

Anomalous heat Generation by surface oxidized Pd wires in a hydrogen atmosphere

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ABSTRACT

Thin Pd wires (diameter 50 micrometers) surface oxidized through joule heating have been loaded in a hydrogen (H₂) atmosphere at pressures in the range 1 - 10 bar. The atomic ratio H/Pd reached in the experimental conditions has been evaluated through its relationship with the electrical resistivity of hydrogen-loaded Pd. It was found that the loading rate of the surface oxidized Pd wires is exceptionally higher than with the untreated ones (full loading in a few minutes as compared with several hours). It was also observed that surface treated wires with H/Pd ≥ 0.75 do not lose hydrogen even when joule heated at temperatures up to about 150°C in a Hydrogen atmosphere. When the wire temperature exceeds 150°C (applied power about 12.4 W) anomalous heat generation (about 3.5 W) was detected.

During an experimental test, the wire was powered with stepwise increased higher power for 500 - 600 seconds at each step, followed by a period of zero power. It was observed that when the power was cut off after powering at 14 W, the wire spontaneously heated for about 70 seconds releasing an estimated heat of 1650 ± 160 J, corresponding to 3940 ± 400 Kcal per mole of Pd. Peak power was $\simeq 16$ W. The wire resistance spontaneously reaches a value $R/R_0 = 2.40$ and then slowly dropped to the original value of 1.80 at room temperature.

In a second experimental test with the same wire similar phenomena have been observed although of lower intensity but lasting over 3000 seconds. After 16 W powering for 500 seconds, the power was cut off. Again the wire heated spontaneously releasing an anomalous heat of 3600 ± 360 J, corresponding to some 13200 ± 130 Kcal per mole of Pd. The peak power was $\simeq 3$ W. The wire resistance increased spontaneously up to $R/R_0 = 2.01$ and then slowly decreased down to 1.90.

Such experiments were performed in 2005 and presented briefly by F. Celani at ICCF12 (Yokohama, Japan 2005). The present paper is in-depth analysis of previous experimental data.

1. Introduction

In a recent paper (J. P. Biberian [1]) it is shown that consistent excess heat is produced when the side walls of a thin Pd tube are crossed by a D₂ flow. The heat generation only occurs if the tube has been previously oxidised in air (at 500°C).

Since 1990, INFN Frascati Labs (Celani *et al.*) developed an experimental procedure for the electrochemical loading of thin Pd tubes. [2] The surface oxidation of the Pd tube (by electrolysis), and later wires, with co-deposition of “proper impurities”, was just one of our innovative technologies previously developed and adopted, more recently, for gas loading tests. We found that proper surface oxidation treatments allowed for a surprisingly rapid loading rate, in experiments conducted in 1994 with “Takahashi-style” Pd plates loaded electrochemically (ICCF5, Montecarlo 1995).

More surprisingly, we observed in 2005 that thin Pd wires (diameter of only 50 μm), warmed up very quickly ($<10\text{ms}$) by Joule heating when in-situ under pressurized H_2 atmosphere. Temperatures rose to about 200°C . The loading ratio remained unchanged only if the surface was previously oxidised and stabilised. In comparison, without proper surface treatments, using DC current with a current density up to 50000 A/cm^2 , Joule heating only caused the H_2 releases from the wire, which followed the usual Pressure-Temperature-Concentration curves.

Preliminary tests performed in a hydrogen atmosphere were called for because the price of this gas is about three orders of magnitude lower than the cost of deuterium. In general, by adopting proper experimental conditions, we were able to check whether comparable (or better) H/Pd loading ratios might be achieved via gas, compared to loading ratios previously obtained via electrolysis.

Because we knew that the tests performed in November 2005 in H_2 (instead of D_2) produced unimpressive loading ratios ($\text{H/Pd} \approx 0.75$ by resistivity methods, not a volumetric Sievert method), we were sure that no emission of excess heat could be expected. When a spontaneous warming up of the wire at “zero applied power” was recorded, we conservatively (and perhaps too hurriedly) attributed the phenomenon to chemical heat generation (absorption), although the amount seemed too large in comparison to a conventional chemical reaction and/or lattice energy.

