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[1]

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Abstract
A peculiar electrolytic protocol has been determinate to achieve very high Hydrogen loading into a thin Palladium wire (H/Pd= 1): electrolysis (with high/low current cycles) has been performed with a very diluted acidic solution (H_2O+HCl) adding a very small quantity of alkaline/earth or heavy metal elements (Sr and/or Hg). A systematic study has been performed with these elements (added to the electrolyte) in order to have a controlled loading dynamics. The aim and the result of this study has been to reproduce H/Pd $\geq$ 1 loading value, just using very low electrolysis voltage and current (7V, 5mA).

Other two independent Research Groups have tested this protocol reproducing similar results.

INTRODUCTION

Since March 1989, after M. Fleischmann and S. Pons claimed to produce a big amount of hentalpy in excess from an electrolytic cell of $D_2O+LiOD$ (0.1 N) using a Pd cathode absorbing high concentration of Deuterium [ref. 1], the main critical point was to achieve high D/Pd values (around 1:1). *Many researchers spent a lot of efforts to reach to this goal but the difficulties were much more than expected and the high absorption reproducibility very poor.*

Our group from many years has studied the Pd cathode over-loading achieving at $D/Pd \cong 1$ with Pd tick plates using a own high voltage, short time, electrolytic pulsed technique [ref. 2]. But working at this very unstable condition, the heat in excess reproducibility was very poor. So that we have substituted bulk Pd plate (very difficult to over-load in homogeneous way) to long thin wires and, instead of high frequency pulse electrolysis (very difficult to study loading parameters, because high electric noise), we used direct current electrolysis.

Many authors have studied different properties of the Pd as function of the loading. In particular, the resistance ratio R/R_0, where R is the actual resistance of the Pd wire and R_0 its hydrogen free resistance, has been analysed [ref. 3, 4]. In order to determinate H(D)/Pd loading value, we can refer to H(D)-Pd resistance curve (Fig. 1) [ref. 5], so that, to have accurate measurements we need to solve these questions:

a) high Pd resistance → long and thin wire;
b) low influence of electrolyte on Pd resistance measurement → very diluted solution and/or distant electrodes;
c) no uncontrolled metallic deposition on cathode → acidic solution (instead of basic) using very pure solvent water;
d) addition of a very low amount of known elements into the solution and production of a quite controlled Pd surface deposition layer.
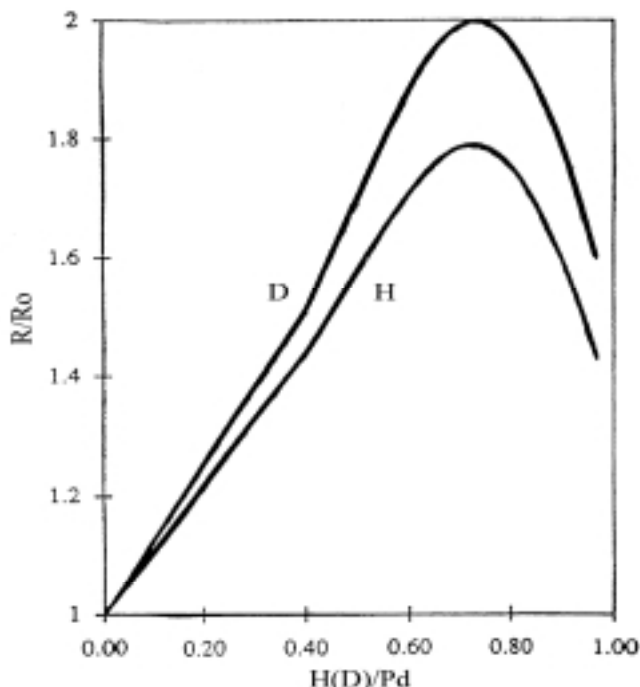
Figure 1 – Normalised Palladium resistance versus Hydrogen (Deuterium) molar fraction of Pd. Peak value is: H/Pd = 0.75, R/Ro=1.78 (Hydrogen) and D/Pd=0.75, R/Ro=2.0 (Deuterium). Maximum known loading is H(D)/Pd = 0.95 at R/Ro=1.4 (1.6).

