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**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**

F. Celani¹, A. Spallone¹, P. Marini², V. di Stefano², M. Nakamura², S. Pace³,
A. Vecchione³, A. Mancini⁴, P. Tripodi⁵, D. Di Gioacchino¹

¹ INFN – Laboratori Nazionali di Frascati Via E. Fermi 40, I-00044 Frascati, Italy

² EURESYS, Via Lero 30, 00129 Roma, Italy

³ INFN – Dep. of Physics, Salerno University, 84081 Salerno, Italy

⁴ ORIM SrL, Via Concordia 65, 62100 Piediripa (MC), Italy

⁵ Stanford Research Institut International, Stanford (CA), USA

Abstract

A new protocol for the electrolytic loading of hydrogen (H) in thin palladium (Pd) wires has been developed. In order to increase the cathodic overvoltage, which is known to be the main parameter capable to enhance the electrolytic H loading of Pd, the catalytic action of the Pd surface versus H-H recombination has been strongly reduced by precipitation of a thin layer of alkaline-earth carbonates on the cathode. A set of electrolytes has been employed, containing small amounts of hydrochloric or sulfuric acid and strontium or calcium ions. The H loading has been continuously evaluated through ac measurements of the Pd wire resistance. Uncommonly low resistivity values, leading to an estimate of exceptionally high H loading, have been observed. Evidence of the existence of a new phase in the very high H content region of the Pd-H system has been inferred on the basis of the determination of the temperature coefficient of the electrical resistivity. Mainly for this purpose a thin layer of Hg was galvanically deposited on the cathodic surface, in order to prevent any H deloading during the measurements.

Our results have been fully reproduced in other 2 well equipped and experienced Laboratories (Italy, USA).

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1 – INTRODUCTION

Among metal-hydrogen systems, the palladium-hydrogen (Pd-H) one has been the most extensively investigated because of its interesting technological applications, that become more and more interesting the higher is the H content that can be achieved [ref. 1, 2, 3, 4, 5].

The palladium-deuterium (Pd-D) system has been also studied in the last few years in connection with the so called “cold fusion phenomena”. Our group is quite active in this field and one of the aims of the present investigation is to find-out a loading procedure able to insure very high and stable loading ratios in the Pd-D system.

High H loading of Pd is usually aimed at by means of two techniques: treatment of the metal with high pressure of H, electrochemical cathodic loading. With the former method a maximum loading of about 0.97 (H/Pd atomic ratio) at an H pressure of 50000 atm. was obtained. Approximately the same loading level has been reached by the electrolytic method. Obviously the latter requires much more simple and economical experimental set-ups. The electrochemical process is equivalent to the physical one in that, a relevant fraction of the cathodic overvoltage can be considered as thermodynamically equivalent to the H pressure in excess of one atmosphere. Therefore, as far as the electrochemical method is concerned, the achieving of high cathodic overvoltages is of paramount importance.

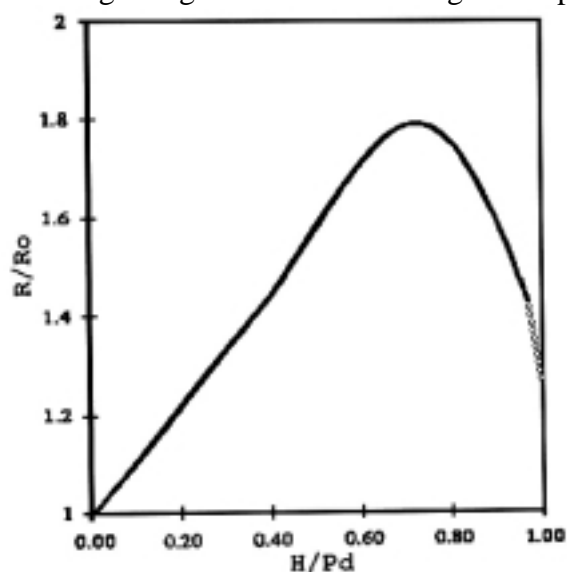


Figure 1 - Hydrogen loading curve.
 From this plot it is possible to calibrate the apparatus, relating the normalised resistance to the atomic Hydrogen concentration into the Palladium lattice. Data from literature are available up to $H/Pd=0.97$ and $R/R_0=1.43$; circle symbols represent a conjectural straight extrapolation of these data up to $H/Pd=1$ at $R/R_0=1.25$.

Any H loading experiment requires a monitoring of the loading level actually achieved. There is a close relationship between the H content and the corresponding Pd resistivity; accordingly, such a monitoring can be conveniently carried out through the measurement of the electrical resistivity ratio $\rho = R/R_0$, where R is the actual resistance of the H loaded Pd wire and R_0 the resistance of the wire free both from H and mechanical strains (due to the cold working). Strains can significantly affect the resistance, especially, as in our case, when the wire is obtained by a cold working down to a very thin gage (50 μm). The resistance ratio ρ shows a monotonic increase up to maximum of about 1.8, corresponding to a value of the H/Pd ratio around 0.75. At higher H/Pd ratio, ρ monotonically decreases. At present, such a relationship is known down to a ρ value of 1.43 corresponding to $H/Pd = 0.97$ (Fig. 1). Accordingly, this relationship is currently used to assess the loading level, taking into account that for the high loading levels, which are commonly referred to (i.e. $H/Pd > 0.75$), as lower are the resistance ratios ρ , as higher are the corresponding H/Pd ratios.

In the last years the efforts to achieve values of ρ significantly lower than 1.4 have been largely unfruitful especially as far as the reproducibility of the results is concerned.

A new approach appears to be necessary.

2 – POISONING OF THE CATHODIC SURFACE

Let us consider the following three cathodic reactions which are part of the electrochemical loading process:

- a) $H^+ + e^- \rightarrow H$ Cathodic discharge;
- b) $H \rightarrow H [Pd]$ Pd loading process (React. 1; a,b,c)
- c) $H + H \rightarrow H_2$ Formation and evolution of molecular Hydrogen gas at the cathodic surface.

The reaction *1c*) is in our case a parasitic reaction, which subtracts H to the Pd loading process *1b*). Normally, the recombination reaction *1c*) reduces in such a way the surface activity of the atomic H that loading levels higher than $H/Pd > 0.85$ can be achieved, with poor reproducibility, only by complicated procedures.

It is well known that the surface of particular metals, specially Pt and unfortunately Pd, is able to catalyse the reaction *1c*). Other metals (like Hg, Pb, Zn) strongly inhibit such a reaction. Accordingly, various attempts have been carried out by our group in order to poison the cathodic surface by a galvanic deposition of thin layers of such metals. Unfortunately, the H diffusion speed through them is extremely slow and it has been found difficult to control their thickness as to match the poisoning effect with a reasonably fast diffusion of H into the Pd cathode.