After the ICCF12 we planned to make more accurate experiments but adverse circumstances prevented that, including: repeated damage to the experimental set-up, budget cuts, man-power reduction, other experiments of higher priority.

On the basis of the work of Jean Paul Biberian [1] and the references therein (especially the experiments of X. Z. Li at Tsinghua University) our old gas loading tests [3] have been revised and deeply analysed: they are the main argument of the present paper.

2. Experimental Setup

Experiments were performed employing a 30 cm long Pd wire (thickness 50 μm , weight 7 mg) inserted in a pressure-tight steel vessel, with mirrored external surfaces. This minimizes heat exchange with the external environment, and it allows high pressure



experiments to be performed. Although pressurized hydrogen gas has excellent thermal conductivity, for the specific tests we performed, that effect is not very significant.

Figure 1. Experimental setup

The resistance of Pd metal is a function of its hydrogen content [4] and is, in principle, the easiest way of determining the state of the Pd electrode (loading ratio H/Pd) as the experiment proceeds.

During the experiment we warmed up the wire by means of a DC current (joule heating) so much that we were able to measure the Pd wire resistance by introducing an AC component, as shown in Fig. 2.

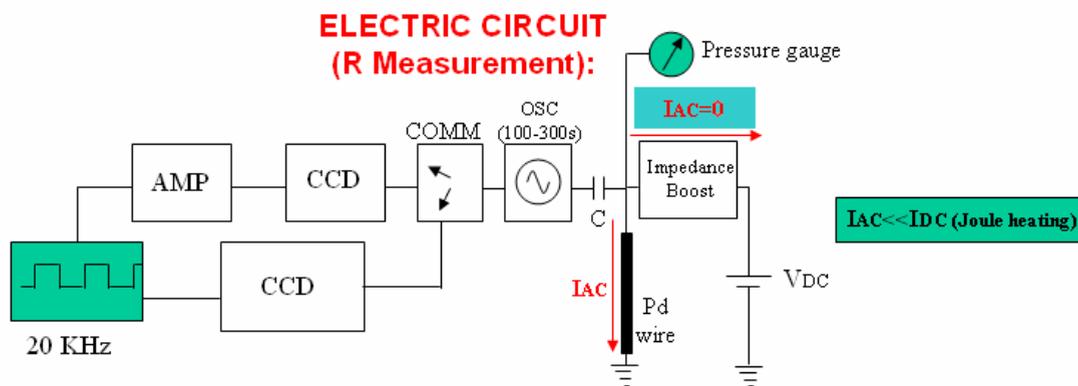
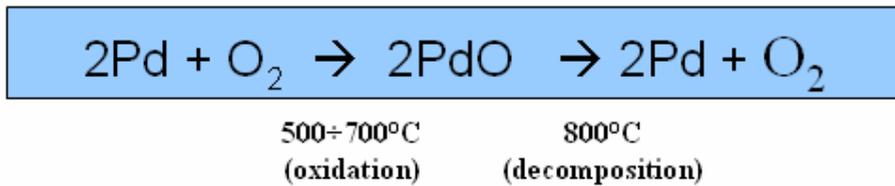


Figure 2. Electric circuit for the measurements of Pd resistance and for joule heating.

3. Results

The Pd wires (thickness 50 μm) selected for the gas loading tests were previously oxidised by joule heating in air, according to the following procedure:

Basic Oxidation/Reduction cycles in air by JOULE HEATING



After the joule heating oxidation, the PdO layer, formed on the wire surface, was stabilised with a further heat treatment. The aim of this treatment, which is still under development, is to prevent (or at least minimise) the collapse due to coalescence and crystallization of the thin and defective Pd layer, ensuing from the H_2 reduction of the previous PdO layer.

