NEW ELECTROLYTIC PROCEDURE FOR THE OBTAINMENT OF VERY HIGH H/Pd LOADING RATIOS. PRELIMINARY ATTEMPTS FOR ITS APPLICATION TO THE D-Pd SYSTEM

A. Spallone[1], F. Celani[1], P. Marini[2], V. Di Stefano[2]

[1] INFN-LNF, Via Enrico Fermi, 00044 Frascati (Roma), Italy

[2] EURESYS, Via Lero 30, 00129 Roma, Italy

Abstract

A new electrolytic protocol is proposed, capable of insuring a very high Hydrogen loading of thin Palladium wires. The main characteristic of the procedure consists in the use of a particular electrolyte containing very small amounts of alkaline-earth metals dissolved in a diluted acid solution (H_2O+HCl).

The addition of alkaline-earth metals to the electrolyte appears to be decisive for the achievement of H/Pd loading ratios close to 1. Two independent Research Groups have tested the protocol with similar results.

Probably because of the presence of contaminants in the heavy water, less satisfactory results have been obtained for the D/Pd loading ratios (best result: R/Ro = 1.52; D/Pd $\cong$ 0.97)

Introduction

It is generally known 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 [Ref. 1].

The poor results, especially from the point of view of their reproducibility, generally achieved by the conventional electrolytic techniques, based on the use of LiOH solutions, induced us to develop a completely different approach.

In order to increase the cathodic overvoltage, which is known to be the main controlling parameter of the H(D) Pd loading, we tried to modify the nature of the cathode, by inducing the formation of a very thin layer of an alkaline-earth carbonate on its surface [Ref. 2].

After the first encouraging results, we decided to carry out a systematic work, starting with light water, in order to define the best composition of the electrolyte and the most effective loading procedure.

With reference to the paper presented by Celani et al. [Ref. 3], which is substantially a comprehensive panorama over all the activities carried out by our group in the last two years, the present one shows in detail the most significant results of the experimental work.

Experimental Apparatus

A schematic diagram of the experimental set-up is shown in Figure 1. The electrolytic cell consists of a Pd cathode (a thin wire - diameter 50 μm – length 19 cm), a Pt anode of the same length (diameter 200 μm) set at a distance of 1.5 - 2 cm form the cathode, both plunged in a glass

beaker filled with about 400 ml of H_2O+HCl solution. The cell is placed into a two litre water bath in order to reduce the temperature fluctuations around the room temperature (usually kept at 22 °C). Cell, bath and room temperatures are continuously monitored and recorded.

The power supply can operate as a constant D.C. current generator or, optionally, as a constant D.C. voltage generator. The cathode is grounded. The voltage is applied to the anode electrode through a home-made impedance adapter circuit (impedance booster), in order to avoid a current feed-back from the A.C. measuring circuit. The latter is essentially composed by a pulse generator (having sinusoidal, square and triangular wave selection) and a ground home-made coupling circuit (ground return, both for the D.C. and A.C. generators).

The D.C. generator can be applied to the edge points A or B of the anode whereas the A.C. generator can be applied to the edge points C or G of the cathode. The Pd wire voltage pick-ups C,D,E,F,G allow for the measurements of the resistances of the correspondent wire segments (CD= bottom, DE=down, EF=up, FG=top). In the present work the length of the CD and FG segments has been set to 0, so that in the following, reference will be made to only two segments, i.e. DE= "down" and EF= "up", both of length 9.5 cm.

The loading ratio is inferred by means of the well known relationship [Ref.s 4,5,6] between resistance and H(D) content in the Pd matrix (Fig. 2) and continuously monitored.

The Pd cathode, because of its favourable surface/volume ratio, allows for a faster Hydrogen absorption and its high resistivity improves both the accuracy and the precision of the measurements. Furthermore, the $1/r$ dependence of the electric field around the wire allows for a sharp increase of the pH value just in its proximity, thus promoting the carbonate precipitation in that region only (see after).

Composition of the electrolyte

The set of experiments which led us to the final choice of the electrolyte composition is extensively described in Reference 2. Here only the essentials will be treated.

