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**A REVIEW OF EXPERIMENTAL STUDIES ABOUT HYDROGEN OVER-LOADING
WITHIN PALLADIUM WIRES (H/Pd ³ 1)**

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Abstract

Many hundred of systematic tests have been performed, at Frascati National Laboratories, in order to achieve very high concentration of Hydrogen (overloading) into Palladium wires. The electrodes (cathode in central position: Pd wires 50 or 100 μm tick; anode: Pt wires 0.5mm tick) were placed in a coaxial geometry into a small cylinder electrolytic cell.

A specific 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 the following alkaline and alkaline-earth metals: Li, Na, K, Ca or Sr. Very small amounts (hundred of nM) of HgCl_2 has been also added to the electrolyte. The addition of Hg ions has been crucial to achieve very high and stable overloading.

To increase the reproducibility of the overloading a peculiar 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/Ro).

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

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1. INTRODUCTION

In the past ten years, a lot of efforts have been done, by LNF Group, to achieve very high H/Pd loading ratios (overloading) by using Pd wires as cathode; the electrolyte was a very diluted (light/heavy water) acid solution. Loading procedures have been tuned up and very high H/Pd loading values ($H/Pd \approx 1$) are been reached, by adding very small amounts of Ca or Sr ions added to electrolytic solution [Ref. 1, 2, 3].

Recently, a systematic study has been performed to test the effectiveness (in terms of H/Pd ratios) of the addition to the electrolyte of small amounts of alkaline and alkaline-earth salts (carbonates and sulphates of Li, K, Na and Ca, Sr).

The role of Hg, to increase, stabilize and make reproducible the hydrogen overloading has been shown in our previous papers; in this study we have tested the addition of Hg ions to those electrolytes (containing alkaline and alkaline-earth salts), which have produced the best loading results.

In all the tests only light water was used for the electrolyte. We have already shown that, when heavy water is used, the loading procedures, capable to insure high D/Pd ratios are different and considerably more complicate [Ref. 4].

2. APPARATUS

The electrolytic cell is a glass beaker filled with about 400 cm³ of an acid solution containing 2ml of HCl at 10 μ M/ml; the electrodes are two parallel (2cm distant) wires (20cm length); the cathode was a very thin Pd wire (diameter 50 μ m); the anode was a Pt wire (0.5mm diameter). The Pd cathode is divided into 2 equal parts (up and down) connected to 3 picks up. The cell is located into a thermostatic water bath, set at room temperature (22°C). Cell, bath and room temperature are continuously recorded (Fig. 1).

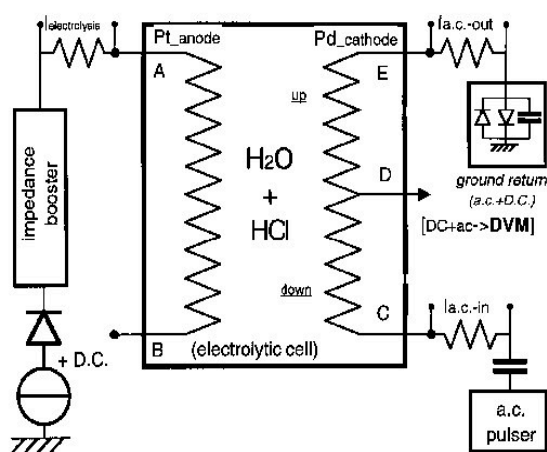


Fig. 1 - The electrolytic cell.

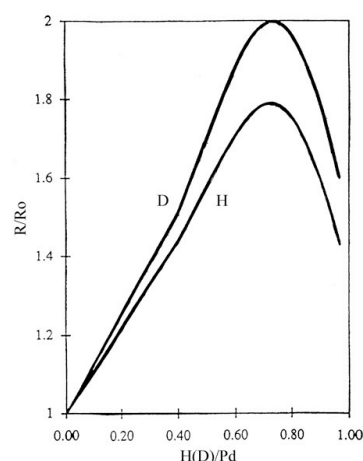


Fig. 2 – Normalized resistance loading curve.

For the assessment of the H/Pd loading we use the relationship between the normalised Palladium resistance and the H(D)/Pd atomic ratio (Fig. 2). Peak value is: H/Pd=0.75, R/Ro=1.78 (Hydrogen); D/Pd=0.75, R/Ro=2.0 (Deuterium). The largest published maximum

loading ratio obtained by the electrolytical techniques are $H(D)/Pd=0.95$ at $R/Ro=1.4$ (1.6) [Ref. 5, 6, 7, 8].