In order to obtain large overvoltage, high anode-cathode voltage is required. On the other hand, to avoid the molecular hydrogen formation at the palladium surface, low density current is necessary.

For these reasons, in this work, we have used a high resistivity electrolyte made of a diluted acidic solution adding small controlled amounts of alkaline metals. During the electrolytic process, the hydrogen loading has been evaluated by mean of resistance ratio measurement and its dependence by alkaline metals has been analysed.

EXPERIMENTAL APPARATUS

The schematic diagram of the experimental set-up is shown in figure 2. The electrolytic cell is a glass beaker filled by about 400 cm^3 of H_2O+HCl solution (with 20 μM of HCl) in which are located two parallel (1.5 ÷ 2 cm distant) thin long (19 cm length) wire electrodes (cathode: Pd, 50 μm 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.

Power supply apparatus is a bipolar direct current generator (optionally it can be used as a direct voltage generator) applied to the anode electrode throughout an impedance adapter home-made circuit (impedance booster) to avoid a current return from the a.c. read-out circuit.

The resistance read-out apparatus is essentially composed by a pulse generator (having sinusoidal, square and triangular waves selection) and a ground home-made coupling circuit (ground return, both for D.C. and a.c. generators).

The D.C. generator can be applied optionally to the edge points A or B of anode whereas the a.c. generator can be applied to the edge points C or G of cathode. The Pd wire voltage picks up C, D, E, F, G are acquired to measure the resistance of these wire segments (CD= bottom, DE=down, EF=up, FG=top, respectively of length 0, 9.5, 9.5, 0 cm).

The thin wire cathode was chosen to enhance the hydrogen absorption by increasing the surface/volume ratio. *Moreover, the 1/r dependence of the electric field around the wire determines large electric fields on the surface of thin wire, which may promote high overvoltage values.* Finally, the higher value of resistance of very thin wires improves the measurements precision.
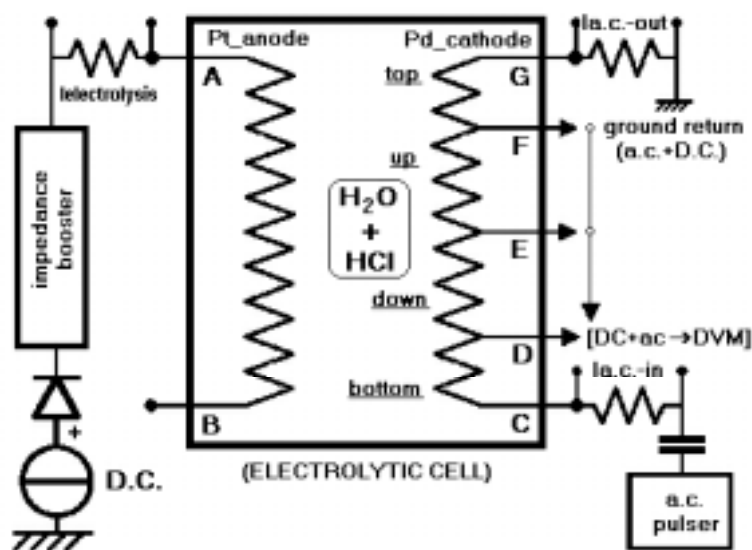
Figure 2 – <u>Apparatus set-up</u>: electrolytic cell, D.C. power supply block and a.c. resistance measurement block; all electric and thermodynamic parameters are acquired by several Digital Voltmeters (DVM) controlled by a computer.

LOADING PROCEDURE

To achieve very high H/Pd loading, we tune up a peculiar protocol regarding the solution, wire preparation and particularly the operation to perform during the electrolysis process. This procedure is the following:

a) Pd is warmed in air (up to roughly 600 °C) flowed by a 500 mA current to desorb residual hydrogen inside and to relax the eventual lattice mechanical stresses due to the wire working.

b) Cell is filled with a pure distilled water (400 cm^3) and its low conductivity is checked using a direct anodic current (impurities occurring into the solution are critic in respect to the high loading, as it will be described in the following)

c) A small quantity of HCl is added (2 cm^3 at 10 µM/cc: solution is at pH around at 4.5) and a low constant electrolytic current is applied (about 5 mA applied to total wire surface), corresponding to a $6 \div 7$ V of electric potential between the electrodes).

d) Several low/high (5/100mA or/and off/on=150V voltage) current cycles are performed distant in the time for many hours at low current (to let to Pd-layer system to slowly stabilise itself).