It is known that Hydrogen can enter a metal only if it is present on its surface in the form of H atoms. In the case of the electrolytic Hydrogen loading of a Pd cathode, after the first rapid absorption (absorption isotherm - $\alpha+\beta$ phase), the Hydrogen loading progressively slows down until it comes to an end, no matter how much is the applied current density. This is mainly due to the catalytic properties of the Pd surface. In fact, even though Hydrogen atoms are continuously formed at the Pd cathode during the electrolysis, they rapidly recombine to form the Hydrogen molecule, thus hindering the absorption process, (a fact consistent with the very low overvoltage measured with Pd cathodes). It is also known that catalytic surfaces can be poisoned by films of adsorbed or deposited substances. On the basis of this assumption we tried to alter the Pd surface through the local precipitation of inorganic substances. The final choice has fallen upon alkaline earth carbonates and among them Strontium carbonate.

The choice of the alkaline earth metals was dictated by the fact that they do not discharge to form a metallic layer, which can eventually hinder the Hydrogen absorption due to the low Hydrogen permeability typical of most metals. Mercury, for example, even though it effectively poisons the Pd surface, is able to stop any Hydrogen exchange. We found it useful only as an extremely thin layer, very hardly controllable through the concentration of Hg ions in the electrolyte. Instead, because of its solubility product, the local precipitation of $SrCO_3$ is easily controlled through Sr^{++} concentration, pH, and current density. Because of their higher solubility product both $CaCO_3$ and $BaCO_3$ are less effective [Ref. 2ùç]. The proper Sr^{++} concentration range is within 30 to 70 $\mu M/l$. Sr^{++} is added as $SrCl_2$. By setting the pH at 4.5 with HCl additions, the proper CO_2 concentration is that one insured by maintaining the electrolyte exposed to open air.

Experimental

Effect of Sr^{++} additions

After a start-up procedure, common to all experiments, consisting in:

1) The Pd wire is Joule heated (500 mA) in air (up to roughly 600 °C) in order to completely eliminate occasional residual Hydrogen and to relax mechanical stresses due to the wire cold-working.

2) The cell is filled with pure distilled water (400 cm^3).

3) A small quantity of HCl is added till the pH of the solution is around 4.5 (the required amount is about 20 μM)

the electrolysis starts with the application of 5 mA current. This current value is maintained until the cathode reaches a first asymptotic loading value (Fig. 3). At this point the electrolysis current is varied according to the following sequence:

Turned off (partial deloading) - turned on (high current loading till next asymptotic value) - turned off (partial deloading)- Turned on (low current loading till next asymptotic value).

It will be referred to this sequence as to the *off-high-off-low* (OHOL) current sequence.

By repeating the sequence, the loading ratios H/Pd tend to become higher until a final asymptotic value is reached, subjected to no further improvement.

In order to point out the effectiveness of the Sr addition to the electrolyte a blank test has been carried out by operating with an electrolyte containing only HCl.

In Figure 4, it is shown that the final maximum loading ratio R/R_0 obtained by the above described procedure is ≈ 1.50.

At this point the current was turned off in order to allow for a complete deloading of the Pd cathode (Fig. 4).

$SrCl_2$ is then added (50 μM) to the electrolyte and the electrolysis is started again with the same set of conditions (5 mA). The OHOL sequence has then been applied and repeated until a final asymptotic value of R/R_0 of 1.15 has been reached (Fig.s 5, 6 and 7). Therefore it is proved that the Sr addition is decisive for the achievement of extremely low R/R_0 values.

Substantially the same results have been obtained by substituting the Cl^- ions with SO_4^- ones.