It is also known that even non metallic substances, adsorbed on the metal Pd surface, are able to poison its catalytic properties. With respect to a galvanic metal layer, a thin and porous coating of organic or inorganic material applied on the electrode surface should not affect consistently the diffusion rate of H into the Pd lattice.

In the electrolysis of water the cathodic discharge of the H ions generates an enrichment of the OH^- ions all around the cathode, with a maximum of the pH value just in the proximity of the electrode surface. In such an ambient a precipitation of various metallic ions can occur in form of insoluble hydroxides, carbonates, sulphides. The precipitation should be mainly localised on the cathode surface, because of the surface energy available for the nucleation process.

It appears therefore possible to profit by an intrinsic property of the electrolytic process to induce a subtle and controlled precipitation of inorganic substances on the cathodic surface.

As far as the choice of the metal ions is concerned, all the ions (e.g. Ag, Co, Cu, Fe, Ni, Pb, Sn) liable to discharge below the overvoltage values (about 1.5 V) typically achieved in the H-Pd loading, must be excluded because they would galvanically deposit over the cathode, thereby stopping the H loading (reaction *1b*).

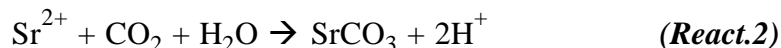
By the way, as regards our final goal, we are aware that most of such ions are normally present in the commercial heavy water.

The alkaline-earth metal ions cannot be discharged, unless the cathodic overvoltage approaches 3V, a value which is practically impossible to reach in the aqueous environment. Moreover these ions can precipitate as hydroxide and carbonates only when the environment

becomes alkaline. *If the starting pH of the solution is in the acid range there will not be any precipitation, but as soon as the electrolysis is started, the increase of the pH value in the proximity of the cathode will induce a hydroxide or carbonate precipitation right on the surface of the cathode itself.*

Considering that alkaline-earth carbonates are less soluble than the corresponding hydroxides, and that carbon dioxide is normally present in the water, carbonate precipitation is largely favoured.

When Sr ions are added, the carbonate precipitation takes place according to the following reaction:



Furthermore, the CO_3^{2-} concentration depends on the pH value according to the relationship:

$$[\text{CO}_3^{2-}] = K_1 \cdot K_2 \cdot [\text{H}_2\text{CO}_3] / [\text{H}^+]^2 \quad (\text{Equat.1})$$

where square brackets stay for the molar concentrations and K_1 , K_2 are the dissociation constants of the carbonic acid:

$$K_1 = 4.3 \cdot 10^{-7}$$

$$K_2 = 5.61 \cdot 10^{-11}$$

It is easily seen that the carbonate precipitation is strongly favoured because of the decrease of $[\text{H}^+]$ ions in proximity of the cathode due to the cathodic H^+ ions discharge (*React.1a*).

In order to check that there are no substantial hindrance to the formation of a layer of carbonates on the cathodic surface, possibly due to bubbling of the H_2 (which may reduce the increase of pH or eventually promote a disbonding of the precipitated layer), a preliminary test has been performed using normal drinking water (in our Laboratory, Frascati, this is particularly rich of calcium bicarbonate) slightly acidified with a small amount of sulphuric acid (until $\text{pH} \approx$

.5). After a 15 minute electrolysis at 25 mA (Pd wire: length 30 cm; diameter 50 μm), a white layer of calcium carbonate was formed on the cathodic surface. The cathode wire was removed from the cell and observed at the optical microscope. The layer was found to be porous and of average thickness around 0.5 mm. The adherence was found so high that, in order to completely clear the wire, a hydrochloric acid attack was required.

Another preliminary experiment (Ref.6) was performed using deionized water with an amount of Ca ions of about 3 mg/litre, about 50 times lower than the Frascati's water (supplied from *CENTRALFARMA*, Montemerano, Italy), in order to strongly reduce the thickness of the coating. This kind of experiment allowed to get R/Ro values lower than 1.43, (i.e. H/Pd values remarkably higher than 0.97) stable for periods of time longer than 10 hours: we get experimental evidence that very small concentrations of Ca ions seemed to be effective.

2.1 – Numerical simulation

Considering that the poisoning is effective in the immediate proximity of the surface, where an intimate contiguity exists between metallic and non-metallic surfaces, in principle, a continuous mono-layer (about 0.5nm of thickness) should be sufficient. In practice, because of the native roughness of cold-worked Pd surface and the growing up of crevices and cracks due

to the increase of the Pd lattice inter-atomic distance (up to 13%), which occurs during the H loading, an average thickness remarkably higher than 0.5 nm seems to be necessary.

In order to acquire some understanding of the parameters which control the amount of precipitation, and therefore the corresponding thickness of the layer, a computer simulation (based on “finite element method”) of the carbonate precipitation process on the cathode during the electrolysis has been developed.

The model considers an electrolytic cell with coaxial cylindrical symmetry: the cathode is a thin wire in the longitudinal axis. The cell has been divided into a number of cylindrical tubes, of the same height of the cell and thickness 250 μm . Each element exchanges ions according to the direction of the current and the direction of the diffusion process (regulated by the difference in concentrations between contiguous elements).

The amount of the exchange is proportional to:

- a)** time interval of the elementary integration step (typically 0.5 ms);
- b)** current density;
- c)** local concentration and transport number values of the various ions;
- d)** diffusion coefficients of the ions.

The mobility values of the ions have been taken from the literature, the diffusion coefficients (D) have been calculated from the corresponding mobility values according to the equation:

$$D = 10^{-7} \cdot \Lambda_{(\pm Z)} \cdot R \cdot T / (Z \cdot F^2) \quad (\text{Equat.2})$$

where:

$R = 8.314 \cdot 10^7 \text{ erg K}^{-1} \text{ mole}^{-1}$;

$T =$ Temperature in K;

$Z =$ Valence of ion;

$F =$ Faraday constant, 96490 Coulomb;

$\Lambda =$ Equivalent ionic conductance at infinite dilution, in water, at 25 $^{\circ}\text{C}$.

We recall that the mobility, in this case, is defined as the “equivalent ionic conductance at infinite dilution”, i.e. completely dissociated electrolyte. The diffusion coefficient D (Equat.2) has been calculated according to [Ref. 7].

Some Λ values of our interest are reported in Tab.1.

Typical simulations for the precipitation of SrCO_3 on the cathodic surface are shown in Fig.s 2 a,b and Fig.s 3 a,b.

Table 1 – Equivalent ionic conductance at infinite dilution, in water, at 25°C.