In order to prevent coalescence, stabilizing surface treatments were effected.

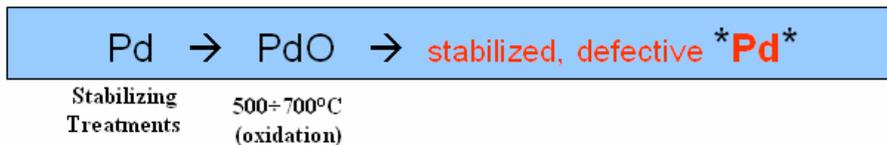
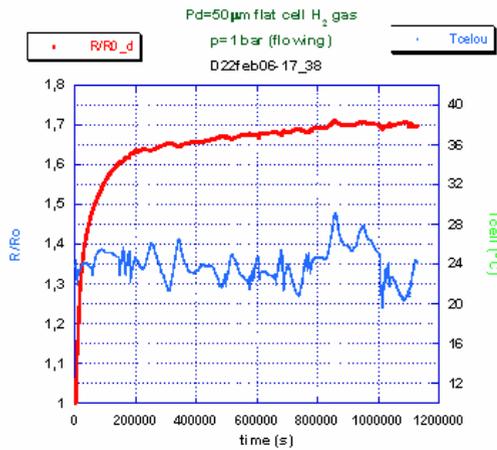


Fig. 3a shows a typical loading rate of a Pd wire in Hydrogen atmosphere (1 bar, fluxing). Thermodynamic equilibrium is reached in about 1Ms (H/Pd ratio = 0.75, at 20°C).

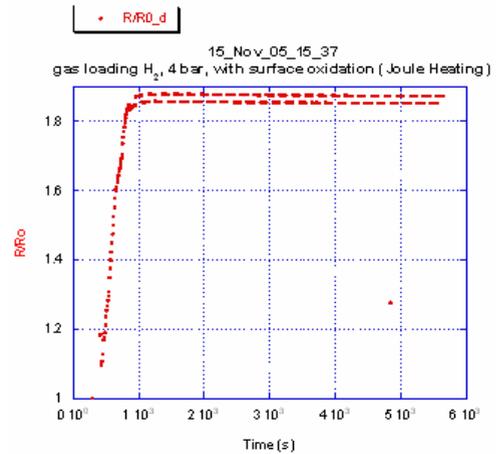
It is well known [4, 5] that such a value corresponds to the maximum of the $R/R_0 = f(\text{H}/\text{Pd})$ curve, where R is the actual electrical resistance of the wire and R_0 is the resistance of the virgin wire ($\text{H}/\text{Pd} = 0$). By comparison, Fig. 3.b shows the loading rate of a similar wire, oxidized in air, with no stabilizing treatment. The loading rate of the wire reaches (equilibrium reached in about 500 sec). Fig. 3.c shows the extremely fast loading rate for a Pd wire oxidized in air and surface-treated. The time to reach thermodynamic equilibrium is just 80 s.

1) Blank: gas loading in H₂ atmosphere, 1bar flux, without any kind of surface treatment. This test is performed in a flat cell, with gas flux (1 bar), and with a 50µm diameter Pd wire



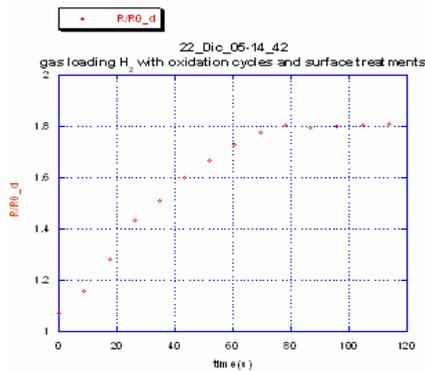
1Ms to thermodynamic equilibrium (R/Ro=1.7, H/Pd≈60%)

2) Gas loading in H₂ atmosphere, 4bar, no flux, only with oxidation cycles, without surface treatment



500 s to thermodynamic equilibrium (R/Ro=1.85, H/Pd≈75%)

3) Gas loading in H₂ atmosphere, 3.6 bar, no flux, with surface treatments and oxidation cycles



80 s to thermodynamic equilibrium (R/Ro=1.8, H/Pd≈75%)

Figure 3. Increase in loading rate with oxidation-stabilizing treatments.