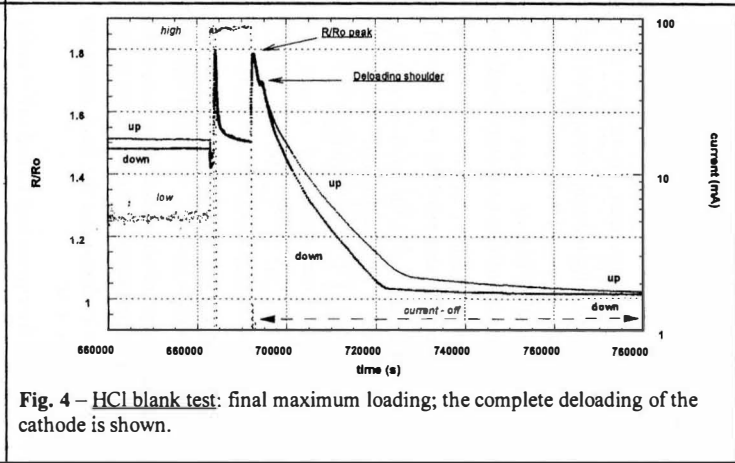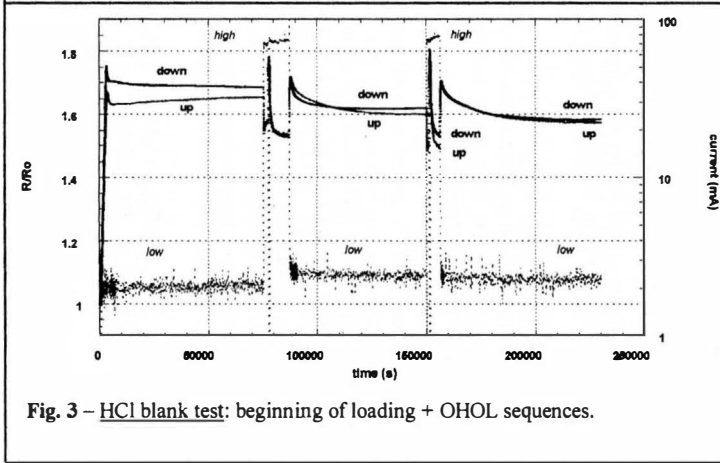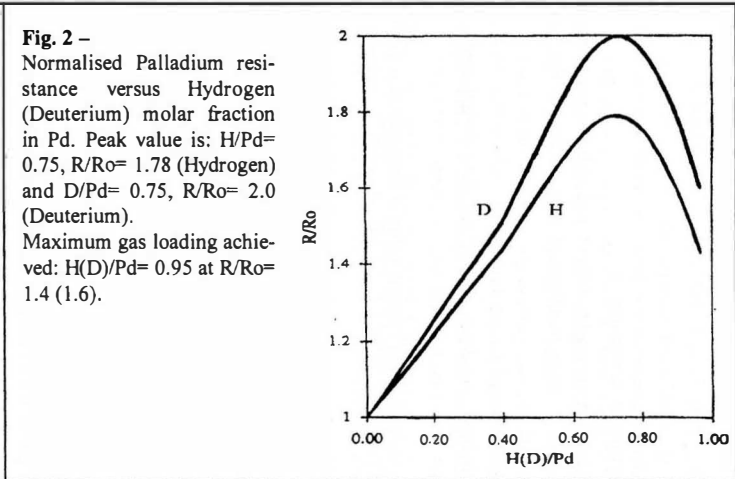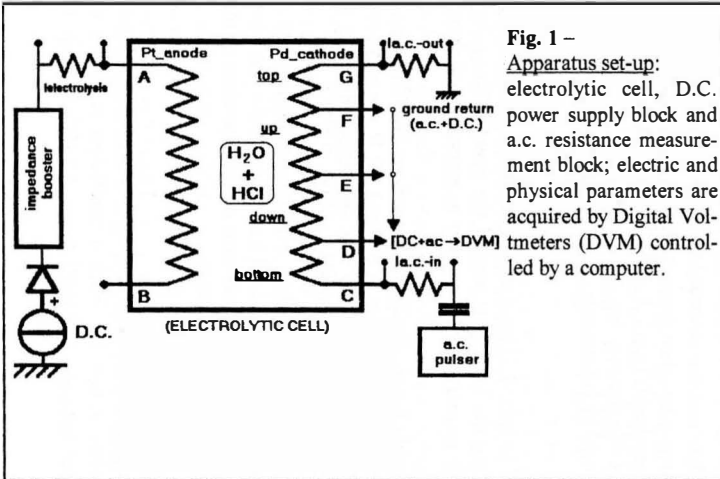### Effect of Hg^{++} additions

Tests using $HgCl_2$ at a concentration of $\approx 10^{-6}$ M (pH=4.5) have shown that a Hg coating forms quickly, thus covering the Pd cathode and blocking the loading at around the peak (R/Ro=1.75). The block could not be removed even by strongly increasing the current or by repeatedly applying the OHOL sequence.

Further tests [Ref. 7] carried out with remarkably lower $HgCl_2$ concentrations ($\approx 10^{-8}$ M) have shown a very slow loading (two days) up to a final asymptotic value of R/Ro=1.35. It was observed that even by turning off the current, the deloading rate was extremely low, suggesting that even at such a low concentration an impermeable Hg layer finally forms on the Pd surface.