CATHIONS	Λ_{o+} ($\Omega^{-1} \text{ cm}^2 \text{ eq.}^{-1}$)	ANIONS	Λ_{o-} ($\Omega^{-1} \text{ cm}^2 \text{ eq.}^{-1}$)
H ⁺	349.8	OH ⁻	198.3
Li ⁺	38.6	F ⁻	55.4
Na ⁺	50.1	Cl ⁻	76.35
K ⁺	73.5	Br ⁻	78.1
Mg ²⁺	53.0	I ⁻	76.8
Ca ²⁺	59.5	HCO ₃ ⁻	44.5
Sr ²⁺	59.4	SO ₄ ²⁻	80.0
Ba ²⁺	63.6	CO ₃ ²⁻	69.3

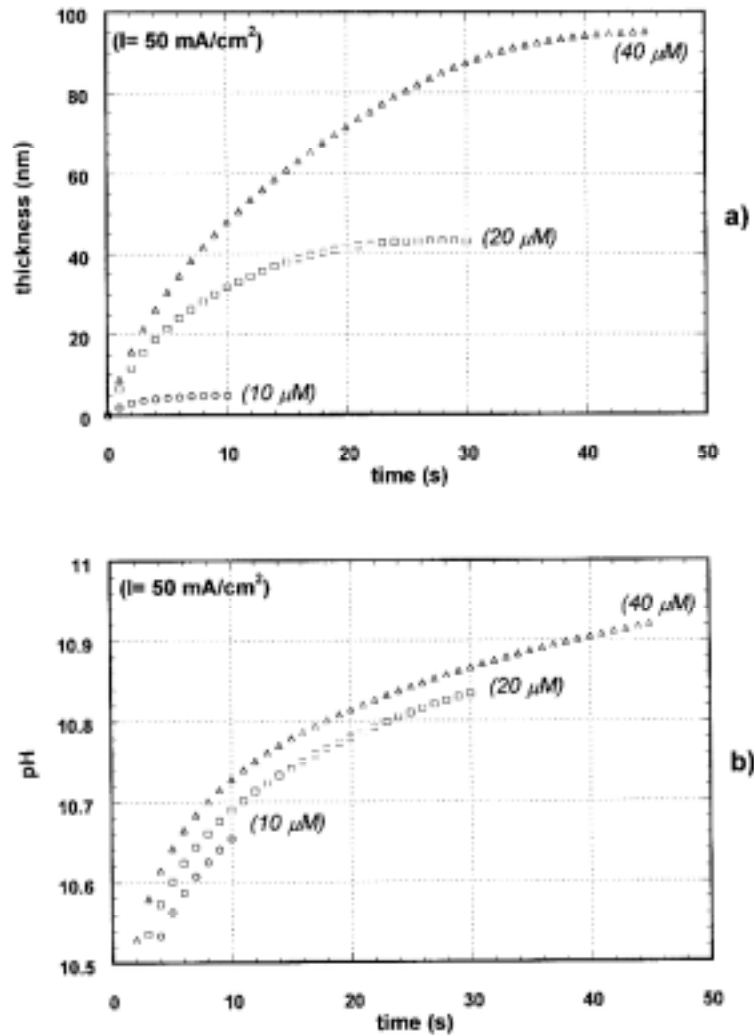


Figure 2 – Computer simulation at constant current density of 50 mA/cm², wire diameter 50 μm. **a)** SrCO₃ deposition thickness, versus time, at 10, 20, 40 μM of Sr²⁺ ions concentrations; **b)** pH variation versus time at 10, 20, 40 μM of Sr²⁺ ions concentrations.

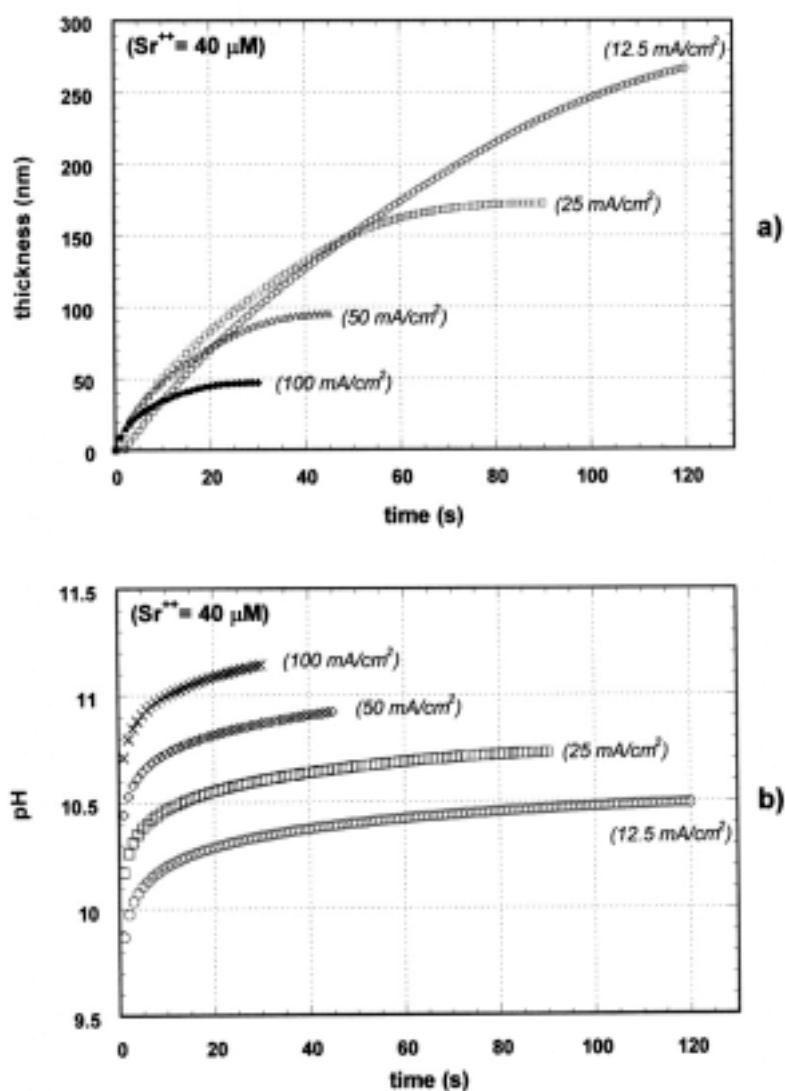


Figure 3 – Computer simulation at constant concentration of $40 \mu\text{M}$ Sr^{++} ion concentration, Pd wire diameter $50 \mu\text{m}$. **a)** SrCO_3 deposition thickness versus time at 12.5, 25, 50, 100 mA/cm^2 current density; **b)** pH variation versus time at 12.5, 25, 50, 100 mA/cm^2 current density.

The results can be summarised as following:

- a)** the pH value in the immediate proximity of the cathode depends on the electrolytic current density and in a few seconds raises to a stable asymptotic value;
- b)** the thickness of the layer reaches, versus time, an asymptotic value which decreases exponentially by increasing the electrolytic current. The density of the coating was assumed equal to the bulk density of SrCO_3 ;
- c)** the thickness of the layer increases by increasing the Sr concentration in the electrolyte before the beginning of the electrolytic process; no (practically) useful precipitation (about 4.8 nm) occurs when this concentration is lower than 10^{-5} M , in our experimental conditions (Pd wire: length 30 cm, diameter $50 \mu\text{m}$);
- d)** it is possible to achieve a very fine control of the thickness.

