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**MEASUREMENTS OF THE TEMPERATURE COEFFICIENT OF ELECTRIC
RESISTIVITY OF HYDROGEN OVERLOADED Pd***

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*EURESYS, Via Lero 30, 00129 Rome, Italy***Abstract**

As reported in previous papers, we performed many electrolytic loading tests using thin Pd wires, achieving loading ratios of $H/Pd \geq 0.95$ (H/Pd over-loading). In particular, we defined a reproducible “loading protocol” suitable for achieving such an over-loading level, based on the use of very diluted acid electrolytic solutions (with additions of tenths of micro-moles of Ca or Sr or Li cations and some hundred nano-moles of Hg ions) and operating with electrolytic current cycles from a few mA up to one hundred mA.

By observing the day/night cyclic fluctuations of electrical resistance, as a function of the corresponding temperature variations, of stable, long term, H/Pd loadings we were able to calculate the temperature coefficient of resistivity (K_0) of the Pd-H system at very high H/Pd loadings.

Many years ago (on 1998) we reported an unexpected value showing that the K_0 parameter values increase when H/Pd exceeds 0.75 (i.e. after that R/Ro goes beyond the 1.8 peak value, i.e. to the right side of the R/Ro / H/Pd curve). This fact was confirmed by the ISR-Stanford Group (McKubre and Tripodi) and Pirelli-Research Group (Gamberale and Garbelli).

In this paper we show several measurements of K_0 at different overloading values of H / Pd up to ≈ 1 (corresponding at R/Ro=1.12) where $K_0 = (13 \pm 1) \cdot 10^{-3} K^{-1}$, i.e. more than six times higher than the minimum value achieved at the R/Ro=1.8 peak value.

This result can corroborate the hypothesis that a new Pd-H phase (full β -phase or the beginning of $\beta+\gamma$ phase) could occur after the H/Pd=0.75 loading ratio (at the end of $\alpha+\beta$ phase), as claimed by many authors as the necessary condition for excess (anomalous) heat from Pd-D system (at D/Pd ≥ 1).

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1 Historical Background

1.1. H/Pd Loading Measurements

It is common opinion that to observe heat in excess from Pd-D system it is necessary to obtain very high values (≥ 0.95) of D/Pd atomic ratio [1,2,3].

Starting from 1998 we decided to perform systematic tests in order to achieve very high H/Pd loading ratio using very diluted electrolytes and thin (50 or 100 μm in diameter) Pd wires as cathodes [4]. Different electrolytic solutions have been tested by adding to the acid solution very low amounts of Ca, Sr, Li and Hg ions. In this way high H/Pd loading ratios have been achieved with a satisfactory grade of reproducibility. Several loading procedures have been performed in a wide range of electrolysis current (from a few mA up to one hundred mA) and at different Hg ion concentrations. The obtained results allowed for the definition of a loading protocol capable to insure very high H/Pd over-loading. Stable $R/R_0 \leq 1.2$ values (corresponding to H/Pd ratios ≥ 0.97) can be currently achieved with an extremely low electrolytic power supply (10 V; 5 mA) [5].

This procedure is based on the increase of the cathodic over-voltage (which is known to be the main controlling parameter of the H(D)-Pd loading) obtained by modifying the nature of the cathodic surface (i.e. by inducing the formation of a very thin layer of an alkaline-earth carbonate on its surface).

1.2. Temperature Coefficient of Resistance trend

The temperature coefficient of electric resistivity (K_θ) of a Pd-H sample is a well known curve in the literature (K_θ is known to decrease from 4.1 to 1.8 mK^{-1} with H/Pd increase from 0 to 0.7) [6,7].

During 1998, after the achievement of a very high and stable H/Pd loading ($\cong 0.95$), we performed a preliminary measurement of K_θ resulting in a value of $(3.2 \pm 0.2) \cdot 10^{-3} \text{ K}^{-1}$ within a temperature range from 77 °K up to 373 °K. For the first time in the literature this value showed that at values of H/Pd higher than 0.7, K_θ increases [8,9]. Further, this fact was confirmed by the ISR-Stanford Group [10] and Pirelli-Research Group [11].

