

Further progress/developments, on surface/bulk treated Constantan wires, for anomalous heat generation by H₂/D₂ interaction

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Outline and motivations

- 1) Path of HT anomalies: from Langmuir (W&H₂) to nano-Constantan.
- 2) Proof, by calibration experiments with Pt wires (different diameters, gases, pressures, power), that main results obtained on 2012 with surface-treated Constant wires, were right. Focused on not-dependence of Anomalous Heat Effects (AHE) on pressure variations inside the transparent glass reactor: **reconfirmed and reinforced previous calibration data (June 2012) using He.**
- 3) Evidence of **unexpected water splitting phenomena**, under vacuum, by “nanodiamonds-coated” Constantan.
- 4) Evidence of correlation between **Resistive Thermal Coefficient (RTC) and resistance ratio (R/R₀)**, i.e. H loading of Constantan. Measurements at T=77-293K (by LN₂) and 20-280°C.
- 5) Evidence of **AHE under vacuum** and different surface treatments on the same wire, varying also the mean local wire temperatures by different power applied. Comparison with Pt.
- 6) Big efforts to develop a procedure to get some AHE even with Constantan wires of poor-quality or damaged: **FOUND**. Key result: AHE depend on **FLUX**, any direction, of H. Same result found by NASA on Dec. 1989 with Pd-D system at T> 300°C. M.M. Kubre formula (1994), on Pd-D system, including flux for AHE, seems ok.
- 7) Conclusions and **next scientific steps toward applications.**

Path of HT anomalies: from Langmuir to nano-Constantan

Nanoscopic anharmonic systems as Maxwell's daemons

- 1) In the preface of the book "Challenges to the Second Law of Thermodynamics" by **Vladislav Čápek** and **Daniel P. Sheehan**, the authors state the possibility of an impending paradigm shift that could invalidate the absolute validity of the second law of thermodynamics. It is pointed out that, over the past 20 years, the second law has been investigated more than in any other time in its history and that studies in this field cross the boundaries between classical and quantum mechanics. Thanks to these studies, the authors believe that the unconditional validity of the second law can no longer be taken for granted, and attempts to overcome it cannot be easily ignored.
- 2) Recently, some Researchers have made assumptions that could achieve this goal by using systems consisting of nanoparticles or nanostructures. **Brian Ahern** (previously at DARPA, USA), an expert in material science, argues that *particles of the size of a few nanometers have different chemical and physical properties compared to macroscopic particles of the same material*. A similar concept (in the LENR studies) was expressed and realized, since 2002, by Prof. **Yoshiaki Arata** (Osaka Univ. Japan) when introduced experimentally the use of Pd nanoparticles (5-20nm), embedded in an abundant (65%) matrix of ZrO₂, in experiments of Deuterium gas loading at high pressures (up to 50 Atm.) and temperatures (up to 250°C). When a particle is composed of only a few thousand atoms, a considerable fraction is located on the surface and is subject to nonlinear binding forces with the internal atoms [1].

- 3) Ahern also mentioned that, already on 1954, Nobel Laureate **Enrico Fermi** (at LANL-USA), the *Fermi-Pasta-Ulam paradox*, found that the conditions for energy localization are the presence of systems (clusters) with countable number of elements (atoms) and the nonlinear coupling between the elements [1,2].
- 4) According to Ahern, and us, in the event that such particles receive a pulse of energy, e.g. from thermo-mechanical oscillations, or from electrical pulses, the energy will not be evenly distributed between all the atoms of the cluster, but will be concentrated on a very small number of atoms. *They will acquire a significantly greater energy than they would in conditions of thermal equilibrium.* This phenomenon could explain catalysis processes. There would be no “lowering of the activation energy”, as normally stated, but are the few atoms that gets a good part of the energy of the nanoparticle that make it available for the activation of chemical reactions that might otherwise happen only at much higher temperatures. Ahern sustains that the phenomenon of localization of energy could even explain the triggering of nuclear fusion reactions at low temperature (LENR) in nanostructures saturated with hydrogen/deuterium [3].
- 5) The "energy localization" of Ahern might therefore “*a fortiori*” be used to explain the ability to split the hydrogen molecule by some special nanostructured alloys [3], even at temperatures much lower than those normally required by the 4.5 eV binding energy of the hydrogen molecule (H₂). Our work, among others (since 2011), was based, for several aspects, on the calculations reported in the paper [3] of **S. Romanowski** (1999).