The not-intuitive behaviours reported at points **a)** and **b)** can be explained through the following cross-linked considerations.

At the cathode there is a strong subtraction of H^+ ions because of their discharge, which

ensues in a rapid increase of the pH value. This generates a rapid increase of CO_3^{2-} concentration (proportional to the square of the OH^- concentration). At the same time there is also an enrichment of Sr^{2+} ions, attracted by the cathodic field. In these conditions the ionic concentration product $[\text{Sr}^{2+}] [\text{CO}_3^{2-}]$ becomes higher than the solubility product and there is precipitation. As the time goes on, more CO_3^{2-} ions are rejected by the cathode than Sr^{2+} ions are attracted, because the mobility of the former is higher than the mobility of the latter. So it happens that the ionic concentration product drops back to the solubility product, thereby arresting the precipitation. This latter process is faster the higher is the current density so, at higher current densities, the precipitation stops earlier and the correspondent thickness of the precipitated layer is smaller.

3 – EXPERIMENTAL APPARATUS

The schematic diagram of the experimental set-up is shown in Fig. 4. The electrolytic cell is a glass cylinder containing 2.4 litres of electrolyte. The cathode is a thin Pd wire (diameter 50 μm , length 30 cm) while a Pt wire with a diameter of 500 μm and a length of 30 cm is the anode. The anode was set at a distance of 5 cm from the cathode. The cell was kept at the fixed temperature of 20°C.

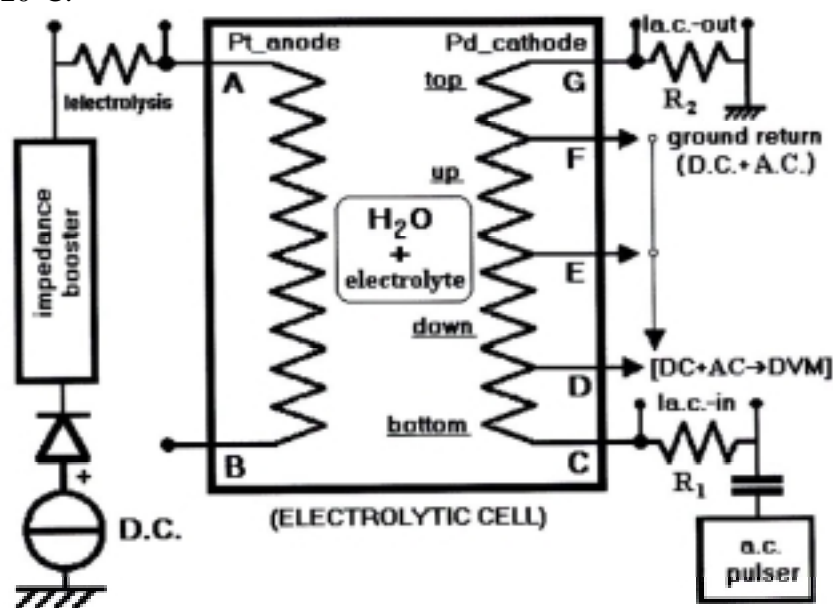


Figure 4 - Apparatus set-up.

Electrolysis cell is composed by anode-cathode electrodes fully immersed into an electrolytic solution ($\text{H}_2\text{O}+\text{HCl}+\text{Alkaline-Earth}$ soluble salt): resistance is measured for “up” and “down” Pd segment wires. External electronic devices are divided in power supply block (DC generator and impedance booster) and measurement block (ac-pulser, ground-return connection and several picks-up connected to Digital VoltMeter). High precision and stability resistances have been used to acquire circuit currents (of D.C. and a.c. generators).

For a sake of experimental simplicity in these experiments, we adopted the parallel geometry of the wire instead of the coaxial one, as reported in the numerical simulation. It can be shown that the electrical paths, about electric field homogeneity at the cathode, are similar to coaxial geometry when the anode-cathode distance is $\gg 20$ radius of the cathode.

The low value for the cathode diameter was chosen both to enhance the H absorption by increasing the surface/volume ratio and to allow for higher current densities which favour the

increase of the pH value at the surface of the cathode, thereby enhancing the carbonate precipitation. Finally, the high value of resistance of very thin wires improves the precision of the measurements.

The cell was supplied by a DC current generator. An impedance adapter circuit (impedance booster in Fig. 4) was connected in series to avoid toward the anode, through the DC power supply, leakage of the AC current used at the cathode for its resistance measurement.

The AC resistance measurement set-up was made by applying an AC-coupled square wave generator to the cathode, able to impose an AC current of about 40 mA r.m.s. at a frequency of 1000 Hz. This current was monitored by means of the voltage drop across the resistance R_1 ($I_{(AC)}$ -in), while, by measuring the voltage across R_2 ($I_{(AC)}$ -out), it was checked the absence of significant current leakage toward the anode. Precise resistance measurements require both high cathode resistance and very low conductivity of the electrolyte. In order to check the influence of the electrolyte on the measured value of the wire resistance, this was measured both in the absence and in the presence of the electrolyte: the differences found were well within 1%. Further tests were performed with DC power supply OFF and ON (anodic condition in respect to Pd wire to avoid H absorption) in order to check the effectiveness of the active booster: it worked properly (<1% error) up to 300mA, 250 Volts.

The assessment of the different loading values in different cathode regions was achieved, as shown in Fig. 4, by continuously monitoring the AC voltage drop, picked up in correspondence of the segments CD (=bottom), DE (=down), EF (= up), FG (= top), of length of 2.5, 12.5, 12.5, 2.5 cm, respectively.

The Pd wire resistance was measured using the “4 contacts method” in order to eliminate the effects of spurious resistance measurements both due to connections cables and resistance contacts at the 2 ends (C, G) of the Pd wire.

Before the electrolytic process, the Pd wire was heated in air (Joule heating up to 600 mA), slowly from room temperature up to about 700 °C (light-red colour) and back: total step-like process (heating and slow cooling) lasted about 1 hour. The procedure guarantees both the desorption of eventual H previously absorbed and relaxes mechanical stresses due to the cold working down to 50 μ m.

The electrolyte was prepared with bi-distilled water (with total impurities lower than 0.3 mg/l), containing the “natural” CO_2 amount ($\approx 1.0 \cdot 10^{-5}$ Molar), by adding HCl or H_2SO_4 (of the order of $5 \cdot 10^{-5}$ equivalents) as to form a slightly acidic solution (hereafter called the “ground solution”) with $\text{pH} \approx 5$.

In order to control the alkaline-earth carbonate precipitation, Ca and Sr ions were added, as chlorides or sulphates, in the order of some 10^{-5} moles. Because of the high resistivity of the resulting solution, the cathode-anode voltage necessary to obtain currents between 10 up to 100 mA is of the order of 20 - 150 Volts.