2 Temperature Coefficient Measure

2.1 Experimental Setup

In an electrolytic cell (solution of one liter of $\text{H}_2\text{O} + \text{HCl}$ at 10^{-4} Moles) the electrodes have been located in the form of 2 parallel wires, of length 25 cm, 6,5 cm apart from each other (the Pd cathode of diameter 50 μm , the Pt anode of diameter 0.5 mm); tenths of micro-moles of Sr and hundreds of nano-moles of Hg have been added to the solution. A junction for a pick up of the voltage divided the Pd cathode in 2 equal segments (named: “up” and “down”).

2.2 Experimental Data and Fit

After applying the procedure to reach H/Pd overloading (OFF/ON current cycles, as shown in Fig. 1), if the loaded sample is found stable, we proceed with the recording of the R/R_0 variations following the day/night cyclic temperature variations. The measurement campaign may last for several day/night cycles. To complete the test, Pd-H wire is de-loaded either by using anodic current or by simply turning the current off for many hours (as reported in Fig. 1) and observing the phase transition at $R/R_0=1.7$ (H/Pd= 0.6).

Generally, as in the latter case, it is possible to check the R/R₀ curve tracing back to the peak value (R/R₀=1.78, H/Pd=0.75) and returning to the initial value of R/R₀=1. By considering the data in the range where the loading is stable, it is possible to record the dependence of the wire resistance on the wire temperature (homogenous with the cell temperature) and once the linearity of these data is confirmed (**Fig. 2**), we can make a fit to calculate the K_θ coefficient according the relation (**A.1**) reported in the Appendix.

To be consider valid to our purpose, resistance data have to be repetitive after each temperature cycle.

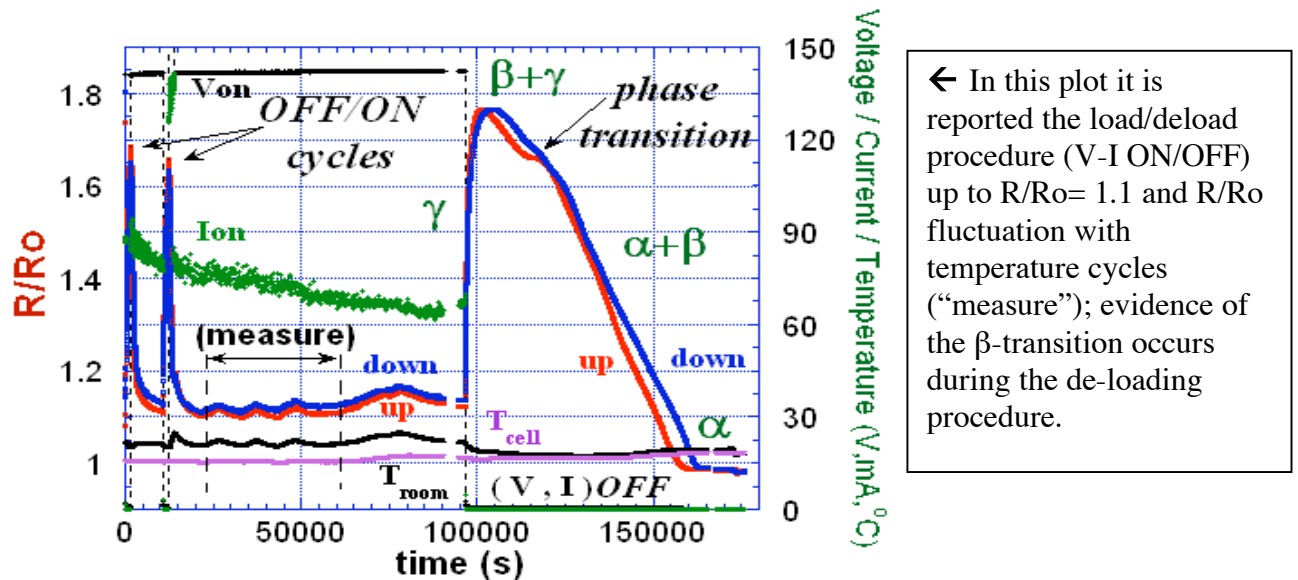


Figure 1. R/R₀ data are meanly stable for a enough long time (from 30,000 to 90,000 seconds range).

