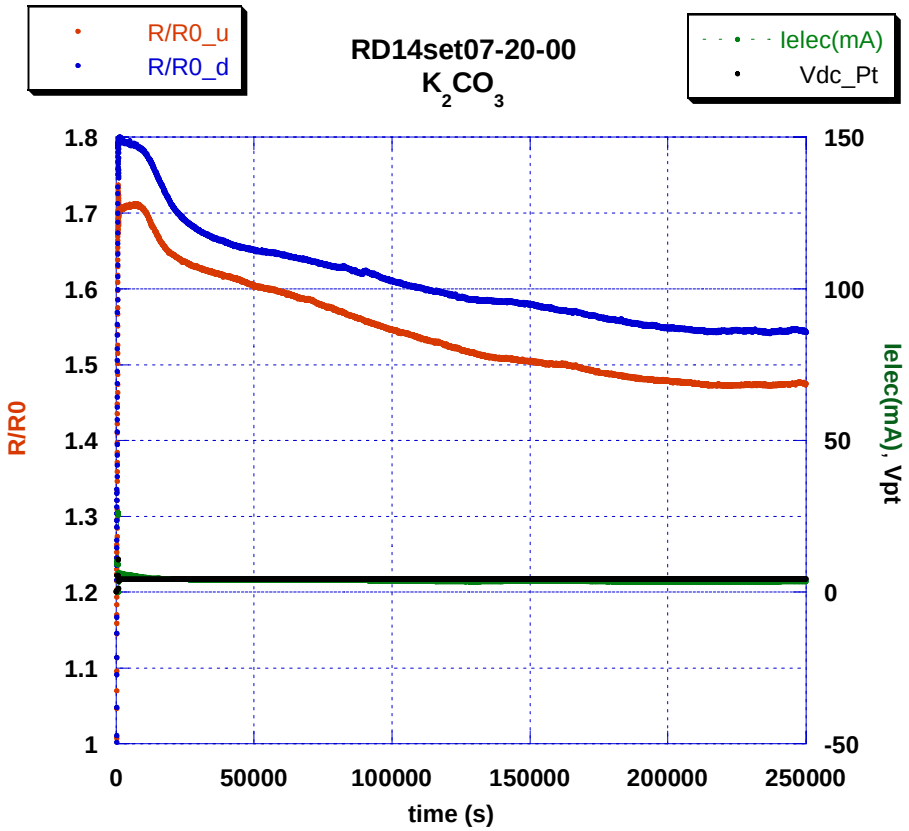


Fig. – *K-carbonate loading trend.*
Loading trend curve (R/Ro vs time) occurred when K-carbonate ions were deposed onto Pd-surface.