4 – RESULTS AND DISCUSSION

Preliminary loading tests were performed using the “ground solution” without any additions. The obtained loading levels were not satisfactory, correspondent to ρ values around 1.7 (H/Pd= 0.80). Additions of alkaline-earth ions (we tested Mg, Ca, Sr, Ba) have resulted in substantially lower values of ρ and correspondingly higher loading values. Among these, the best results were obtained with Ca and Sr and are reported hereafter.

In Figs 5 and 6, measurements of electric resistance ratios of the “up” (EF) and “down” (DE) wire sections (see fig. 4) are presented as function of time, adopting the Ca^{++} ($7.0 \cdot 10^{-5} \text{ M}$) and Sr^{++} ($3.5 \cdot 10^{-5} \text{ M}$) electrolytes, respectively. The graphic representations of the loading process (ρ versus log time) show a first stage, lasting about 300 seconds, during which ρ goes from 1 up to a maximum of 1.78-1,80, corresponding to a loading level $x=H/Pd=0.75$, according to the Baranowski diagram. Afterwards, as the loading proceeds the value of ρ decreases. The course of this decrease shows a “shoulder”, after which ρ drops asymptotically toward minimum values, usually different in the various segments of the wire and depending on the alkaline-earth ion added to the “ground solution”.

In Ca-based electrolyte after 12 hours, loading corresponding to $\rho_{\text{up}}=1.28$ and $\rho_{\text{down}}=1.38$ were obtained (see Fig. 5).

In Sr-based electrolyte the course is very similar, the final values obtained were even better: $\rho_{\text{up}}= 1.13$ and $\rho_{\text{down}}=1.15$ (Fig. 6).

At these values, the effective cathode loading cannot be determined directly from the Baranowski curve. A reasonable and conservative extrapolation indicates exceptionally high loading levels, around $x=0.99$ or even higher.

In order to check the correctness of the results, the electrolytic process was stopped to allow the complete de-loading of the cathode and to control that the ρ values go back to the maximum and then decrease to the initial $\rho=1$ value. Fig. 7 shows a complete de-loading of a cathode previously loaded down to $\rho=1.13$. The complete de-loading required about 16 hours. Several loading/de-loading cycles were performed and substantially confirmed the obtained results.

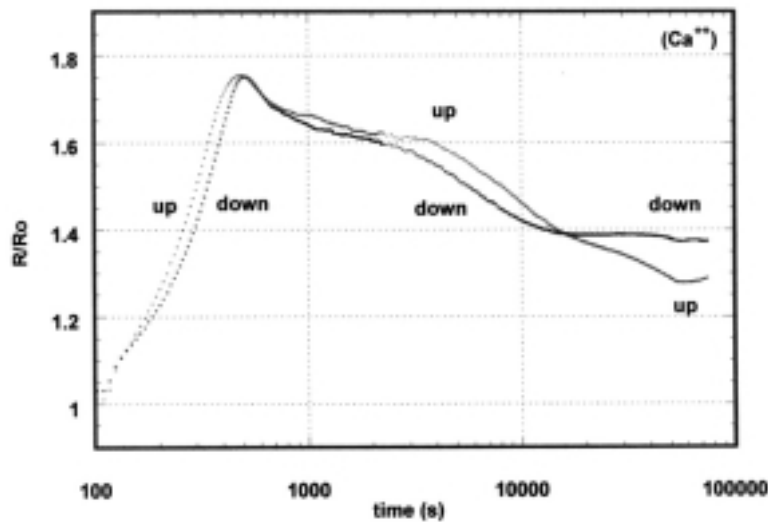


Figure 5 – Calcium loading trend.

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

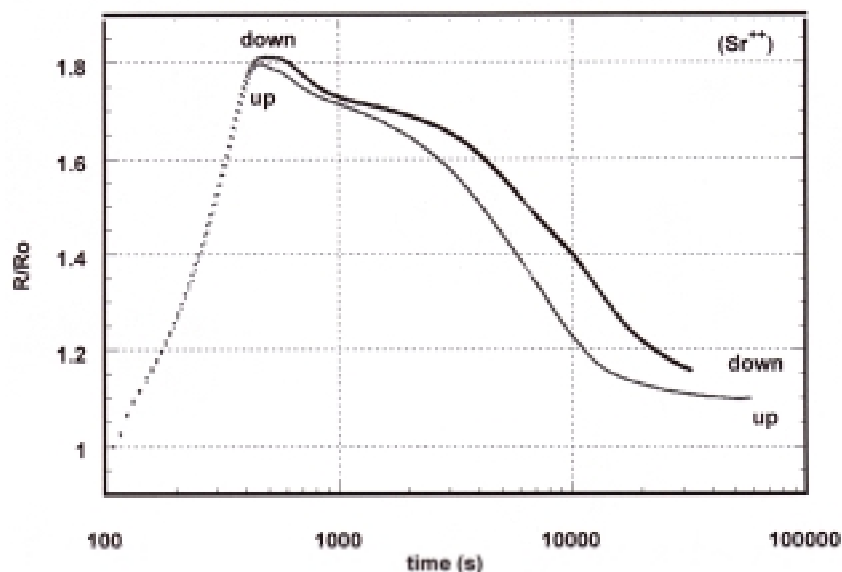


Figure 6 – Strontium loading trend.

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

4.1 – Evidence of a new phase in the system Pd-H

Experiments with the Sr containing electrolyte have shown a remarkable phenomenon: once the ultimate loading level was reached, corresponding to $\rho=1.13$, the electrolysis was interrupted and the wire was allowed to de-load toward the maximum value of ρ : the electrolysis was restarted at $R/R_o=1.7$ ($H/Pd=0.8$). It was observed that the re-loading was so rapid that in about 20 minutes the value of ρ dropped to 1.2. The subsequent lowering to the starting value of 1.13 was reached within the next 40 minutes (Fig. 8).

The occurrence of very rapid re-loading after the first loading is highly reproducible, in the sense that it happens every time ρ becomes lower than 1.4.

If the wire is made to lose H beyond the $\rho=1.80$, that is under $x=0.75$, a clear “shoulder” appears in the course of the de-loading (Fig 7), meaning that some process which slows down the de-loading is taking place. If the de-loading is carried out beyond this “shoulder” the re-loading process is found to be as slow as any first loading. Furthermore, such a “shoulder” is observable only when the loading has been carried out down to $\rho < 1.4$ (i.e. $H/Pd > 0.97$).

The described behaviour suggests that, during the first loading, a slow process of nucleation of a solid phase in the Pd-H system may take place. This new phase should be able to absorb hydrogen at a relatively high rate. Metastable nuclei of this phase would then “survive” a partial de-loading (before the above said “shoulder”) and then allow for the rapid re-loading, while if the wire is de-loaded further-on, they disappear and the whole process, including their slow formation, has to start again.