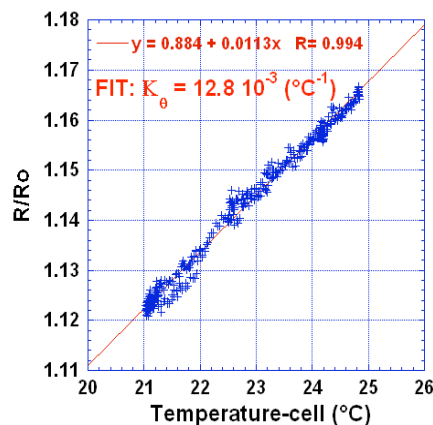


Figure 2. Partial data of a full temperature cycle (40,000->60,000 s) well fitted by a simple line.

H/Pd	(up)		(down)		Note
	R/Ro ± 0.1	K _θ (mK ⁻¹)	R/Ro ± 0.1	K _θ (mK ⁻¹)	
0.00	1.0	4.1 ± 0.1	1.0	4.1 ± 0.1	(a)
0.85	1.75	2.8 ± 0.3	1.75	2.6 ± 0.3	(b)
0.88÷0.90	1.58	7.2 ± 1	1.61	6.7 ± 0.5	(c)
0.91	1.52	≈ 7 ± 1.5	1.52	≈ 7 ± 1.5	(c)
0.92÷0.93	1.44	≅ 8.3 ± 1	1.46	≅ 8.4 ± 1	(c)
0.96÷0.98	1.19	9.9 ± 0.5	1.24	9.6 ± 0.5	(c)
0.97÷0.98	1.18	10.7 ± 0.5	1.21	10.6 ± 0.5	(c)
0.99÷0.995	1.10	≅ 13 ± 1.5	1.13	12.8 ± 0.5	(c)

Table 1. Values of K_{\square} as resulting from several tests performed at stable loading conditions and ratios (ref. Troom at 20°C):

- The first value is in agreement with the expected value for $K_{\theta} = 4.1$.
- At the R/Ro peak value the thermal coefficient is a little higher (30%) than the one reported in the literature ($K_{\theta} \cong 2.0$).
- At all values, beyond the R/Ro peak, the thermal coefficient shows rapid increase.

2.3 Results

Out of several hundred tests, only a few tens have shown a loading stability suitable for the calculation of the K_{θ} parameter. We report in **Table 1** some values corresponding to different values of Pd loading.

In this table, measured values of R/Ro are reported for each of the two wire sectors “up” and “down” (generally showing similar loading values); tests ranged along a period of a year during which different wires, electrolytes and procedures were used.

H/Pd values reported in the table are taken from literature data up to R/Ro peak value and after this point we refer to Mc Kubre experimental and theoretical data, as previously reported [12].

In **Fig. 3** we report known literature data (“+” points below the R/Ro peak) in addition to the new experimental data (“o” points beyond the R/Ro peak) which show the progressive increase of K_{θ} as the H/Pd value increases (overloading); *the arrows show the trend of K_{θ} with increasing loading ratio*.

Similarly, in **Fig. 4** we report data from the literature and the experiments; they show clearly the rapid progressive increase of K_{θ} at H/Pd overloading.