RESULTS AND DISCUSSION

Studying the dependence of H/Pd maximum loading by the electrolyte composition, we found the following statements:

a) Just HCl diluted acidic solution is unuseful to achieve high loading (Fig. 3, 4);

b) Adding to the acid solution (produced with a very pure water) some alkaline elements (such as *Sr*) in a proper low quantity, loading can be increased to very high values (Fig. 5, 6, 7);

c) Heavy metal elements (as well as *Hg*) have been tested but they did not produce interesting loading if they are used by alone; instead a mixing of a low amount of *Sr+Hg* can be useful for high and long-term stable loading (Fig. 8).

d) Just Hg (with HCl solution and no Sr) can be useful if it is present in a very low amount ($<< 10^{-7}$ M), but in this condition it is critic for the loading reproducibility (Fig. 9).

e) When a high loading (R/R= 1.15) at very low current (5 mA) is achieved, a peculiar layer seems to be deposit on to the Pd surface (de-loading tests show it clearly).
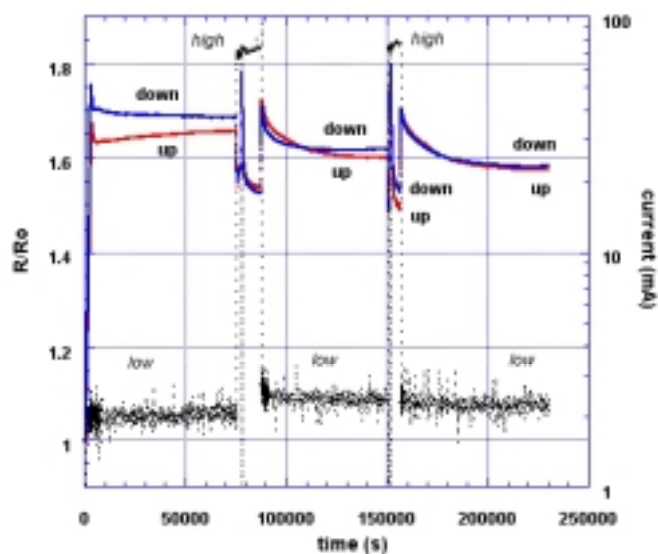
Figure 3 – HCl blank test: beginning of loading + low/high/off current cycles. In the time, because impurities coming from the air, loading lightly increases.
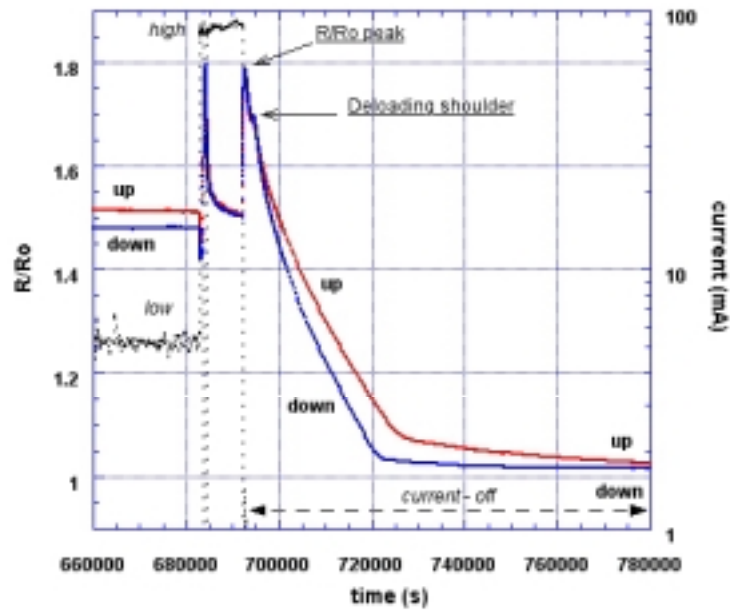
Figure 4 – <u>HCl blank test</u>: end of loading; wire deloading with electrolysis off. After long time, loading achieved interesting value (R/Ro= 1.5). De-loading curve clearly shows a typical shoulder at R/Ro=1.7; R/Ro peak (1.78) and initial R/Ro (1.02) values are in agreement with those ones expected.
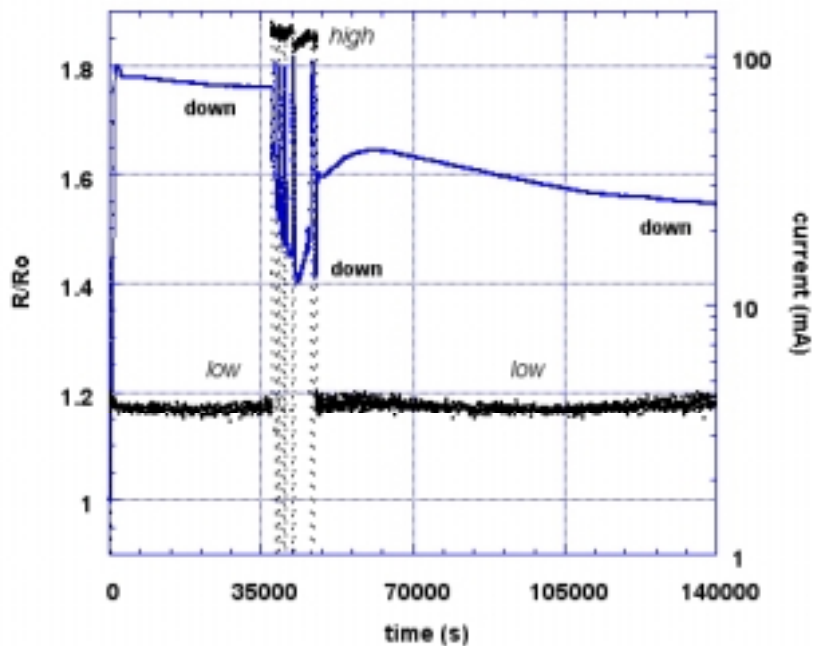
Figure 5 – <u>Sr test</u>: beginning of loading + low/high/off current cycles; after these cycles, loading has increased and R/Ro has reduced from 1.7 to 1.5 (returning to operate at low current).