In order to evaluate the degassing rate as a function of temperature, the wires were oxidised with the procedure described above and preloaded at $H/Pd = 0.75$, and kept constantly in contact with the H_2 atmosphere. They were then warmed up by joule heating with currents of increasing intensity. The results are presented in Fig. 4.

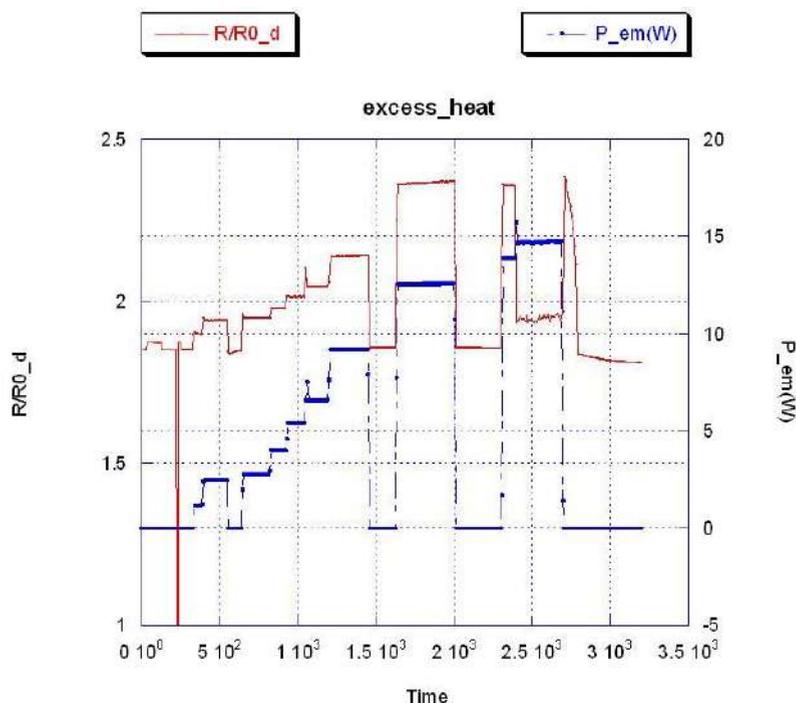


Figure 4. The wire was warmed up with amperage of increasing intensity

In Fig. 4 the sudden change of resistance is shown (red line) due to the applied electrical power (blue line). The starting R/R_0 value of the wire (30 cm long and $50 \mu m$ thick) was 1.85 ($H/Pd \approx 0.75$); the gas temperature was $35^\circ C$. It appears that, when the power is on, the equilibrium temperature of the wire, because of its small thermal capacity, is reached almost instantaneously (within the 10 second cycle of the data acquisition system). When the power is off the cooling down of the wire to the ambient temperature ($35^\circ C$) is as rapid as the heating.

In Table 1, the tests shown in Fig. 4 has been labelled from 1 to 12. The table shows the R/R_0 values, the relative applied electrical power and the calculated wire temperatures.

Table 1. R/Ro values, applied electrical power and wire temperature for the 12 tests shown in Fig. 4.

Tests	1	2	3	4	5	6	7	8	9	10	11	12
R/Ro	1.85	1.95	1.98	2.02	2.06	2.14	1.85	2.37	1.85	2.36	1.92	2.39→1.82
Watt	0	2.6	3.9	5.2	6.7	9.2	0	12.4	0	13.6	14.7	0
t wire (°C)	35	67	76	89	102	128	35	201	35	?	?	?

Tests 1 through 9 will be analysed and discussed first. Tests 10, 11 and 12, the most important ones, will be treated separately.