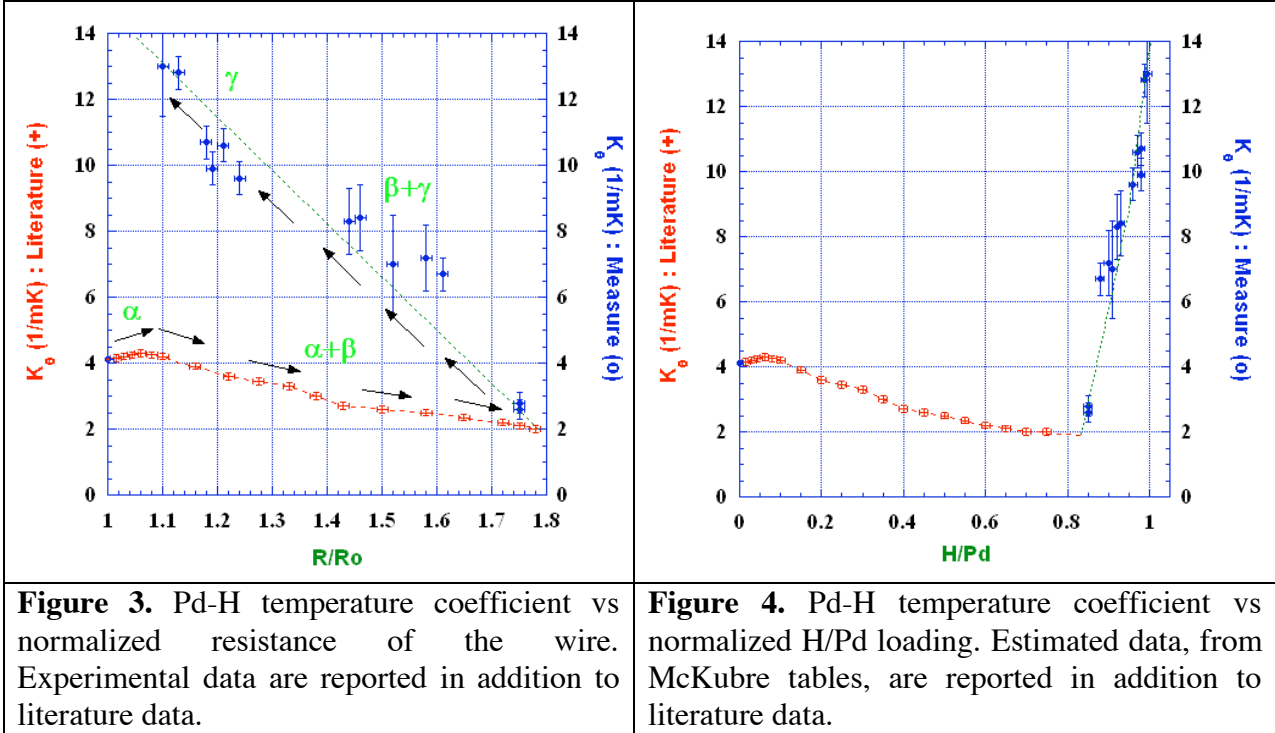


Figure 3. Pd-H temperature coefficient vs normalized resistance of the wire. Experimental data are reported in addition to literature data.

Figure 4. Pd-H temperature coefficient vs normalized H/Pd loading. Estimated data, from McKubre tables, are reported in addition to literature data.

3 Discussion

3.1 Phase hypothesis

From the literature [2,3,6] is known that at room temperature the system Pd-H_x occurs in different phase conditions (\square -phase at $H/Pd=0 \square 0.1$ and $\square+\square$ phase at $H/Pd=0.1 \square 0.6$). Because of the change of dimension occurring for R/R_0 at the peak value of 1.8 when H/Pd is ranging from $0.7 \square 0.8$ [1], it is possible to suppose a phase transition is taking place as it is pointed by an arrow in Fig. 1 at $R/R_0=1.7$. At this R/R_0 peak we hypothesize a new phase, named “ $\beta+\gamma$ ” phase. If, at high H/Pd loading, this R/R_0 peak is surpassed, we can assume that a peculiar \square -phase occurs in correlation with the change of slope of the K_0 vs temperature curve (Fig.4) so that this new phase is peculiar of H/Pd high loadings.

3.2 Conclusion

In conclusion, we stress the following points:

- We are able to achieve $H/Pd \approx 1$ staying stable for a long time;
- We can calculate Thermal Coefficient of Resistance at high Pd-H loadings;
- At high loadings as the R/R_0 strongly decreases, the thermal coefficient of electrical resistivity strongly increases;
- We can conjecture a new important phase occurring at high loadings.

Because all tests were performed using Hydrogen (i.e. light water) instead of Deuterium (i.e. heavy water) we do not expect any anomalous heat in excess produced by the wire (i.e. Fleishmann and Pons effect), in fact we never detect thermal anomalies using light water in electrolysis solution. If such an anomaly occurred, wire temperature increasing (in respect to

solution temperature) could alter the thermal coefficient measurement, but just this change of expected value could be an indication of anomalous excess heat.

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Appendix

We used the known formula to calculate K_θ :

$$\mathbf{R}(\mathbf{x}, \theta) = \mathbf{R}_0(\mathbf{x}) \cdot (1 + \mathbf{K}_\theta(\mathbf{x}) \cdot \theta) \quad (\text{A.1})$$

where R (in Ω) is the electric resistance of the wire (related to a fixed $x = H/Pd$ loading ratio) and depending on the wire temperature θ (in Celsius Centigrade); R_0 is the wire resistance at 0 °C of temperature. K_θ is the temperature coefficient of resistance (in °C⁻¹).

We consider K_θ constant within a large range of temperature; indeed we have checked this constancy (within 5% of variation) from 200 °K up to 373 °K with a overloaded wire.

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