- 6) As a consequence, the nanoparticles may be seen as **Maxwell's daemons** able to transform part of thermal energy of the nanoparticles into valuable high potential chemical energy due to the splitting of the hydrogen molecule. The second principle would only apparently be violated, but in reality, since it is a statistical principle, it simply cannot be applied to systems consisting of a relatively small number of atoms. The non-applicability can also be extended to a macroscopic system consisting of relatively isolated nanoscopic structures (e.g. clusters).
- 7) In order to verify this hypothesis, a stream of molecular hydrogen could be sent over an appropriate catalyst functioning above a critical temperature T_1 , and then part of the monatomic hydrogen formed in the catalyst could be recombined in a second time and place, thereby generating a temperature $T_2 \gg T_1$. This system, thanks to the strongly endothermic nature of the decomposition of molecular hydrogen, would also allow to cool intense and localized heat sources.
- 8) In addition to Ahern, **Thomas Prevenslik** also recently noted the extraordinary thermodynamic properties of nanometer-sized objects. Prevenslik supports the possibility of nanoscopic particles to behave as frequency multipliers able to generate high-energy photons from a much larger number of photons of lower energy. In this case also, we would have a mechanism potentially able to "violate" the second law of thermodynamics and, according to Prevenslik, even able to explain most the effect found in Low Energy Nuclear Reactions experiments [5].

- 9) This mechanism could also generate photons with energy much higher than the kT and could therefore explain the possibility of some nanostructured systems to split the hydrogen molecule at relatively low temperatures ($\ll 3000$ K).
- 10) Nobel Laureate **Irving Langmuir** in his paper "Flames of Atomic Hydrogen" [6] has pointed out that the heat carried away from an incandescent wire by an inert gas increases roughly proportionally as the 1.9th power of the temperature of the filament and that many gases as nitrogen, argon, and mercury vapor, up to the temperature of melting tungsten 3660 K, follow this law. Langmuir noted that, with experiments at high temperatures, in the case of hydrogen, very different results were obtained. Up to about 1700 K the normal exponent of 1.9 was observed, but, at higher temperatures, the exponent increased until at 2600 K and above it was about 5.0. At 3400 K the heat conducted by hydrogen was 23 times as great as that carried by nitrogen under similar conditions. The fraction of the molecules which have been dissociated, grows rapidly with temperature. At atmospheric pressure, at 1000 K, was found to be 3.71×10^{-9} , 0.256 at 3400 K and reaches 0.9469 at 5000 K [fig. 1].
- 11) It's possible that the thermal anomalies, found by some of Researchers (**U. Mastromatteo** at STMicroelectronics-Italy; the **MFMP** International Collaboration, France-Switzerland-USA; **ourselves**) on recent experiments with special surface-processed constantan wires, may be partially explained by a very efficient catalytic action of the nanostructures on the surfaces of wire that uses their "Maxwell's daemon like" behavior for H_2 molecule splitting, even at temperatures < 800 K.

- 12) The hypothesis of Maxwell's daemon is also supported by the pressure dependence of apparent excess heat in these experiments. At lower pressures spontaneous recombination of monatomic hydrogen is less probable: the mechanism of H₂ splitting (in sub-micrometric Constantan wires) and subsequent recombination at "cold" internal surface of the glass, create a very efficient mechanism of heat transfer, not present in "blank" experiments (e.g. He, Ar, air gas instead of H₂). The increase in temperature of both wire and external glass surface however seems indicate that this consideration is not sufficient for a comprehensive understanding of the experimental results. Obviously, more dedicated and cross-check experiments are needed, ASAP.
- 13) At the end, the very recent experiments, presented by **A. Kitamura** and **A. Takahashi** (Kobe University and Technova R&D, Japan) at this Conference, seems to enhance the hypothesis of a real unknown internal heat source in Ni_{80%}-Cu_{20%} nanostructured compound (absorbed into mesoporous silica and dispersed among gamma-Al₂O₃) experiments under H₂ gas interaction at mild temperatures (200-300°C).

[1] B. Ahern, “Energy Localization, the key to understanding energy in nanotechnology and nature”,

<http://lenr-canr.org/acrobat/AhernBSenergyloca.pdf>

[2] E. Fermi, J. Pasta, S. Ulam “Studies of nonlinear problems”, Los Alamos National Laboratories, Document LA-1940, May 1955.

[3] S. Romanowski, W. M. Bartczak and R. Wesołkowski “Density Functional Calculations of the Hydrogen Adsorption on Transition Metals and Their Alloys. An Application to Catalysis”, *Langmuir*, 1999, 15 (18), pp 5773–5780.

[4] WO1996035215, “Method of maximizing anharmonic oscillations in deuterated alloys”.

[5] T. Prevenslik, “QED induced cold fusion”,

<http://www.nanoqed.org/resources/2011/Bologna.pdf>

[6] Irving Langmuir, “Flames of Atomic Hydrogen”, *Industrial and Engineering Chemistry*, vol. 19, n. 6, pp.667-674, June 1927.