In the following we investigate in more detail these experimental facts.

--- *HCl blank tests*

First test just using bi-distilled water with HCl (we consider it as a blank) does not show interesting high loading at the beginning of charging up (Fig. 3), achieving quickly R/Ro=1.7, neither after trying high/low current cycles (almost R/Ro=1.55 after many days). Because

some impurities coming from the air (cell working open at the top), after about a week (Fig. 4), maximum loading occurred at R/Ro=1.5 or 1.4 (low or high current). Leaving the wire to de-load spontaneously (having switched off the electrolytic current), very soon the resistance reaches the peak value (R/Ro=1.78); after a peculiar resistance shoulder (at R/Ro=1.7, a condition indicating a sort of Pd-H lattice phase change transition), in some hours the wire resistance return to the initial value (about R/Ro=1).

--- HCl + Sr tests

Following test has been performed adding a small quantity of $SrCl_2$ (50 µM) to the solution. The loading (at first at low current and later with high/off current cycles) has been performed at same condition as blank test and the initial loading trend is very similar (Fig. 5); situation sharply changes during the current cycles (Fig. 6) and after this test, returning to initial low current condition, something has changed for the loading (from R/Ro=1.7 to R/Ro=1.6 firstly and slowly in about one day to R/Ro=1.5). The operation has been repeated along a few days and finally after a cycle (Fig. 7) loading achieves the best result (from R/Ro=1.4 to R/Ro=1.15 at 5 mA, 7V and R/Ro=1.05 at 120 mA, 100V).
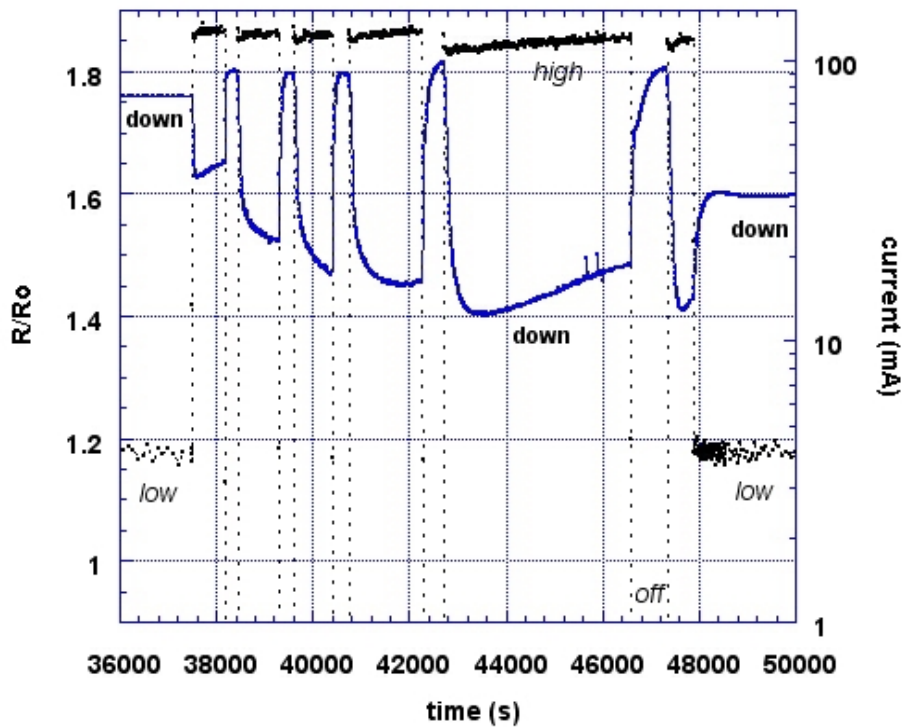
Figure 6 – <u>Sr test</u>: a detail of low/high/off current cycles; in off condition, time of de-loading to the R/Ro peak seems to increase cycle by cycle.
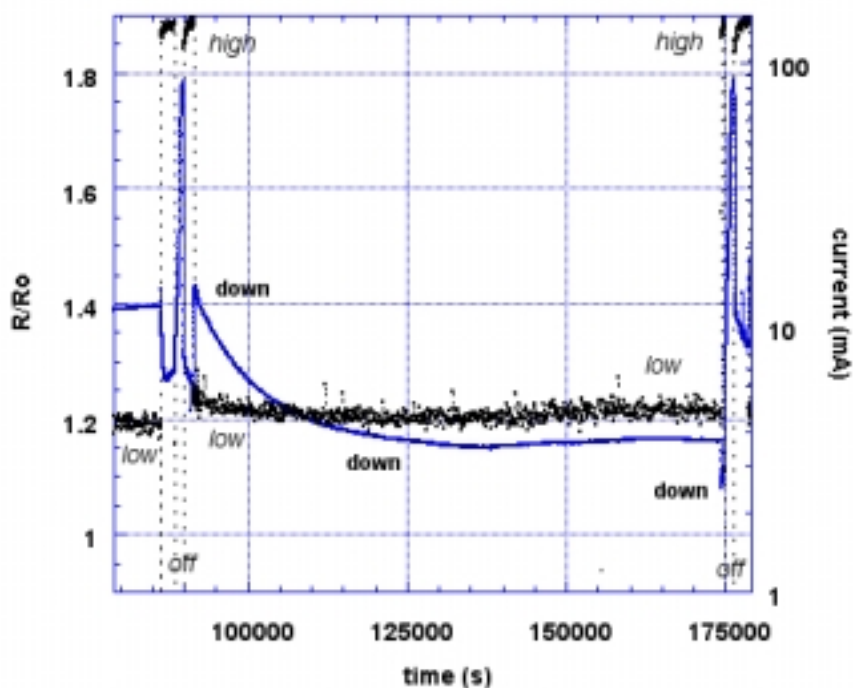
Figure 7 – <u>Sr test</u>: after a current cycle, maximum loading has been achieved (R/Ro=1.15 at low current and 1.05 at high current); it is possible to see that loading is very stable in the long time operating at 5 mA, 7 V (electrolysis power supply).
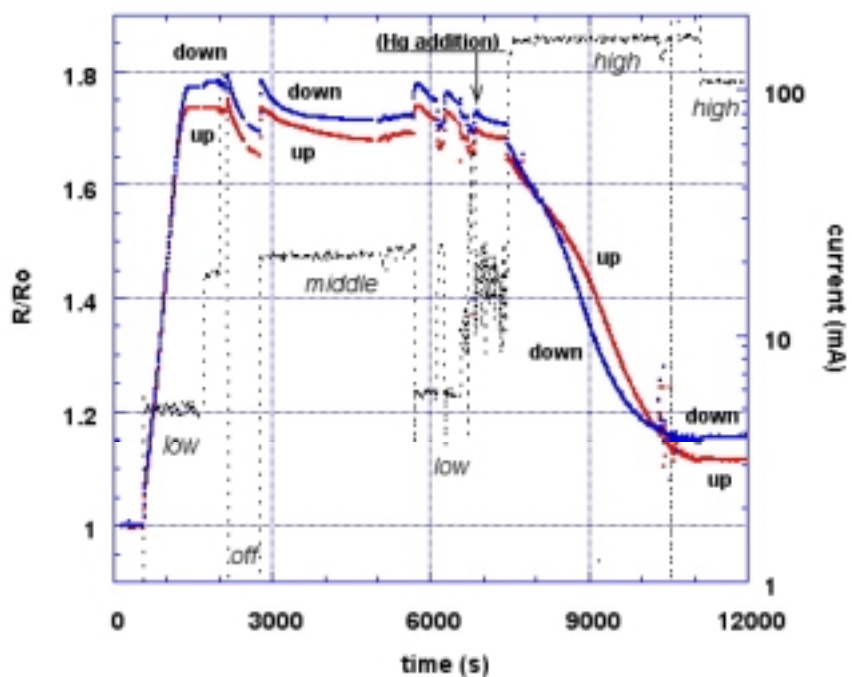

