

A Review of Experimental studies about Hydrogen over-loading within Palladium wires ($H/Pd \geq 1$)

A. Spallone ⁽¹⁾, A. Marmigi ⁽¹⁾, F. Celani ⁽¹⁾, P. Marini ⁽²⁾, V. Di Stefano ⁽²⁾

(1) INFN-LNF, Via E. Fermi 40, 00044 Frascati, (Italy)

(2) EURESYS, Via Lero 30, 00129 Roma, (Italy)

ABSTRACT

Many hundreds of systematic tests have been performed at Frascati National Laboratories in order to achieve very high concentration of hydrogen (overloading) in palladium wires.

The electrodes (cathode in central position: Pd wires 50 or 100 μm thick and anode: Pt wires 0.5 mm thick) were placed in a coaxial geometry into a small cylindrical electrolytic cell.

A special study has been performed in order to optimise the electrolytic solution based on H_2O (400 cm^3) + HCl ($50 \div 200 \mu\text{M}$) and small amounts (tenth of μM) of salts (carbonate or sulphates) of one of these alkaline and alkaline-earth metals: Li, Na, K, Ca or Sr. Very small amounts (hundreds of nM) of HgCl_2 has been added to the solution. The addition of Hg ions has been crucial to achieve very high and stable H/Pd overloading.

To increase the reproducibility of the over-loading a special loading protocol based on high/low (or OFF/ON) cathodic current cycles has been tested successfully.

The H/Pd loading ratios have been estimated by the on-line measurement of the normalised wire resistance (R/R_0).

The loading results are quite satisfactory: $H/Pd \geq 0.97$ ($R/R_0 \leq 1.30$; input electrolytic current/voltage: 7V, 5mA) are typically reached and sometimes $H/Pd \geq 1$ ($R/R_0 \cong 1.15$; input current/voltage: 11V, 2.5 mA) has also been achieved. The reproducibility of the results is quite satisfactory.

1. Introduction

Over the past ten years, a great deal of effort has been made by the LNF Group to achieve very high H/Pd loading ratios (overloading) by using electrolysis with Pd wires as cathodes in acid solutions extremely diluted with light/heavy water. Loading procedures have been optimized and very high H/Pd loading values ($H/Pd \cong 1$) are been reached, using a very small quantity of Ca or Sr added to electrolytic solution [1,2,3].

Recently a systematic study has been performed to test alkaline elements (such as Li, K, Na or Ca, Sr) in composed salts (carbonate or sulphate) in relation to H/Pd overloading in our loading procedures.

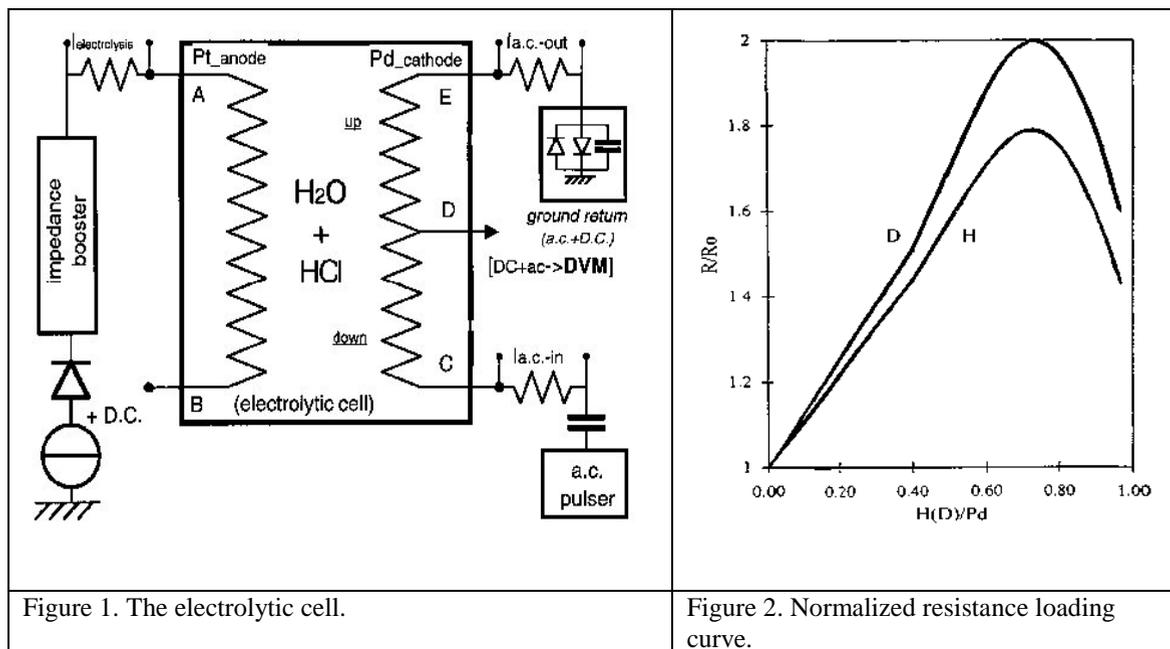
The role of Hg in increasing overloading and achieving stable and reproducible loading has been shown in our previous papers. In this study we have tested the addition of Hg ions to electrolytes containing alkaline and alkaline-earth salts, elements which have produced the best loading results.