Temperature dependence of fraction of dissociated Hydrogen molecules at different pressures (Atm) in Tungsten:

(P= 0.01 red, 0.1 green, 1 black, 10 blue)

From equations in [6], p. 668:

$$\log_{10}(K) = -21200/T + 1.765 * \log_{10}T - 9.85 * 10^{-5} * T - 0.256.$$

with:

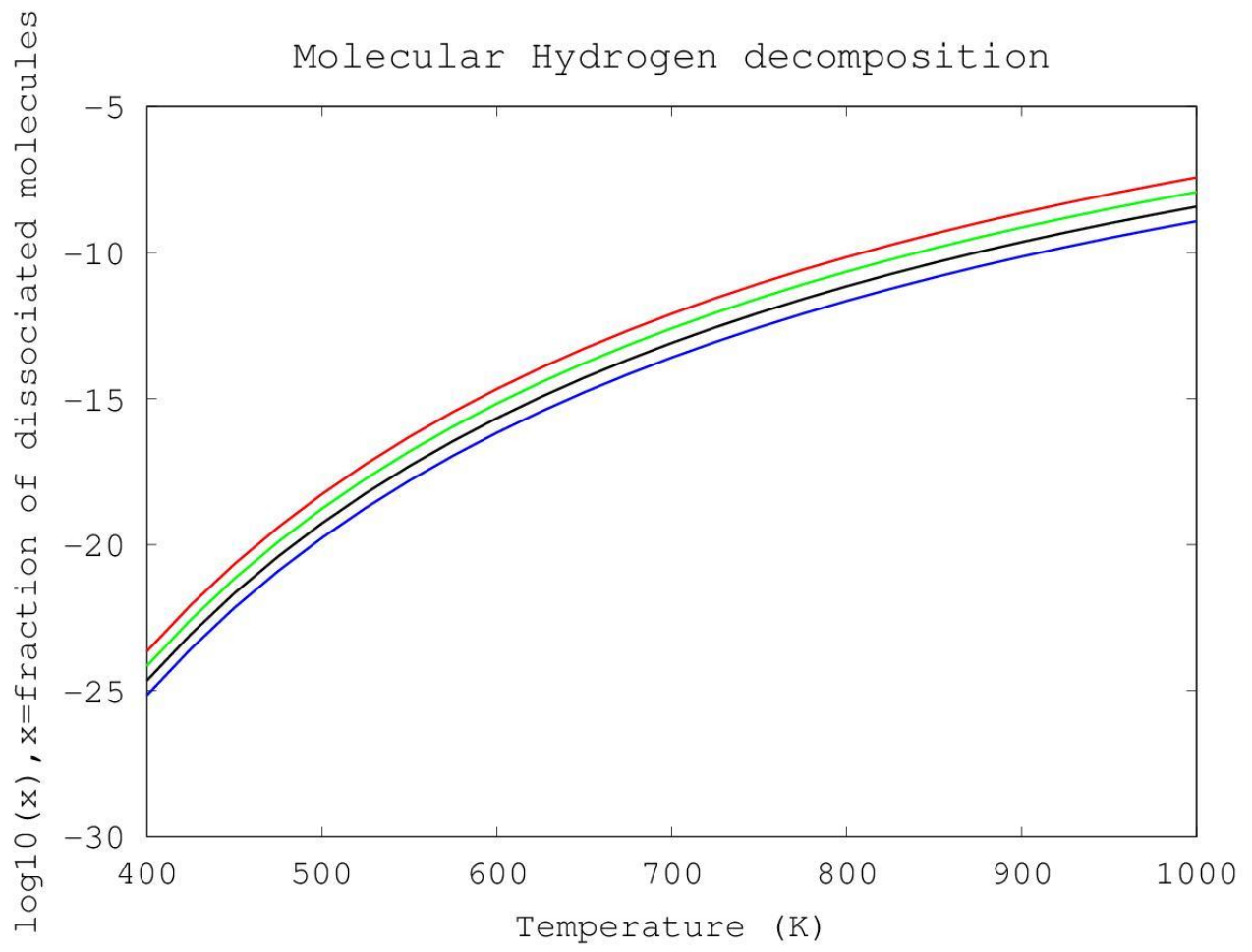
T= Temperature (Kelvin)