3. LOADING RESULTS

We report in Tab. 1 a summary of all the tests performed by changing the salts added to the electrolyte. We can observe that the best loading results occur when Strontium salts (particularly sulphate) are used ($R/Ro= 1.2$, $H/Pd\cong 0.97$). We noticed that the thickness of the layer of Strontium sulphate, deposited on the Pd cathode surface, is more difficult to be controlled during the electrolysis with respect to the Strontium carbonate.

We developed a peculiar electrolytic loading procedure, which operates with a low/high (L/H) regime of current density and/or with a switching on/off (ON/OFF) of the power supply [Ref. 9]. Even though we have not yet a full comprehension of the complex phenomena occurring at the Pd surface, we found that this procedure is very effective for the achievement of a high (H-D/Pd loading ratio).

Tab. 1 – Systematic tests performed using alkaline an alkaline earth salts.

<i>electrolyte (NO-Hg)</i>	$CO_3^{=}$	$SO_4^{=}$
H₂O + HCl (50 μ mol) <i>Loading at R/Ro-peak: (R/Ro=1.75, H/Pd=0.67)</i>	----	---
Na₂CO₃	Concentration: 20mg/400ml Procedure: L/H current Result: R/Ro=1.6 , H/Pd=0.9	----
Li₂CO₃ - Li₂SO₄	Concentration: 200 μ mol Procedure: Low current Result: R/Ro=1.52 , H/Pd=0.92	Concentration: 30 μ mol Procedure: L/H current Result: R/Ro=1.40 , H/Pd=0.94
K₂CO₃ - K₂SO₄	Concentration: 25 mg/400ml Procedure: Low current Result: R/Ro=1.50 , H/Pd=0.92	Concentration: 10mg/400ml Procedure: L/H/L Result: R/Ro=1.43 , H/Pd=0.94
SrCO₃ - SrSO₄	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
CaCO₃ (OLD TEST)	Concentration: 70 μ mol Procedure: Middle current Result: R/Ro=1.30 , H/Pd=0.96	----

In Fig. 3 and Fig. 4 (R/Ro versus time) are shown the results achieved by using Sr carbonate and sulphate; the role played by the L/H procedure in the case of SrSO₄ is clearly evident (Fig. 4b).

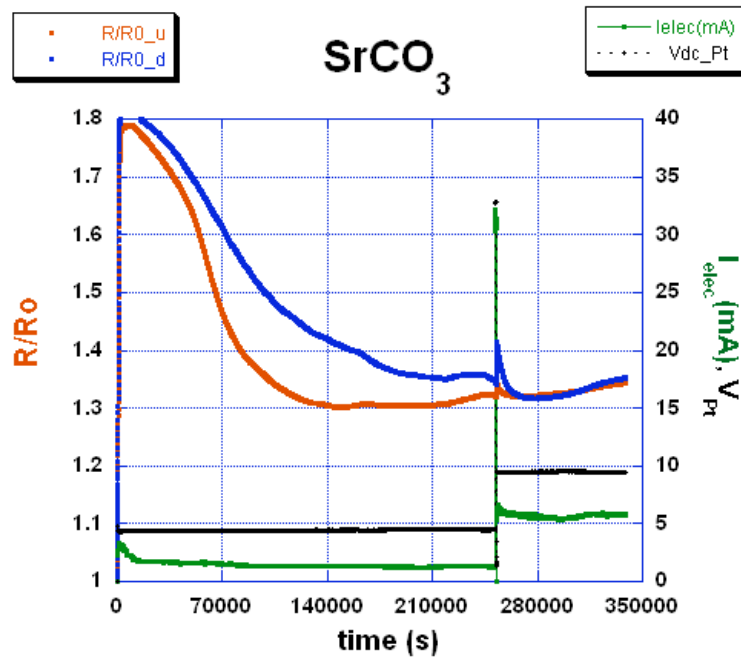


Fig. 3 - Loading with $SrCO_3$, and L/H current procedure implementation.

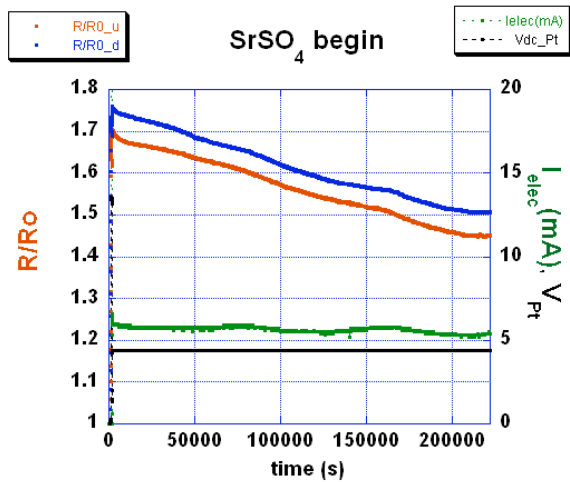


Fig. 4a – Loading with $SrSO_4$. at the beginning of electrolysis.