This is also supported by the presence of another “shoulder” referred to in Fig. 6, and characteristic of the first loading. It appears reasonable to think that in the “first-loading shoulder time” there is a slow nucleation of this new phase at $x > 0.9$. The fact that an analogous “shoulder” presents itself during de-loading at $x \approx 0.7$, strongly suggests the occurrence of a hysteresis which can be just bound first to the nucleation and growth of a phase and then to its disappearance.

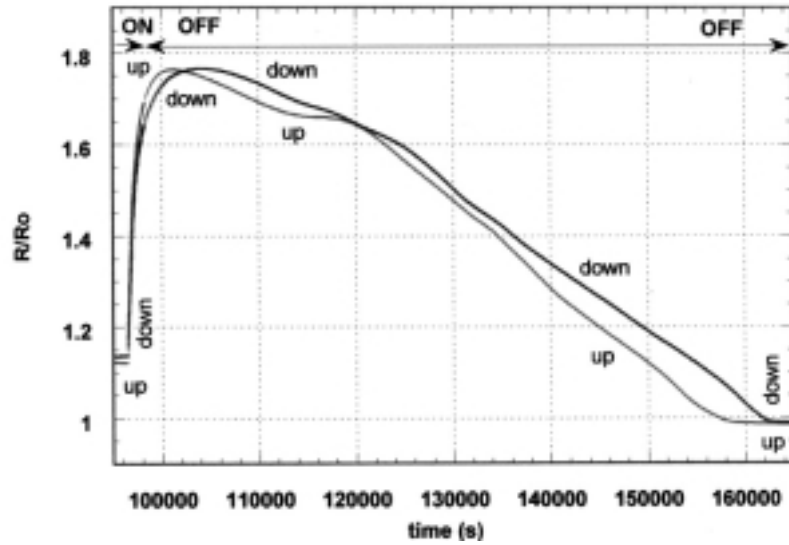


Figure 7 – Deloading trend.

The plot shows Hydrogen deloading versus time. Electrolysis current has been switch off (“OFF” condition) after “ON” condition ($R/R_o=1.13$ at $23\text{ }^\circ\text{C}$) and in about one hour loading peak was achieved ($R/R_o=1.77$ at $23\text{ }^\circ\text{C}$). A visible deloading shoulder lasts, about half hour, at $R/R_o=1.65$; full deloading process requires about 16 hours: both “up” and “down” wire segments return to their initial R_o resistance values.

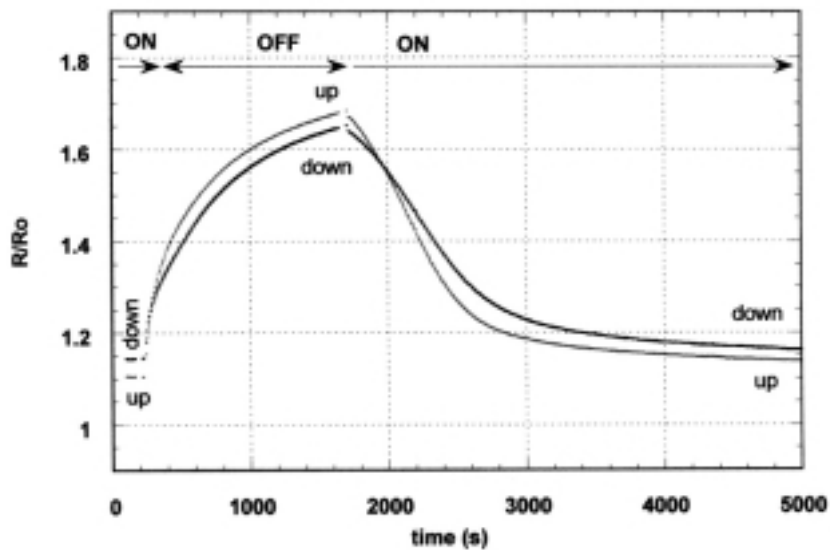


Figure 8 – Fast re-loading test.

Typical test of OFF/ON current cycle: starting from a high loading condition ($R/R_o=1.10$ at $22\text{ }^\circ\text{C}$), 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/R_o value. Sometimes this procedure, operated cyclically, can be useful to achieve high loading values.

4.2 – The thermal coefficient of the resistivity in the Pd-H system

Let's take the following equation as a first good approximation of the resistivity growth rate with temperature:

$$R_t = R_0 \cdot (1 + \alpha t) \quad (\text{Equat.3})$$

where:

R_t is the resistivity at the temperature t expressed in $^{\circ}\text{C}$;
 R_0 is the resistivity at 0°C ;
 α is the resistivity thermal coefficient (RTC).

Previous assessments in the range of x ($=\text{H}/\text{Pd}$) between 0 and 0.70, have shown that the RTC starts with a value of $4.1 \cdot 10^{-3} \text{ }^{\circ}\text{C}^{-1}$ at $x=0$ and increases between $x=0$ and $x=0.08$, up to $4.35 \cdot 10^{-3} \text{ }^{\circ}\text{C}^{-1}$, then decreases monotonically as x increases (Fig. 9). Our measurements are substantially consistent with those in the literature [ref. 7]. At $x=0.75$ the value found for α is $1.7 \cdot 10^{-3} \text{ }^{\circ}\text{C}^{-1}$, which is very close to the value of $(1.5\text{--}1.6) \cdot 10^{-3}$ obtainable by extrapolating the values of Fig. 9.

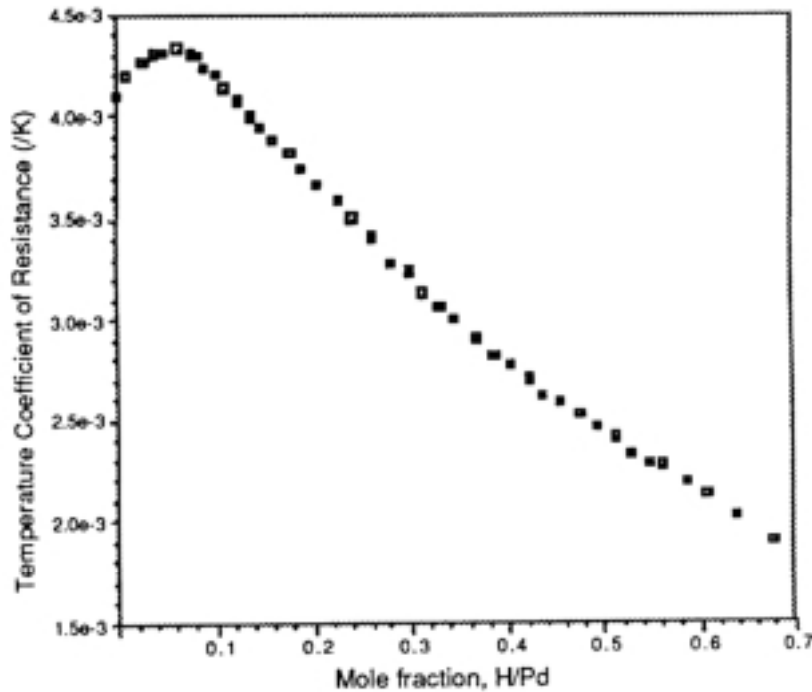


Figure 9 - *H/Pd* resistance temperature coefficient.