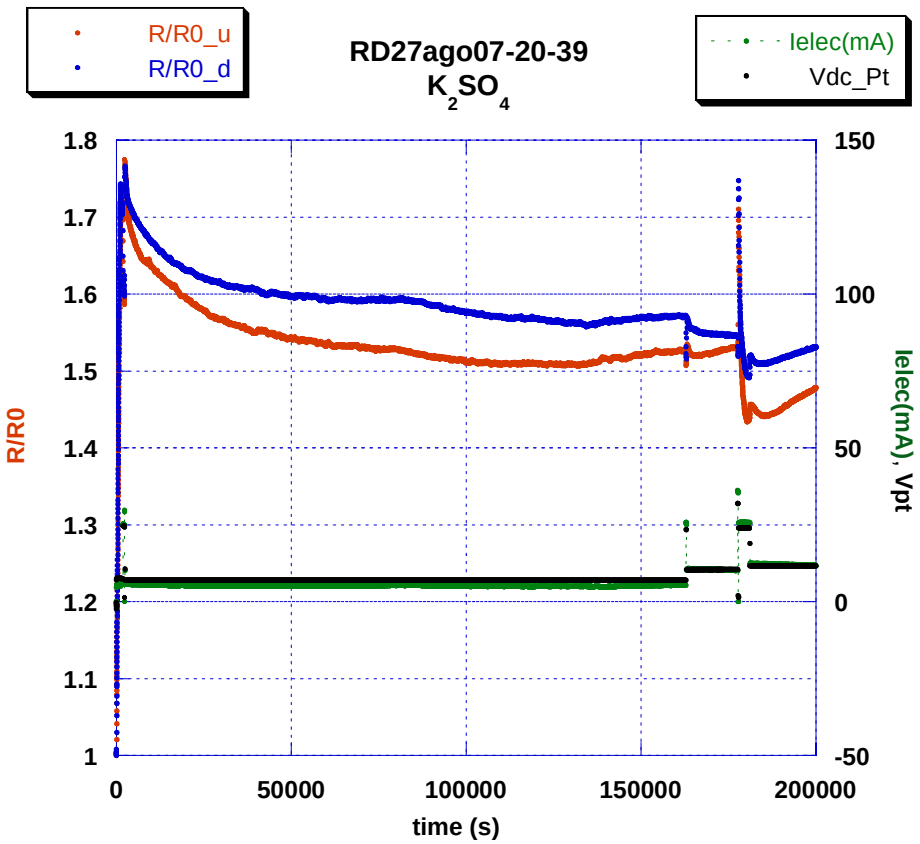


Fig. – *K-sulfate loading trend.*
Loading trend curve (R/Ro vs time) occurred when K-sulfate ions were deposed onto Pd-surface.

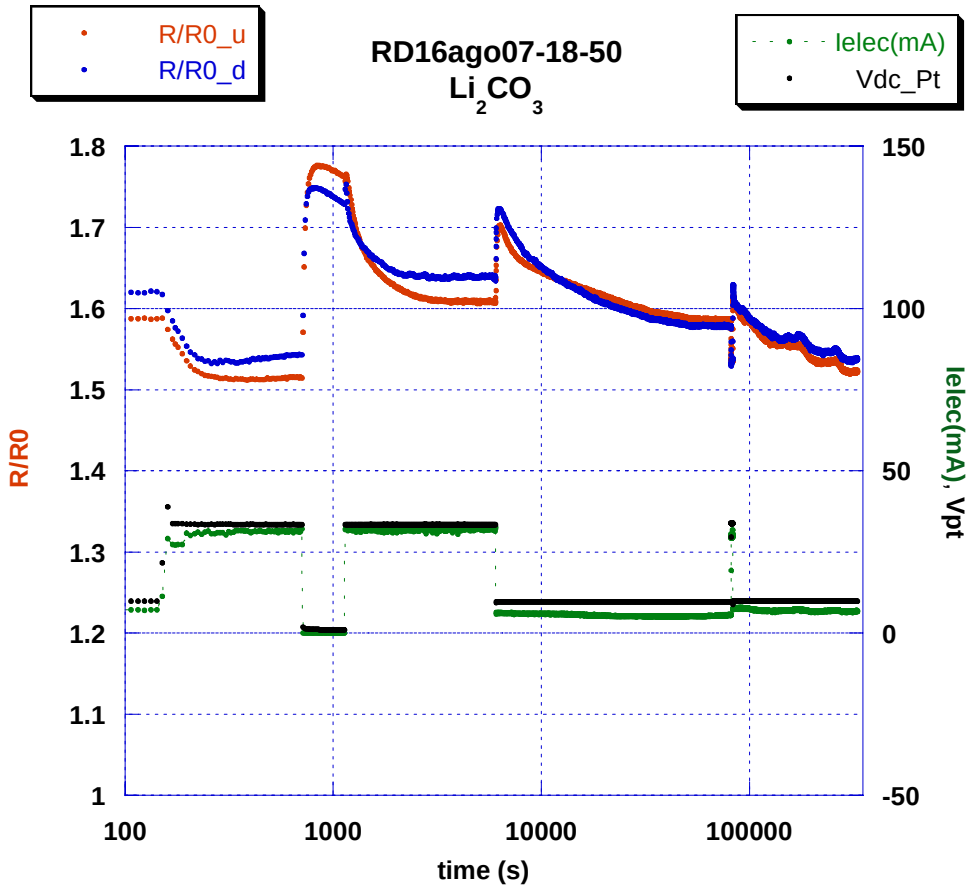


Fig. – *Li-carbonate loading trend.*
Loading trend curve (R/Ro vs time) occurred when Li-carbonate ions were deposed onto Pd-surface.