In another experiment (Fig. 8), to the Sr^{++} containing electrolyte, $HgCl_2$ was added up to a concentration of 10^{-5} M. A strong loading occurred (R/Ro= 1.10 and 1.15 respectively for "up" and "down" sectors). This suggests that Mercury could not form a continuous coating because of the presence on the cathode surface of a previously precipitated $SrCO_3$ layer.

Thermal resistivity coefficient of the Pd-H cathode.

As described in an our previous works [Ref. 8], for the first time we measured the thermal resistivity coefficient of the Pd cathode (α_T), when R/R_0= 1.2. Such a coefficient is known to decrease as the H concentration in Pd increases between H/Pd=0.1 (α_T= $4.1 \cdot 10^{-3}$ K^{-1}) up to

Fig. 1 –
<u>Apparatus set-up</u>: electrolytic cell, D.C. power supply block and a.c. resistance measurement block; electric and physical parameters are acquired by Digital Voltmeters (DVM) controlled by a computer.

Fig. 2 –
Normalised Palladium resistance versus Hydrogen (Deuterium) molar fraction in Pd. Peak value is: H/Pd= 0.75, R/Ro= 1.78 (Hydrogen) and D/Pd= 0.75, R/Ro= 2.0 (Deuterium).
Maximum gas loading achieved: H(D)/Pd= 0.95 at R/Ro= 1.4 (1.6).

Fig. 3 – <u>HCl blank test</u>: beginning of loading + OHOL sequences.

Fig. 4 – <u>HCl blank test</u>: final maximum loading; the complete deloading of the cathode is shown.

H/Pd=0.7 ($2.0\,10^{-3}$ K^{-1}), which is the maximum H concentration for which there were available data [Ref. 9]. The result of our measurements at R/R_0=1.2 (H/Pd close to 1) is $\alpha_T = 3.5\,10^{-3}$ K^{-1}.

A further value of $\alpha_T \cong 6.0\,10^{-3}$ K^{-1} has been found at H/Pd a bit closer to 1 (R/Ro = 1.15). These results show that between H/Pd=0.7 and H/Pd $\approx$ 1, there must be a minimum value of α_T, probably rising rapidly in the H/Pd region close to 1. This strongly suggests that a new phase is starting to nucleate inside the Pd-H β phase.

Finally, the existence of a change of phase seems to be indicated by the presence of a characteristic shoulder (Fig. 4), which appears in the R/Ro versus time deloading curve, just after the peak has been overcome. The occurrence of the shoulder (roughly around H/Pd=0.65) after the peak, might be connected with the end of β phase and the beginning of $\alpha+\beta$ phase, sequentially occurring during the deloading.

Preliminary Pd-D loading experiments

When our batch of commercial heavy water was used for preparing the electrolytic solution, according to the above described protocol, the best loading obtained was D/Pd=0.75. Taking into account that our procedure requires the absence of any foreign substance in the electrolyte apart from Sr^{++} ions and CO_2, it will be clear that even the small amounts of impurities (inorganic, organic and biologic materials) normally present into that commercial heavy water, could have seriously impaired the proper formation of the thin layer of $SrCO_3$ on the Pd surface.

Another batch of guaranteed higher purity heavy water was employed and the composition of the electrolyte was the same one used for H loading.

High purity heavy water is remarkably hygroscopic. Consequently, the electrolytic cell was excluded from the contact with ambient air. The necessary supply of CO_2 was assured by a flow of air, dried by bubbling it into concentrated sulphuric acid, and subsequently into heavy water.

It is to be noted that with the experimental set-up used for D loading, both ends of the up and down sectors of the Pd wires were protected with a drop of silicone sealant for a total length of roughly 4 mm (about 4% of their length). These portions of the cathode are not in contact with the electrolyte and cannot be directly loaded. In this conditions it was found that the maximum numerical value of R/Ro read by the instruments was 1.96 instead of 2.0. Therefore the values of R/Ro, reported in the Figures from 9 to 12 are about 2% lower than the correct ones.

In Figure 9 the effect of the OHOL sequence is shown with some detail. These results are rather inferior if compared with the ones obtained with H loading.