In all these tests only light water has been used for the electrolyte. We have already shown that when heavy water is used, the loading procedures capable of insuring high D/Pd ratios are different and considerably more complicated. [4]

2. Apparatus

The electrolytic cell is a glass beaker filled with about 400 cm³ of an acid solution containing 2 ml of HCl at 10 μM/ml. The electrodes are thin, long wires (20 cm length) placed parallel 2 cm apart. The cathode is Pd, 50 μm diameter; the anode is Pt, 0.5 mm diameters. The Pd wire is composed by 2 equal parts (top and bottom) connected to 3 pickups. The cell is located into a thermostatic water bath set at room temperature (22°C). The cell, bath and room temperatures are continuously recorded (Fig. 1).

To obtain a reference value of H/Pd loading we use the normalised Pd resistance versus hydrogen (or deuterium) molar fraction of Pd (Fig. 2). The peak value is: H/Pd=0.75, R/Ro=1.78 (with hydrogen) and D/Pd=0.75, R/Ro=2.0 (with deuterium). In the published literature, the highest loading ratio obtained by the electrolytic is H(D)/Pd=0.95 at R/Ro=1.4 (1.6) [5,6,7,8].



3. Loading results

Table 1 shows a summary of all electrolysis tests performed changing the alkaline elements (Na, Li, K, Sr, Ca) and compounds (carbonate and sulphate) in the electrolysis solution. We see that the best loading results occur when Sr is used particularly in sulphate compound ($R/R_0 = 1.2$, $H/Pd \cong 0.97$). We observed that the thickness of the layer of strontium sulphate deposited on the Pd cathode surface is more difficult to control during electrolysis compared to strontium carbonate.

We developed a special procedure during electrolysis operating with electrolytic current in low/high (L/H) regime and switching on/off the power supply [9]. This procedure plays an important role to increase the loading. This is clear, even though we do not yet have full comprehension of the phenomena occurring onto the Pd surface.

Table 1. Systematic tests performed using alkaline elements (I and II group of periodic table)

Electrolyte (NO-Hg)	CO₃	SO₄
H₂O + HCl (50 μmol) <i>Loading at R/Ro- peak: (R/Ro=1.75, H/Pd=0.67)</i>	----	----
+ 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 (OLD TEST)	Concentration: 70 μmol Procedure: Middle current Result: R/Ro=1.30 , H/Pd=0.96	----

In Fig. 3 and Fig. 4, R/Ro versus time is shown for the over-loadings using Sr in carbonate and sulphate compounds. The role played by L/H procedure to reach the overloading in the case of SrSO₄ should be noted (Fig. 4b).