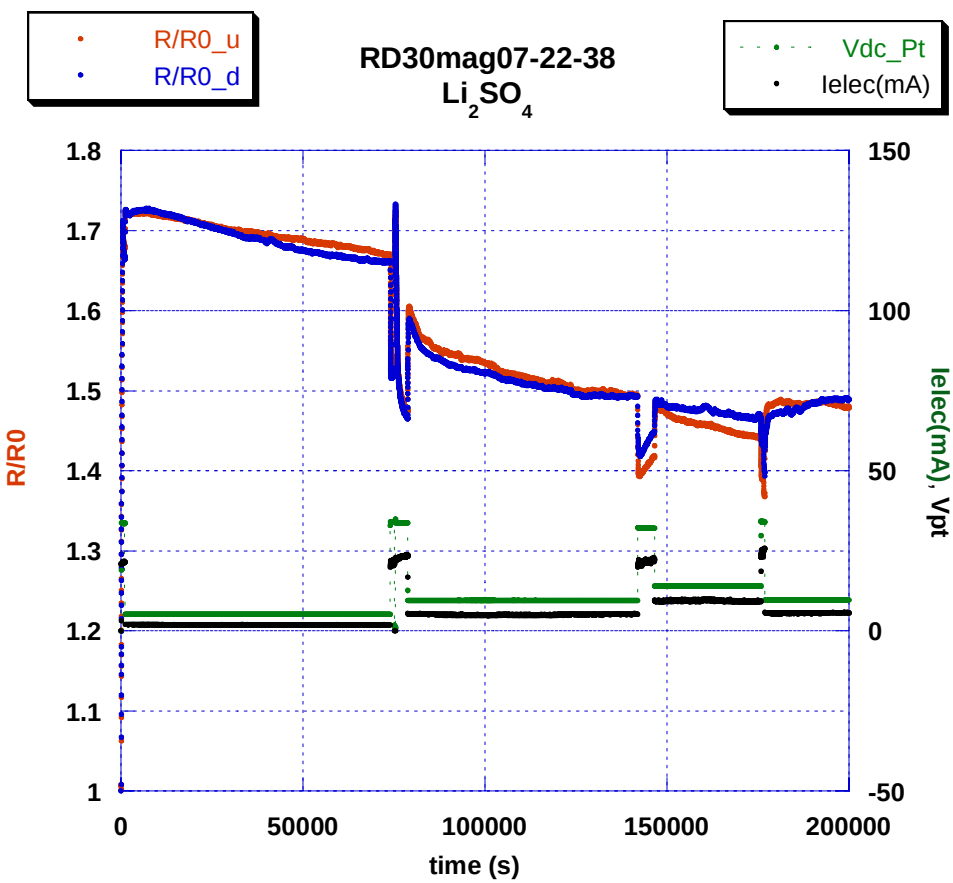


Fig. – *Li-sulfate loading trend.*
Loading trend curve (R/Ro vs time) occurred when Li-sulfate ions were deposed onto Pd-surface.

+ Hg + Sr(Cl2 or CO3)	+ Hg-oxide +Sr *(surface treatment)*
Concentration: powder (saturation) Procedure: Very low current Result: **R/Ro=1.25**, H/Pd=**0.97**	Concentration: very low (+**pre-deposition**) Procedure: HIGH voltage/current Result: **R/Ro=1.15**, H/Pd=**0.99**

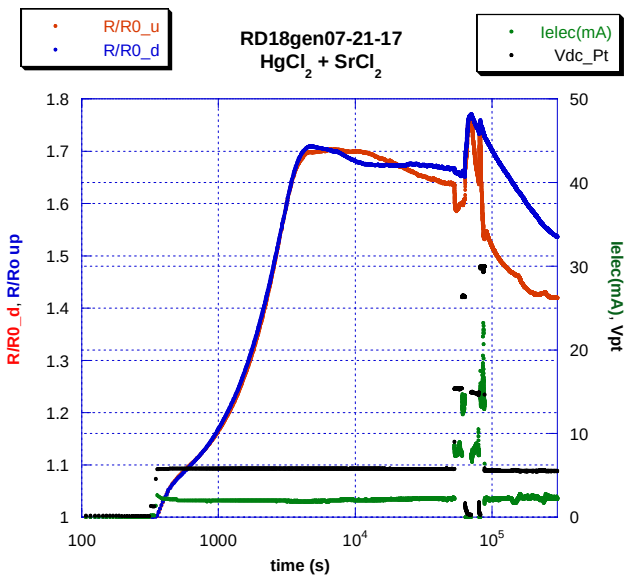


Fig. – *Hg+Sr, loading trend.*
with Hg+Sr ions deposed onto Pd-surface.