Both Fig. 4 and Table 1 show that no degassing occurs when the electric current is crossing the wire. In fact, when the power is switched off, in tests 7 and 9, the R/Ro value comes back immediately to its starting value (R/Ro = 1.85).

By increasing the applied power (Fig. 3), the R/Ro values (tests 1 through 6) increase linearly, according to the relationship:

$$\frac{R}{R_o} = 0.03 \cdot W + 1.86 \quad (1)$$

The linear correlation: R/Ro = f(W) directly demonstrates that, in spite of the increase in temperature of the wire due to the supplied power input, the loading ratio (H/Pd = 0.75) remains unchanged; (i.e: no degassing occurs). In fact, let us consider the following two expressions, which correlate the wire temperature with the wire resistance and the applied electrical power:

$$\frac{R_t}{R_o} = R_o \cdot (1 + \alpha \cdot t_w) \quad (2)$$

$$t_w = (W + h t_g) / h \quad (3)$$

Where: R_t = wire resistance at the wire temperature (t_w);

R_o = wire resistance at 20°C when $H/Pd = 0$ (virgin wire)

R_o^* = wire resistance at 0°C when $H/Pd = 0.75$ ($R_o^* = f(H/Pd)$)

α = thermal resistivity coefficient ($\alpha = f(H/Pd)$)

t_w = actual wire temperature

W = applied power input

h = thermal exchange coefficient

t_g = gas temperature (considered constant and equal to 35°C)

By combining (2) and (3) we have:

$$\frac{R_t}{R_o} = R_o^* \cdot \left[1 + \alpha \cdot \frac{(W + h \cdot t_g)}{h} \right] \quad (4)$$

Equation (4) is the explicit form of the experimentally demonstrated relationship (1). Taking into account that R_o^* and α are both dependant on the H/Pd ratio, the linear dependence requires that, while the wire is being warmed up, the loading ratio H/Pd remains constant (as it does in tests 1 through 9).

After establishing that the wire does not degas, it is possible to calculate with the equation (2) the wire temperatures. It is known [5] that when $H/Pd = 0.75$ the value of the thermal resistance coefficient is:

$$\alpha = 1.8 \cdot 10^{-3} \text{ } ^\circ\text{C}^{-1}$$

It is necessary first to calculate the R_o^* value; as the starting temperature is 35°C, we have:

$$R_o^* = 1.85 / (1 + 1.8 \cdot 10^{-3} \cdot 35) = 1.740 \quad (5)$$

by inserting the R_o^* value in equation (2) it is possible to obtain the wire temperature. The calculated values are reported in Table 1.

Looking at the Fig 4, it appears that the coordinates (R/R_o versus W) of Test 8 are placed much above the prolongation of the straight line (1). In order to justify such a displacement, according to equation (1), the applied power would have been 16.7 Watt, instead of 12.4 Watt actually supplied; that is: 4.3 Watt in excess. It should be noted that

because the mass of the wire is small (≈ 7 mg), the excess power amounts to 0.61 KW per gram of wire!

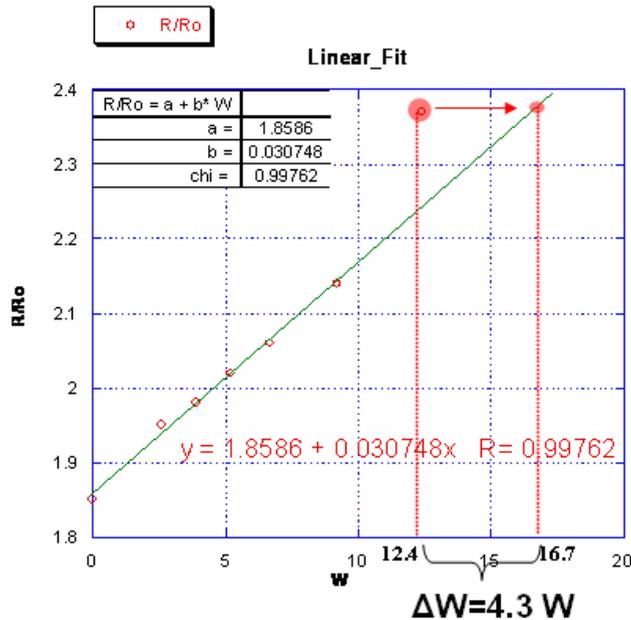


Figure 5. First evidence of excess heat.