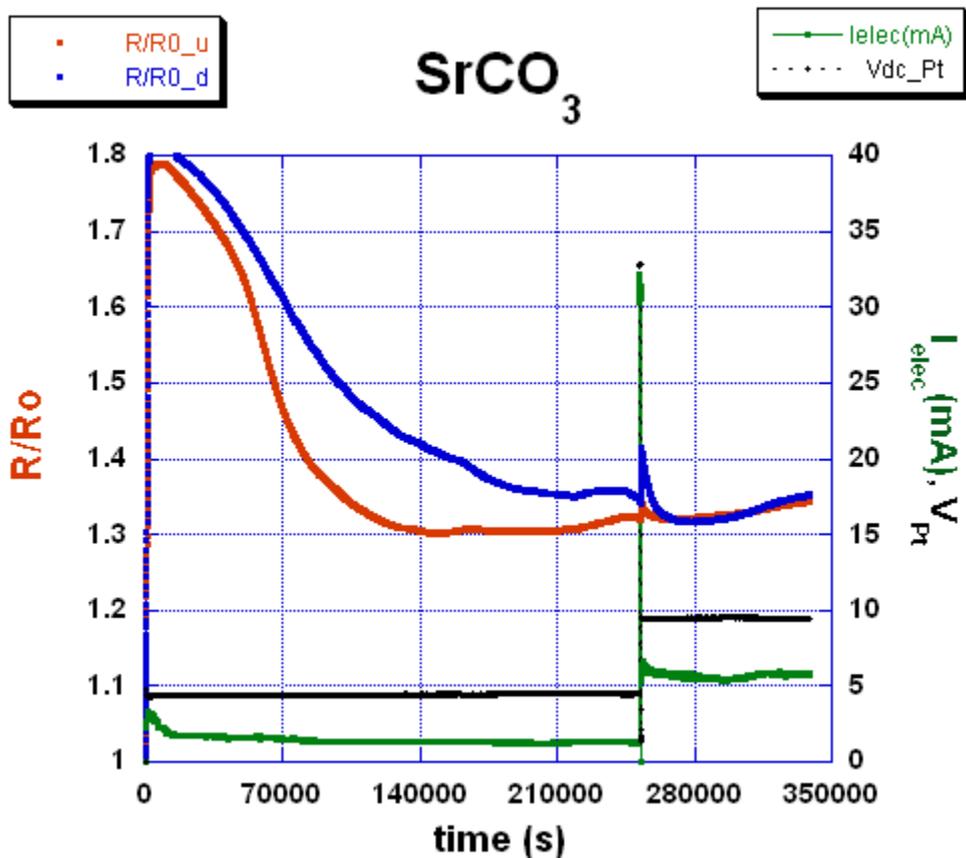
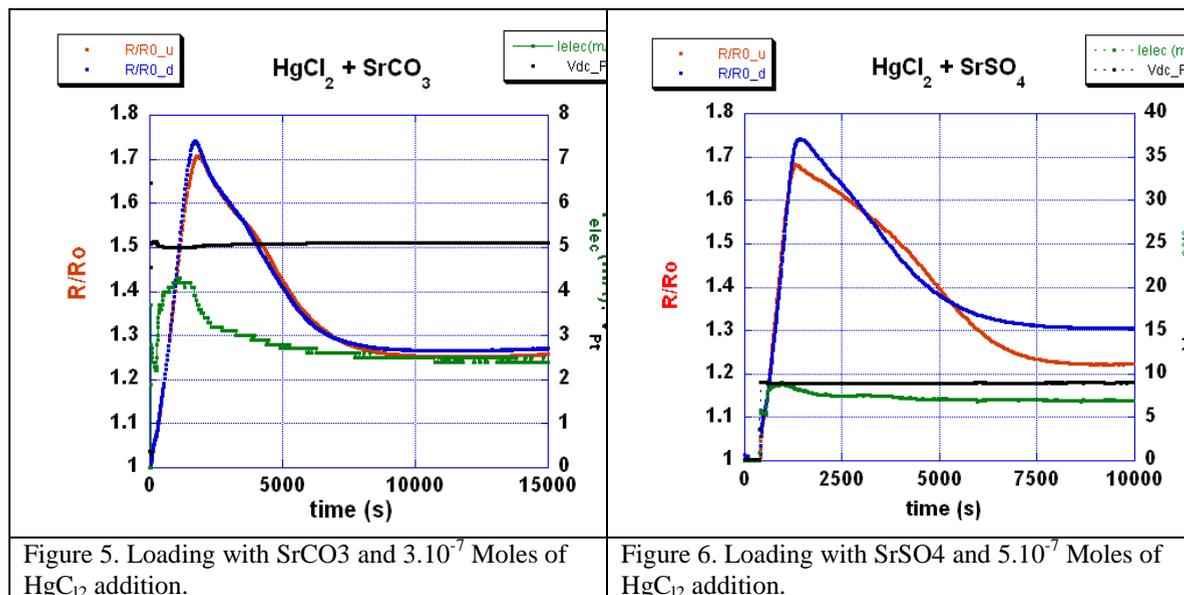