Figure 8 – <u>Hg test</u>: an addition of Hg to the solution (containing Sr) and a sharp increasing of electrolytic current, seem to be effective to produce an overload for both sectors (up, down).
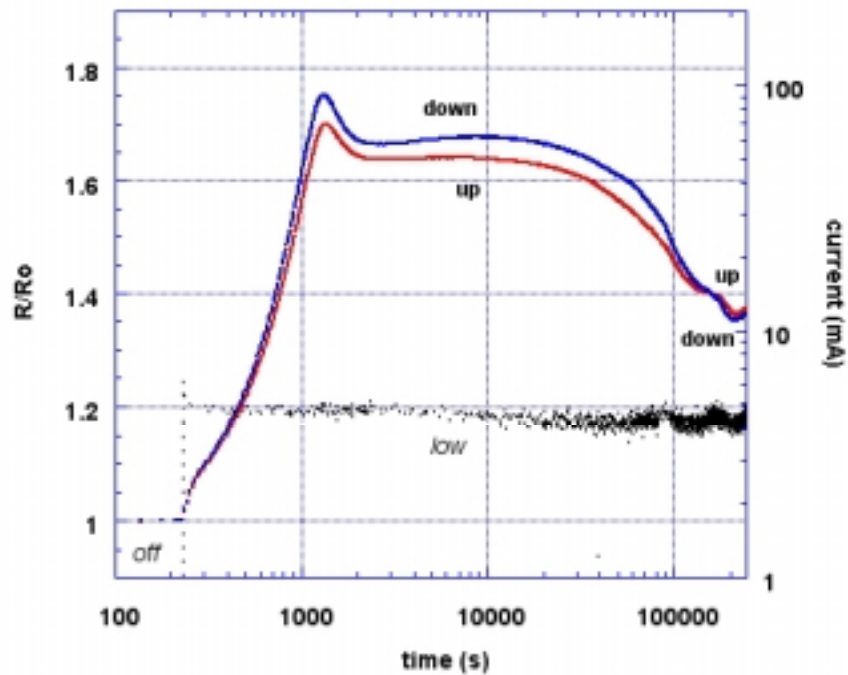
Figure 9 – <u>Hg test</u>: a very low amount of Hg ($<< 10^{-7}$ M) added to solution (with no Sr) and a low constant current seem to be effective to produce an overload for both sectors (up, down); again at R/Ro$\cong$ 1.7 a loading shoulder is occurring.
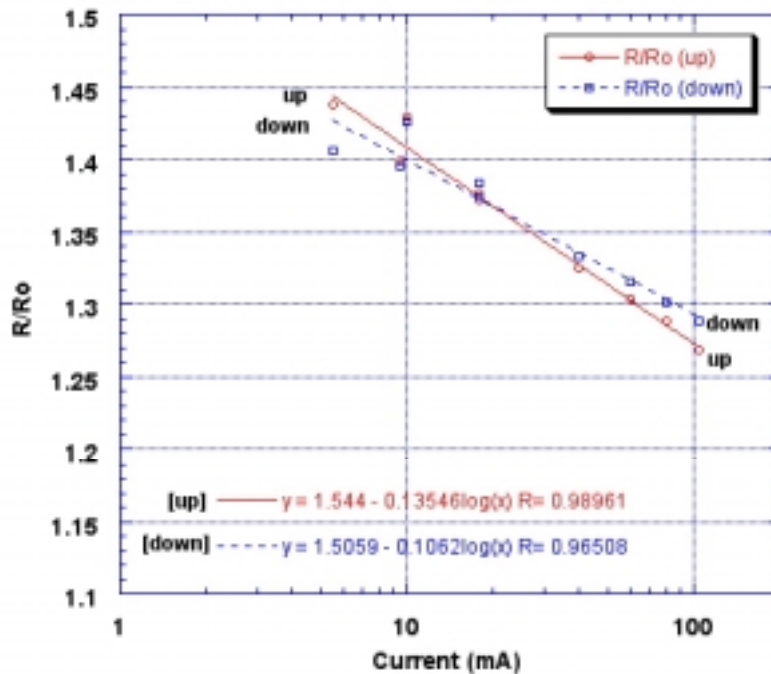
Figure 10 – <u>Tafel test</u>: both sectors (up, down) follow a R/Ro logarithm-fit dependence with the current. A comparison with other fits indicates that the slope of the curve becomes more flat when the loading (at low current) is very high.