It also appears that the observed excess heat requires a triggering temperature, which is somewhere between 128°C and 152°C . This temperature corresponds to the power of 12.4 W during a calibration when no excess heat is produced.

Obviously, Test 8 is the most interesting, and the test that most encourages additional research.

Test 12 shows that when power is switched off R/R_o increases up to 2.4. We know that the the R/R_o can only go above 1.8 is when the wire is warming up. (R_o is not corrected for temperature.)

The R/R_o of the wire stays over 1.8 for about 100 seconds, before returning to 1.8. The integral of excess power yield is about 1 KJ, or 4 Mcal per gram-atom of Pd. So, it exceeds the limits of chemical heat production.

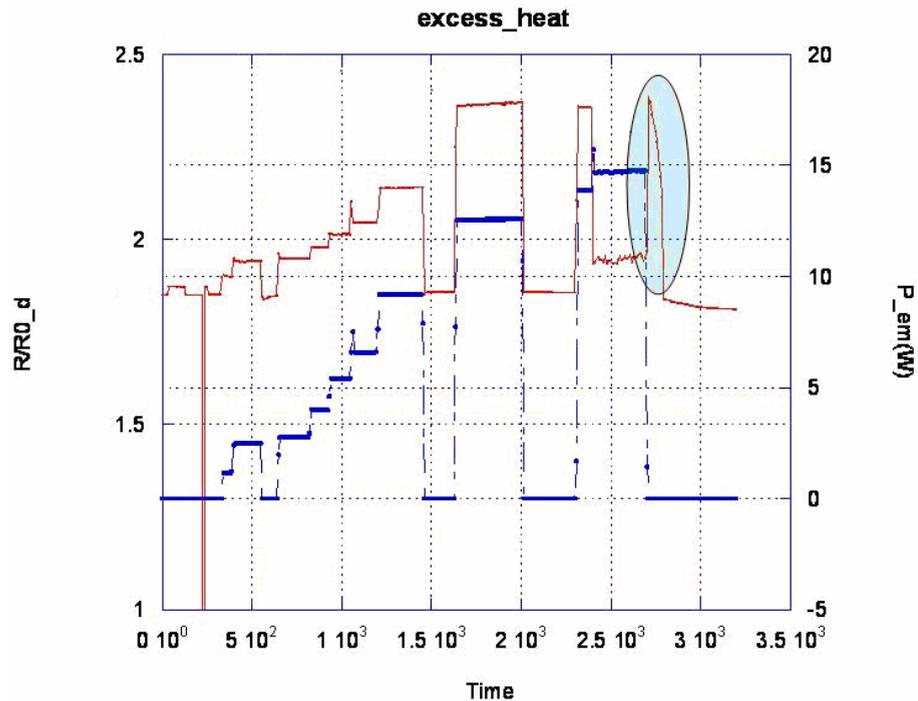


Figure 6. Evidence of excess heat at $W=0$.

4. Conclusions

Gas loading of thin Pd wire has been studied:

- a) Blank loading \rightarrow 1Ms to thermodynamic equilibrium
- b) After surface oxidation \rightarrow 500 s to thermodynamic equilibrium
- c) After surface stabilising treatment \rightarrow 80 s to thermodynamic equilibrium

Excess heat was found in a loading gas experiment:

- a) No degassing observed
- b) Excess power of 4 W was found when power applied was 12.4 W
- c) Excess heat of 4 Mcal/mol was found when power applied was 0 W
- d) Experiment was reproduced

References

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