After several attempts it was found effective to increase the deloading time during the off portion of the OHOL sequence, allowing for an almost complete deloading. Some of the results are shown in Figure 10. After several new OHOL sequence applications a final asymptotic value of R/Ro=1.62 (at 25 °C) was achieved. The current was then increased up to 30 mA. It can be seen that an R/Ro value of 1.55 was rapidly achieved. By lowering the applied current the R/Ro value rose to 1.65. By again increasing the current up to 90 mA a R/Ro value of 1.52 was obtained (Fig. 11). In the same figure it is shown that by turning the current off, the deloading process proceeds regularly with a peak of R/Ro at 1.95. It should be noted that the deloading rate of the D loaded wire is significantly lower than that observed with the deloading of the H-loaded wire (Fig. 4). Such a difference could be due to the difference between the length of the deloading time within the OHOL sequence.

The previously reported "loading ramps" effect [Ref. 10] has been observed to occur sometimes when loading is quite high (R/Ro< 1.75). We observed this effect to occur several times especially in the "up" wire sector (Fig. 12), when R/Ro decreases under 1.65 (cycles oscillating between 1.643 and 1.647, with a period roughly of 1 hour, even lasting for about 1 day and disappearing when R/Ro rises up over 1.66).

In a previous paper [Ref. 11], we conjectured that this effect could be located within just a few small fractions of the wire achieving very high loading (R/Ro< 1.5), thus giving rise to "bursts" of
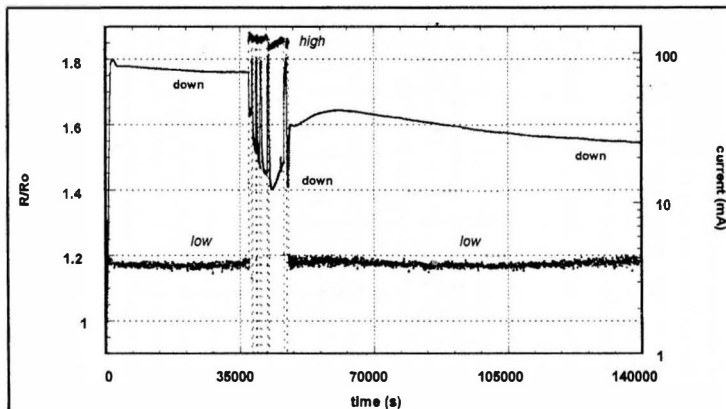
Fig. 5 – Sr test: beginning of the loading + OHOL sequence; R/Ro is reduced from 1.75 to 1.55 (back to low current).
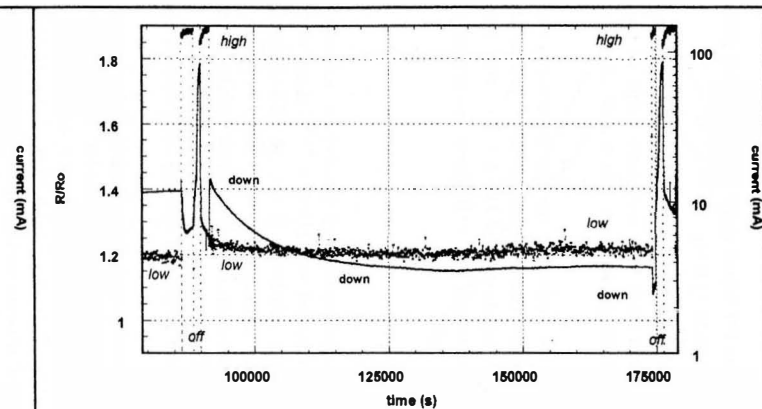

Fig. 7 – Sr test: maximum final loadings: R/Ro= 1.15 at low current (5 mA, 7 V) and 1.05 at high current (120 mA).
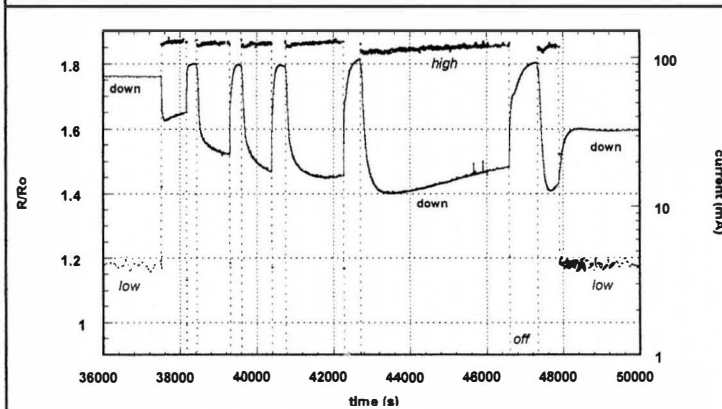