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

If in the Pd-H system a new phase nucleated at higher loading levels, it is probable that also the RTC would undergo a significant variation. In other words, if beyond certain H/Pd values there is a significant change in the RTC course, it would be reasonable to think that a new phase has nucleated and grown.

A correct assessment of the value of α requires that the value of $x = H/\text{Pd}$ remains stable while the temperature is made to change and the correspondent measurements of the resistance are effected.

The stability of the loading values has been obtained by profiting of the barrier effect produced by electrolytic coatings on the cathode, with metals which were found to strongly inhibit the intake of H (see reaction *Ib*, above), therefore able to hinder its outgoing as well. Among the possible metals the choice fell over Hg because it forms *amalgams* with Pd (0.06 wt% at 20°C , Ref. 9). Such room-temperature formation of solid solutions allows for complete and rather uniform coatings of the "physical" surface and, as extra bonus, the covering of possible surface defects like, for example, micro-crevices.

In practice, once a sufficiently high loading level was achieved ($\rho=1.16$), 10^{-5} moles of HgCl_2 have been added to the electrolyte, while the current was maintained at about 20mA. When the value of ρ had dropped to 1.10, due to the contribution of the Hg coating (notice that the resistivity of Hg is ten fold higher than that of the pure Pd; the thickness of the Hg film was estimated to be around 5 μm), the current was cut-down. It was observed that the ρ value remained stable for several hours at room-temperature, showing that the Hg coating reduces strongly the H de-loading. The temperature of the cell was then raised up to 100 °C and the electrolyte made to gently boil for one hour. After cooling down to 20 °C it was found that the value of ρ differed from the value reached before heating of a few percent. The wire was then taken out of the cell and put into liquid nitrogen for storage, before the measurements for the assessment of the value of α at $\rho=1.16$.

In Fig. 10 there are reported the values of ρ between 20 and 100 °C, while in Fig. 11, the temperature range is extended down to 77 °K. It can be seen that the results are well aligned one another. The average value for α was found to be $3.2 \cdot 10^{-3} \text{ }^\circ\text{C}^{-1}$, which is definitely higher than the minimum value reported in Fig. 9 correspondent to a value of $\rho=1.8 \cdot 10^{-3} \text{ }^\circ\text{C}^{-1}$, beyond which no value for α is available. The contribution of the Hg film can be easily estimated to be of a few percent and therefore cannot significantly affect the validity of the results.

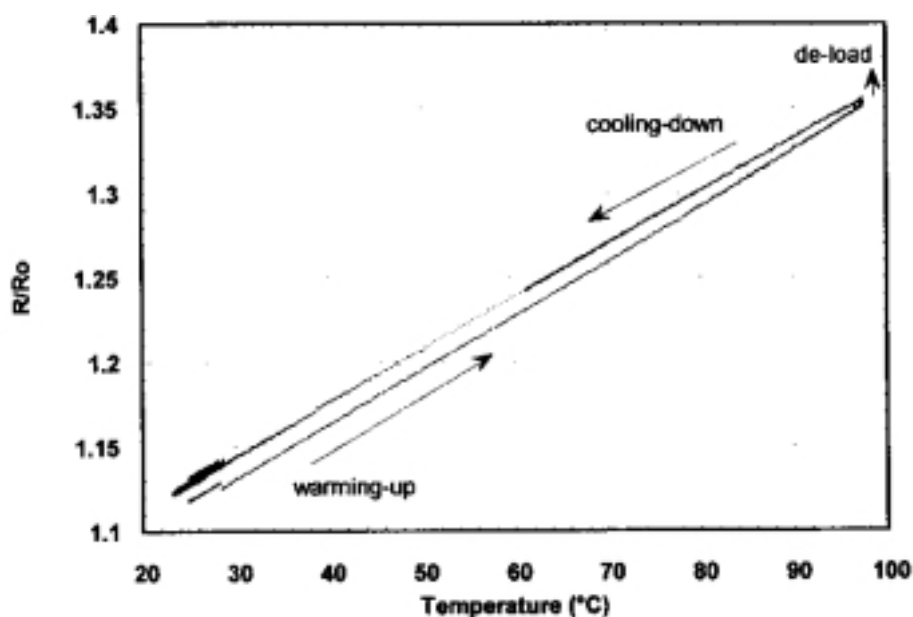


Figure 10 – Hg coated wire, high temperature measurements. After achieving $R/R_o=1.1$, the Pd surface has been coated with Hg (by HgCl_2 electrolysis) and a cycle of “high temperature test” was performed. Only a weak de-loading occurred at 100 °C (2 hours at ebullition state). In this experiment the temperature coefficient (α_{T_w}) was estimated to be $3.2 \cdot 10^{-3} \text{ }^\circ\text{C}^{-1}$.

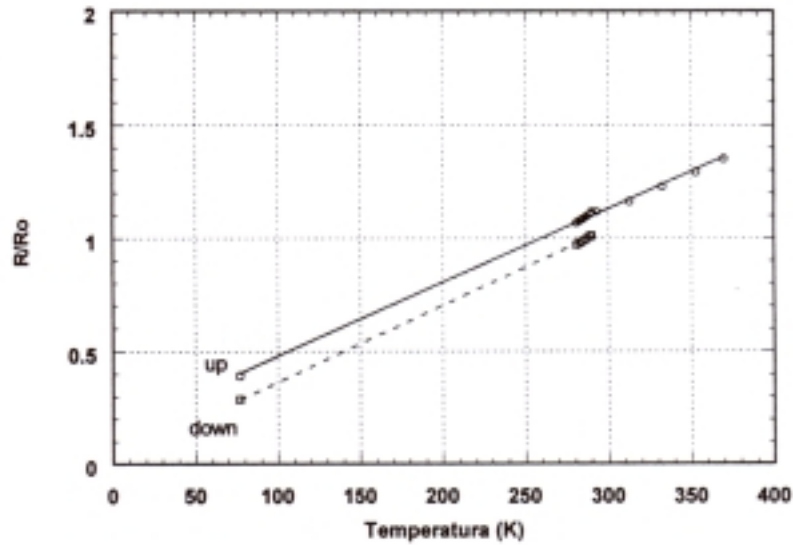


Figure 11 – Hg coated wire, test at very low temperatures. After achieving $R/R_o=1.1$, the Pd surface was coated with Hg and a cycle of low temperature test (up to liquid nitrogen) was performed. For sector “up” both high and low temperatures data are available: they are roughly on the same line. In the range $77\div 300$ K the temperature coefficient, α_T , was estimated to be $3.3 \div 3.4 \cdot 10^{-3} \text{ }^\circ\text{C}^{-1}$.