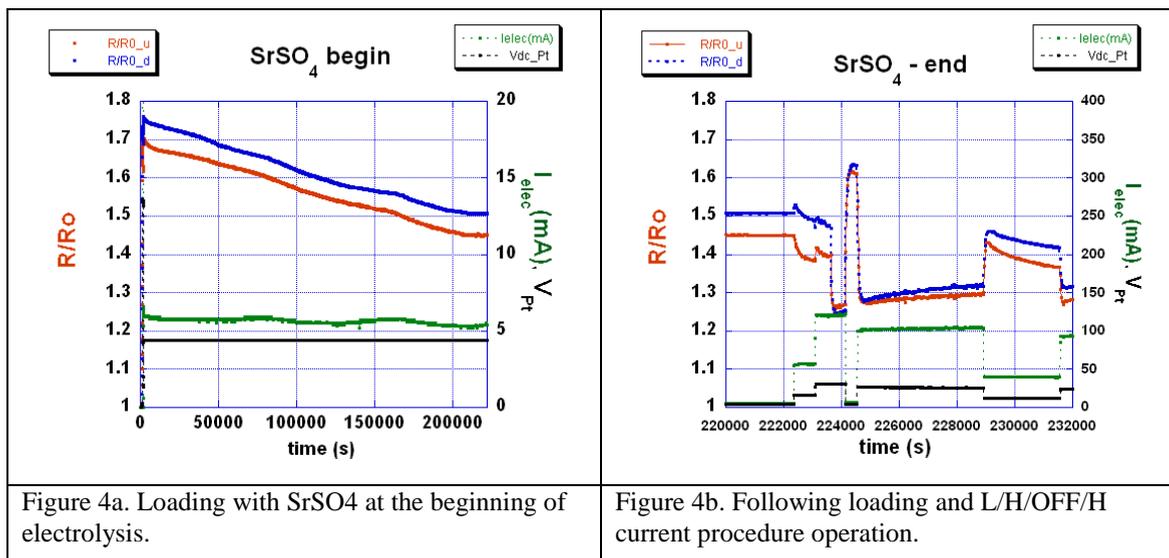