This evidence seems to be consistent with a peculiar thin layer, slowly deposited onto the Pd surface, enhanced by these opportune current cycles.

--- *Hg tests*

Because others alkaline-earth elements have been tested and some of them (as Ca) have been found effective (these tests will be reported in a next paper), we have been going to test the effectively of metals such as Mercury (other metals as Fe, Cu did not seem to be effective).
In a peculiar test (Fig. 8) we have begun with a $SrSO_4$ salt in addition to the solution (instead of HCl) but no interesting loading effect has occurred; neither changing it with H_2SO_4 and operating low/high current cycles we got any result. After that, an addition of $HgCl_2$ (10^{-5} M) and a sharp increasing of current has shown a quite fast (about 1 hour) and strong loading (R/Ro= 1.10 and 1.15 for "up" and "down" sectors). In this case Hg, occurring with Sr in the same solution can be considered useful to achieve, quickly and in a stable way, overloading even if the electrolytic current has been reduced (from 150 mA to 100 mA).

Further tests (Fig. 9), just using HCl and a very low amount of $HgCl_2$ ($<< 10^{-7}$ M) with no Sr, have shown (starting from beginning with a new wire) in about 2 days a very slow loading up to R/Ro=1.35, working all the time at low constant current (5 mA); in this plot (Fig. 9) is visible the loading peak at 1.78 and the long time staying new phase shoulder at 1.7. Instead, tests using just Hg but at higher concentration ($\geq 10^{-6}$ M) have shown that Hg covers quickly the Pd cathode leaving locked the loading at around the peak (R/Ro=1.75) even increasing strongly the current or switching off the electrolysis for many days.

These tests with Hg show that it is very critic (speaking about the concentration into the solution and the deposit layer onto the Pd) in respect to the overloading; many tests, performed with unwanted and unpredictable low amount (just a few tracks) of the Hg remained into the solution (or deposited onto the electrodes), have carried out apparently contradictory loading results!

--- *Equivalent-Tafel tests*

Several tests have been performed (Fig. 10) when Pd loading was stable at low current (a few mA), increasing to high current (hundred of mA) and fitting data with logarithm curve (in equivalent way to empirical Tafel law (1905)) as the following formula: *R/Ro = **a** + **b** log(I)*. We have observed that these parameters ("a" and "b" supposed to be roughly constant in the literature) are depending by the loading ratio: increasing the loading, both them strongly decrease (in module). In fact, as an indication of that, in the 5 → 100 mA current range, we report very different R/Ro variation depending by initial loading: at <u>high</u> loading R/Ro= 1.5 → 1.2 while at <u>very high</u> loading R/Ro= 1.15 → 1.08.

A sort of structural change on the Pd cathode surface can be an explanation of this unexpected result.

--- *Resistivity coefficient of temperature observation*

In an our previous works [ref. 6], for the first time, we have shown an unexpected high enhancing of this temperature coefficient [ref. 7] ($\alpha_T = 2 \cdot 10^{-3}$ K^{-1} at H/Pd= 0.7 and R/Ro= 1.7) corresponding to $\alpha_T \cong 3.5 \cdot 10^{-3}$ K^{-1} at R/Ro$\cong$ 1.2 (H/Pd > 0.97). According to the whole tests previously reported we can confirm that this measurement is essentially correct: in our condition at R/Ro $\cong$ 1.15 at room temperature (ranging of some degrees) roughly is $\alpha_T > 3.5 \cdot 10^{-3}$ K^{-1} (in the range of 4.5 ÷ 7.5).

All the tests above reported have been performed changing often the Pd wire and always de-loading the Pd electrode or by switching off the electrolytic current (slow process) or with an anodic current (faster process); in the whole of cases the R/Ro value has been observed to

return to 1.0 and we observed the de-load shoulder at R/Ro=1.7 (after overcoming the peak) indicating a sort of a new Pd-H lattice phase.

CONCLUSIONS

Experiments performed permit us to conclude that electrolyte composition in a d.c. voltage electrolysis is determinative to achieve very high H/Pd ($\geq$ 1) thin wires loading and loading dynamics seems related to a very low and optimal quantity of particular alkaline elements (Sr) or heavy metals (Hg).

Moreover, a peculiar "low/high-off" current cycles procedure seems to be very effective to achieve very high loading (R/Ro$\leq$ 1.4) in a few days.

All tests, based on impurities addition and current loading procedure, are in agreement with a formation of a peculiar very <u>thin layer</u> ($\leq$ 1μm) <u>deposit</u> onto the Pd surface; such a status provides a very high H/Pd loading ($\cong$ 1) corresponding to R/Ro= 1,15 (at 5mA electrolysis current). That can be consistent to interpret the obtained results with a sort of a metastable H-Pd condition able to absorb big hydrogen amount through the palladium wire surface.

This our loading protocol has been, sequentially in the time, checked by Pirelli-Cavi SpA Research Laboratory (Milan), by Dr. D. Garbelli Group (under the supervision of Ing. F. Fontana) and Stanford Research Institute (CA), by Dr P. Tripodi Group (under the direction of Dr M. Mckubre). Both they have found that it is effective, getting very similar results; in particular way Pirelli Group, which has adopted a similar apparatus, they have shown detailed studies of the deposit layer on the Pd using a SEM [ref. 8].

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