Fig. 6 – Sr test: detail of OHOL sequence ("down" sector); R/Ro= 1.40 is achieved at high current.
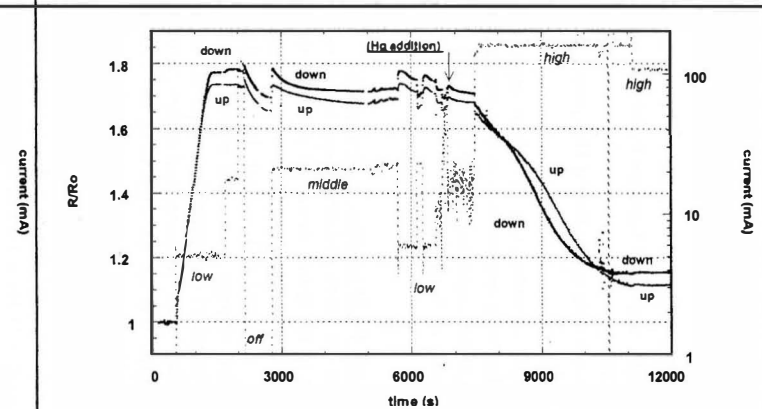

Fig. 8 – Hg test: an addition of Hg to the solution (containing Sr) and a sharp increase of electrolytic current, allow for a fast and strong loading .
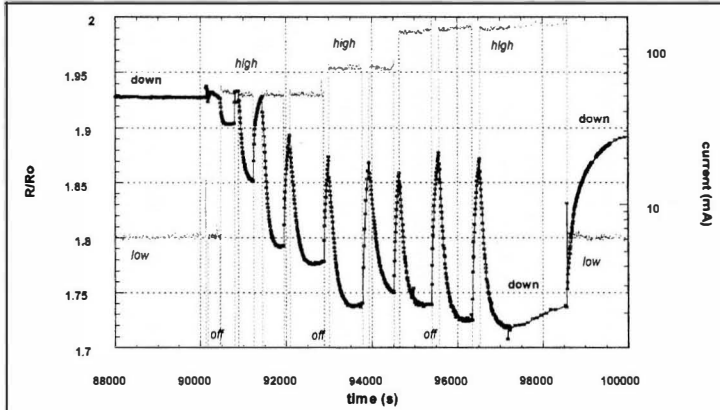
Fig. 9 – D$_2$O test: detail of OHOL sequence; maximum loading: R/Ro → 1.72

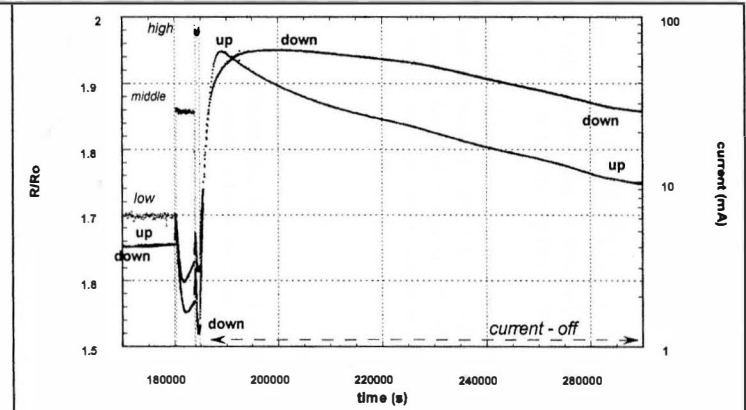**Fig. 11** – D$_2$O test: starting from R/Ro= 1.65, by increasing the current up to 90 mA, R/Ro= 1.52 was obtained. In OFF, a very slow deloading occurs.
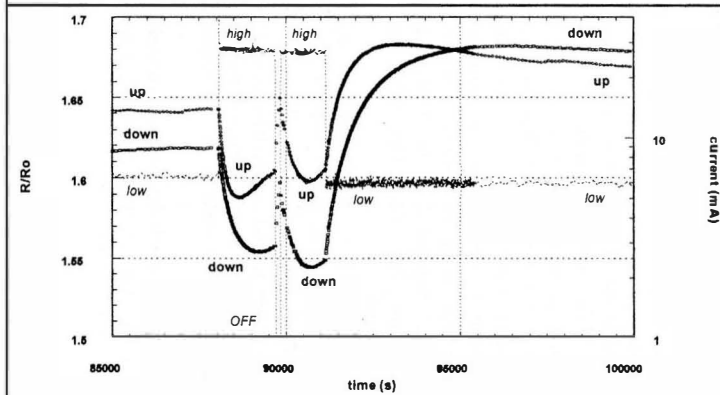