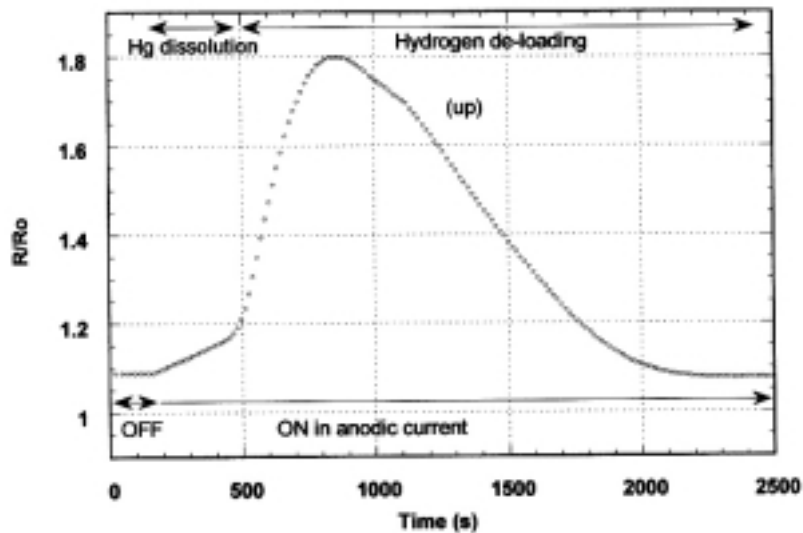


Figure 12 – Hg removing and Hydrogen de-loading. Starting from very high loading ($R/R_o=1.1$), anodic electrolytic current was applied: in few minutes Hg deposit (about $4\div 6 \mu\text{m}$) at the Pd surface was time-linearly removed. Later on, hydrogen come out from the Pd following the expected trend (peak at about $R/R_o \approx 1.8$, shoulder at $R/R_o \approx 1.7$) up to the initial resistance value ($R/R_o \approx 1$).

After the measurement campaign the wire has been put back in the cell and anodically de-loaded. In Fig. 12 the ρ value is reported against time at constant anodic current. It can be seen how, at the beginning of the electrolysis, there is an interval of time during which there is an increase of ρ between 1.1 up to 1.18 with a slope proportional to the current. This is clearly due to the dissolution of the Hg coating. When this is completely gone, the slope becomes steeper, due to H de-loading.

Going back to fig. 9, in the range of $x = \text{H/Pd}$ between 0.1 and 0.7, the value of α

decreases regularly as x increases. According to our measurements, beyond $x=0.7$ there is a definite inversion of the course of α versus x , and this is in favour of the hypothesis of the nucleation and growth of a new phase.

5 – CONCLUSIONS AND FURTHER DEVELOPMENTS

A thin layer of alkaline-earth carbonates on the Pd surface appears to be effective in order to achieve very high H loading.

We have shown that, when $\rho > 1.4$, it is possible to observe the occurrence of two symmetrical shoulders during the loading and de-loading processes. Such a behaviour strongly suggests that a new metastable phase is able to nucleate during the loading process.

Direct measurements of the thermal coefficient of resistivity α , in the H ultra-rich region of the Pd-H system, have been carried out. Previous measurements have shown that such α coefficient regularly decreases with the increase of the H/Pd ratio; our measurements demonstrate that α sharply increases when the H/Pd ratio is higher than 0.97, in agreement with the hypothesis of the nucleation of a new phase.

Successful experiments, i.e. showing H/Pd ratio $\gg 0.97$, were over 20 in our Laboratory. They were made changing each time the Pd wire (99.97% purity, batches BR 5545_'96 and BR 8582_'97): all come from Johnson Matthey Company (J/M).

The new procedure described in this report has been successfully reproduced in others 2 well equipped and experienced Laboratories:

- a) Pirelli Cavi e Sistemi S.p.a, Advanced Research Lab., Milan (Italy); group led by F. Fontana; the *same batch* of Pd we used and that they provided to us;
- b) Stanford Research Institute International, Stanford (USA); group led by M.C. H. McKubre; different batches of Pd coming both from J/M and Enghelard.

The “replication” experimental results were reported during “4th Asti Workshop on Anomalies in Hydrogen/Deuterium Loaded Metals”, 22-24 Oct.1999, Asti (Italy) and are publishing by Italian Physical Society as Conference Proceedings.

As stated in the introduction, our final goal is the overloading of deuterium in palladium and we do hope that it will be possible to transfer to D the loading procedure developed for H loading.

Obviously, we'll have to use the commercially available heavy water. The total impurities (amount and type) usually present in the “reactor grade” heavy water (isotopic purity $>99.94\%$) are quite larger in comparison to those in the bi-distilled light water and of different “nature”. Up to now, in addition to inorganic compounds (about 10 mg/litre), were detected organic compounds (about 10 mg/litre, Ref. 10) and even several kinds of biological contaminants (Ref. 11). It will be therefore necessary to develop specific procedures in order to conveniently purify the reactor grade heavy water.

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7 – REFERENCES

- [1] Baranosky B. “Hydrogen in Metals” G.Alefed and J Voelkl (eds) Top. Appl. Phys 29, 1978, pp.157-200.
- [2] Baranosky B., Tkacz M., Majachrzak S., “Molecular Systems under High Pressure, R. Pucci and G. Piccitto (eds), Elsevier Science Publ.1991, pp. 139-156.
- [3] Hemley R. J., Mao H. K., Hanfland M., *ibid.* pp. 223-244.
- [4] Silvera I. F., Eggert J.H., Goettel K.A., Lorenzana H.E., *ibid.* pp.181-200.
- [5] Ashcroft N.W. *ibid.* pp. 201-222.
- [6] F. Celani et al., Società Italiana di Fisica, LXXXIV Congresso Nazionale 1998, Salerno, poster IX-31, pg. 152.
- [7] Patrizio GALLONE, “Principi dei processi elettrochimici”, Tamburini Editore Milano, 1970, pp. 197—199, (IN ITALIAN).
- [8] B.Baranowski and R.Wisniewshi, Phys. Stat. Sol.35, 1969, pg. 539.
- [9] Comprehensive Inorganic Chemistry, Pergamon Press, 1973, pp. 283—285.
- [10] Naoto Asami, Institute of Applied Energy, Tokyo (Japan), May 1999; private communication.
- [11] F. Celani et al. “A study on the electrochemistry parameters to achieve reproducible H/Pd and D/Pd values in relation to ‘anomalous’ excess heat; proteobacteria contamination problematic”. Presented at.: *4th Asti Workshop on Anomalies in Hydrogen/Deuterium Loaded Metals*, 22-24 Oct.1999, Asti (Italy), publishing by Italian Physical Society as Conference Proceedings.