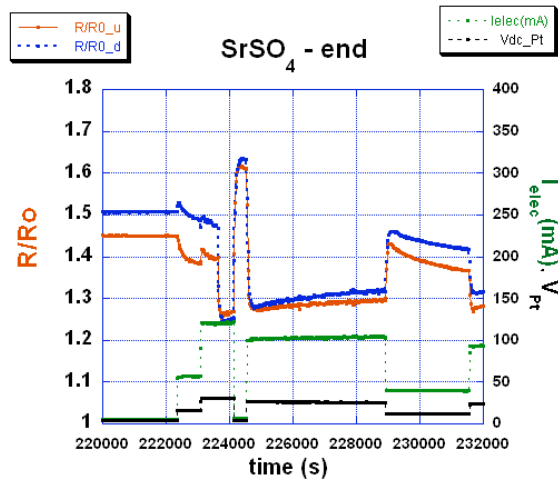


Fig. 4b – Following loading and L/H/OFF/H current procedure operation.

The effectiveness of Hg ions to achieve stable and reproducible over-loading is shown in Fig. 5 ($HgCl_2 + SrCO_3$) and Fig. 6 ($HgCl_2 + SrSO_4$). In Fig. 5, Hg^{++} is added in a very low amount (about $3 \cdot 10^{-7}$ Moles). In Fig. 6, relating to the sulphate, we added a little more quantity of $HgCl_2$ ($5 \cdot 10^{-7}$ Moles) and a little higher overloading was achieved. We have to take into account that the addition of larger amounts of Hg ions tends to produce a higher thickness of the layer deposited at the Pd surface, as far as to cause a complete block for the diffusion of Hydrogen into the Pd bulk.

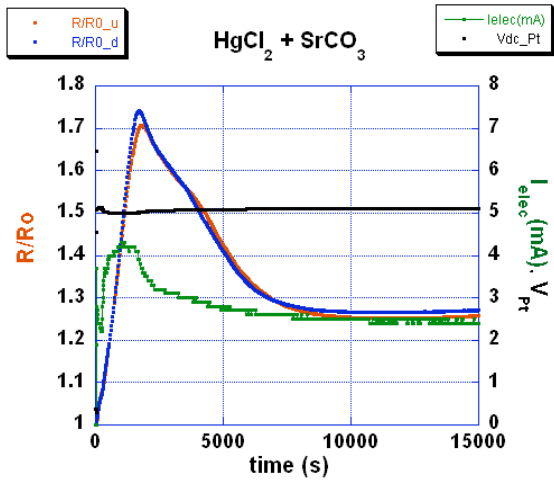


Fig. 5 – Loading with $SrCO_3$ and addition of $3 \cdot 10^{-7}$ Moles of $HgCl_2$.

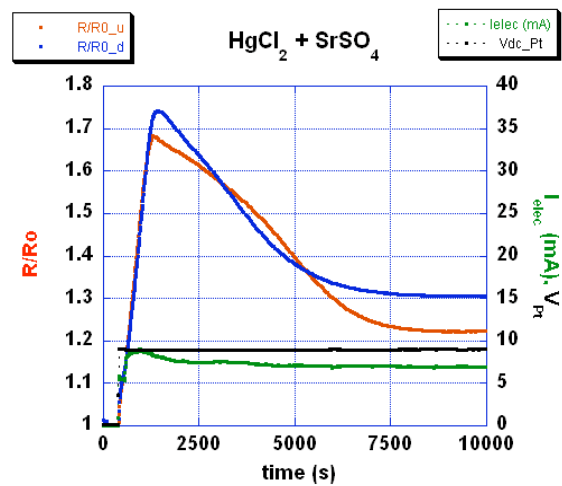


Fig. 6 – Loading with $SrSO_4$ and $5 \cdot 10^{-7}$ Moles of $HgCl_2$ addition.

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

For this reason Calcium or Strontium carbonates, completely dissolved in the electrolyte, can precipitate, in form of a thin layer, just and only 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 such an amount of these salts to the electrolyte, as far as to obtain an almost saturated solution. In this case only, 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 tick deposit)
<i>High current request</i>	<i>Low current request</i>
<i>Alcaline solution request</i>	<i>Acid solution request</i>

CONCLUSIONS

In order to achieve overloading, very diluted 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 responsible of the overloading, has to be analysed in more details.

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

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