Figure 3. Loading with SrCO₃, and L/H current procedure implementation.

The effectiveness of Hg ions in achieving stable and reproducible over-loading is shown in Fig. 5 (HgCl₂ + SrCO₃) and Fig. 6 (HgCl₂ + SrSO₄). In Fig. 5, Hg⁺⁺ is added in very low amounts, about of $3 \cdot 10^{-7}$ Moles. In Fig. 6, relating to the sulphate, we added a little more HgCl₂ ($5 \cdot 10^{-7}$ Moles) and slightly higher over-loading was achieved. We have to take into account that the addition of larger amounts of Hg ions tends to produce a thicker deposit on the Pd surface, which has the effect of blocking the diffusion of hydrogen into the Pd bulk.



It is known that the solubility of the alkaline earth carbonates, because of the weakness of the carbonic acid, strongly increases by increasing the acidity of the solution. Whereas the solubility of the corresponding sulphates is only slightly dependent on the pH value.

During electrolysis, the region around the cathode is more alkaline than the rest of the solution.

For this reason, calcium or strontium carbonates, completely dissolved in the electrolyte, can precipitate in the form of a thin layer. This only happens on the cathode surface. In order to produce a proper thin layer on the cathode surface when calcium or strontium sulphate are used, it is necessary to add just enough of these salts to the electrolyte obtain an almost-saturated solution. Because of the increase of pH in the cathode region, it is possible to obtain the proper thickness of the salts layer on the cathode surface.

In case of inadequate thickness of the layer on the cathode surface it is possible to make the following corrections:

Too high solubility (very thin deposit)	Too low solubility (very thick deposit)
<i>High current needed</i>	<i>Low current needed</i>
<i>Alkaline solution needed</i>	<i>Acid solution needed</i>

Conclusions

In order to achieve overloading, very dilute electrolytes should be used. The addition to the electrolyte of very small amounts of carbonate and/or sulphates of Ca and Sr, together with extremely small amounts of Hg ions, is strongly effective. The thickness, structure and composition of the thin layer of precipitated salts on the cathode surface, which seems to be the main factor causing the overloading, has to be analysed in more detail.

Further studies are in progress to optimise the composition of the electrolyte, in particular when heavy water is used.

References

1. 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.*” INFN: LNF-00/006 (P), 6 March 2000.
2. A. Spallone, F. Celani, P. Marini and V. di Stefano, “*Experimental studies to achieve H/Pd loading ratio close to 1 in thin wires, using different electrolytic solutions.*” Proceedings of the 9th International Conference on Cold Fusion, “Condensed Matter Nuclear Science” pg 319-322, Beijing (China), 19-24 May 2002; Edited by Xing Z. Li. ISBN: 7-302-06489-X
3. A. Spallone et al., “*An overview of experimental studies about H/Pd over-loading with thin Pd wires and several different electrolytic solutions.*” Proceedings of the 11th International Conference on Cold Fusion, Marseilles (France), 01-05 Nov. 2004; Edited by J.P.Biberian. World Scientific, pg. 392-404; ISBN: 981-256-640-6.

4. F. Celani et al. "*High Hydrogen loading into thin Palladium wires through precipitate of alkaline-earth carbonate on the surface of the cathode: evidence of new phases in the Pd-H and unexpected problems due to bacteria contamination in the heavy water*". Proc. of the 8th International Conference on Cold Fusion. Lerici, 21-26 May 2000. Edited by Editrice Compositori, Pg. 181-190, ISBN: 88-7794-256-8
5. J.C. Barton, F.A. Lewis and I. Woodward (1963), *Trans. Faraday Soc.* **59**, 1201.
6. B. Baranowski and R. Wisniewski, *Phys. Stat. Sol.* **35**, p.539 (1969).
7. B. Baranowski et al., *J. Less Common Met.*, **158**, p.347 (1990).
8. M.C.H. McKubre et al., "*Calorimetry and Electrochemistry in the D/Pd System*, "Proceedings of the First Annual Conference on Cold Fusion, Salt Lake City, Utah, March 23-31, 1990.
9. A. Spallone, F. Celani, P. Marini and V. di Stefano. "*Measurements of the Temperature Coefficient of Electric Resistivity of Hydrogen Overloaded Pd.*" Proceedings of the 12th International Conference on Cold Fusion, "Condensed Matter Nuclear Science" pg 404-410, Yokohama (Japan), 27 Nov. - 02 Dec. 2005; Edited by Akito Takahashi, World Scientific , Condensed Matter Nuclear Science series, pg.404-410; ISBN: 981-256-901-4.