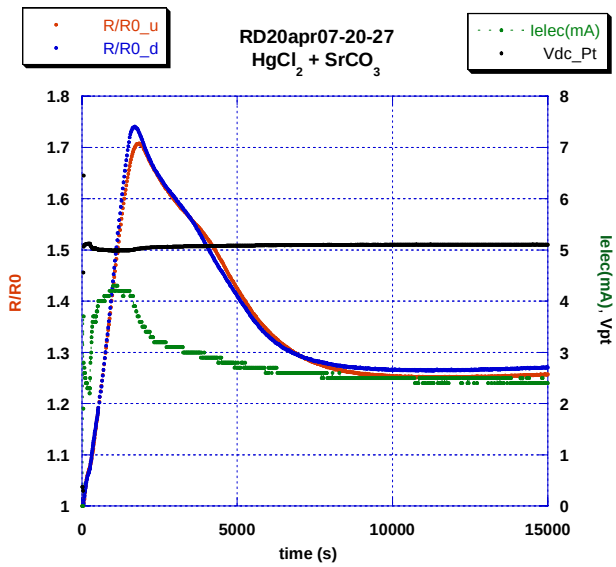


Fig. – *Hg-oxide+Sr, loading trend.*
with Hg-oxide+Sr ions deposed onto Pd-surface.

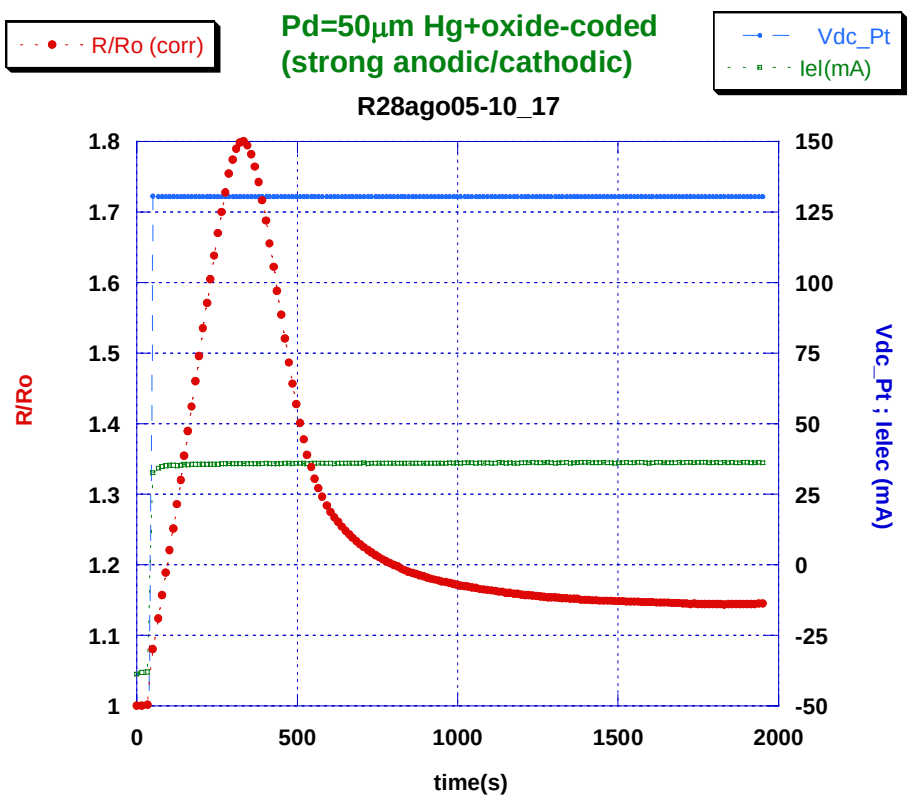


Fig. – *Hg-oxide+surface treatment, loading trend.*
Loading trend curve (R/Ro vs time) occurred when "opportune elements" **were pre-deposed** onto Pd-surface.

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 and low amount of some alkaline elements (+Sr, +Hg) (at very low electrolysis power ≅50 mW;**

2) **A systematic study about addition of carbonate or sulphate of alkaline elements occurring during electrolysis has stated that the over-loading time and magnitude are depending by the alkaline compounds and deposition procedure (Low/High-OFF/ON current).**

3) **Addition of Hg ions improves the over-loading (increasing the over-voltage on the Pd-deposition surface) reducing the loading time and minimizing the electrolysis current.**

H/Pd CONCLUSIONs

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

1. **Alkaline (Li, Na, K, Sr, Ca and maybe others…) elements (in carbonate or sulfate compounds) addition to acid solution**
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…**

→ BUT a new promising "Celani-procedure" with a surface pre-treatment is under test…