Fig. 10 – D$_2$O test: final value after the new OHOL sequence (R/Ro ≅ 1.62); the current was switched up to 30 mA and R/Ro = 1.55 was achieved.
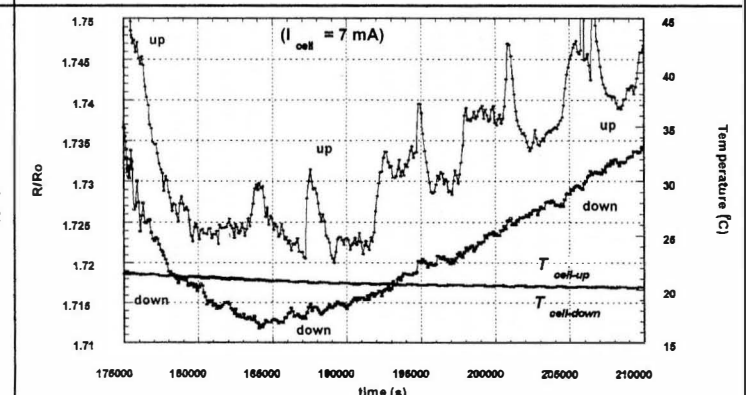

Fig. 12 – D$_2$O test: detail of some typical loading "ramps" occurring (for R/Ro< 1.75) at low current for the "up" sector only.

heat production which locally rise the wire resistance, but that are on the average too small to be detected by the sensors as cell temperature rise.

Conclusions

In conclusion a protocol for the obtainment of high H/Pd and D/Pd values has been developed, in agreement with the hypothesis of a modification of the catalytic properties of the Pd-cathode surface, through the formation of thin layers of $SrCO_3$, by local precipitation due to pH increase at the cathode surface.

The Pd-H loading protocol has been tested by Pirelli-Cavi SpA Research Laboratory (Milan), by Dr D. Garbelli Group (under the supervision of Ing. F. Fontana) and the Stanford Research Institute (CA), by Dr P. Tripodi Group (under the direction of Dr M. McKubre) and was found to be effective. In particular by the Pirelli Group has shown detailed evidence of the deposited layer on the Pd surface through the use of a SEM apparatus (as it is reported by Dr Garbelli at this same Congress).

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 of thin Palladium wires through alkaline-earth carbonates' precipitation on the cathodic surface. Evidence of a new phase in the Pd-H system." Published by *LNF-00/006 (P), 6 Marzo 2000* --- To be published by *Physics Letter A*

[3] F. Celani, A. Spallone et al. "A study on the electrochemistry parameters to achieve reproducible high H/Pd values in relation to 'anomalous' excess heat; proteobacteria contamination problematic." Submitted to the *IV Workshop on Anomalies in Hydrogen/Deuterium Loaded Metals*, Conf. Proc. 22-24 Oct. 1999, Asti, Italy

[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] A. Spallone, F. Celani et al. "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." Submitted to the *IV Workshop on Anomalies in Hydrogen/Deuterium Loaded Metals*, Conf. Proc. 22-24 Oct. 1999, Asti, Italy --- Published by INFN: *LNF-00/017 (P), 27 Giugno 2000*

[8] P. Marini et al. *XXI Secolo Scienza e Tecnologia*, Anno **X** - Num. **1**, pg. 34-41 (1999)

[9] B. Baranowski, Filipek et al. (1990), *J. Less Common Metals*, **158**, 347

[10] F. Celani, A. Spallone, P. Tripodi et al. "Deuterium overloading of palladium wires by means of high power μs pulsed electrolysis and electromigration: suggestions of a 'phase transition' and related excess heat." *Physics Letters A*, 214 (1996) 1-13

[11] A. Spallone, F. Celani et al. "A preliminary D/Pd study: anomalous resistivity transition effect." *"Asti Workshop on Anomalies in Hydrogen/Deuterium Loaded Metals"* (SIF-Conf. Proc. Vol. 64 pg 7-16, Asti 27-30 Nov. 1997) Edit by W.J.M.F. Collis, Compositori–Bologna, Italy (1999).