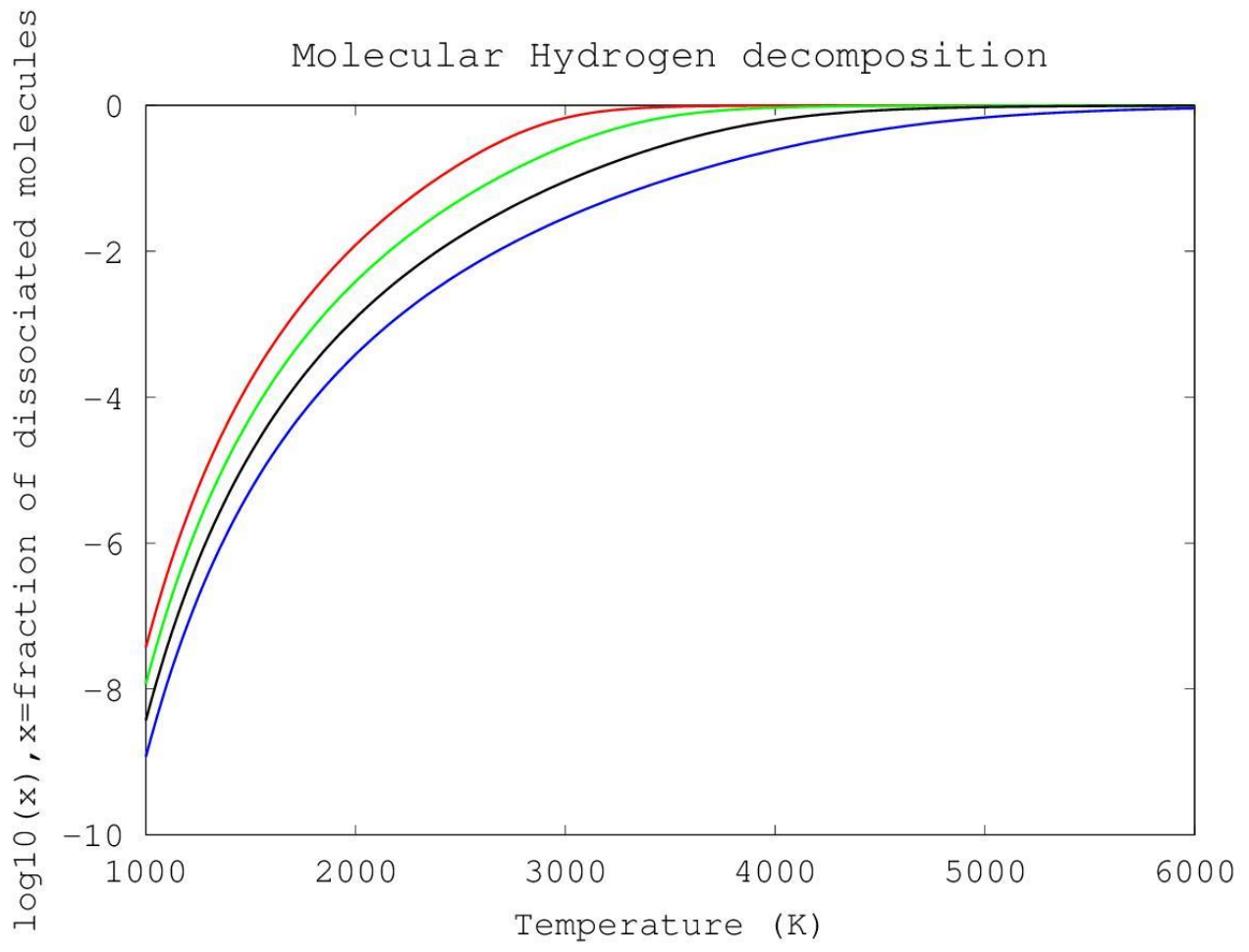
P=Pressure (Atm)

$K=10^{\log K}$

$K=4 * P * x^2 / (1-x^2)$

$$x = (K / (4 * P + K))^{0.5}$$





Some key points presented at ICCF17 (2012)

The Constantan has extremely large values of measured catalytic power (ΔE , in eV) in respect to the dissociation of H_2 (Ref. 1), as following:

$$\mathbf{Ni_{0.3750}-Cu_{0.6250} \implies +3.16eV}$$

$$\mathbf{Ni_{0.6250}-Cu_{0.3750} \implies +2.86eV}$$

$$\mathbf{Ni_{0.8125}-Cu_{0.1875} \implies +2.10eV}$$

$$\mathbf{Ni \implies +1.74eV}$$

$$\mathbf{Ni_{0.1825}-Cu_{0.8175} \implies +1.57eV}$$

$$\mathbf{Ag_{0.8125}-Pd_{0.1875} \implies +0.57eV}$$

$$\mathbf{Ag_{0.625}-Pd_{0.375} \implies +0.51eV}$$

$$\mathbf{Ag_{0.1875}-Pd_{0.8125} \implies +0.51eV}$$

$$\mathbf{Pd \implies +0.42eV}$$

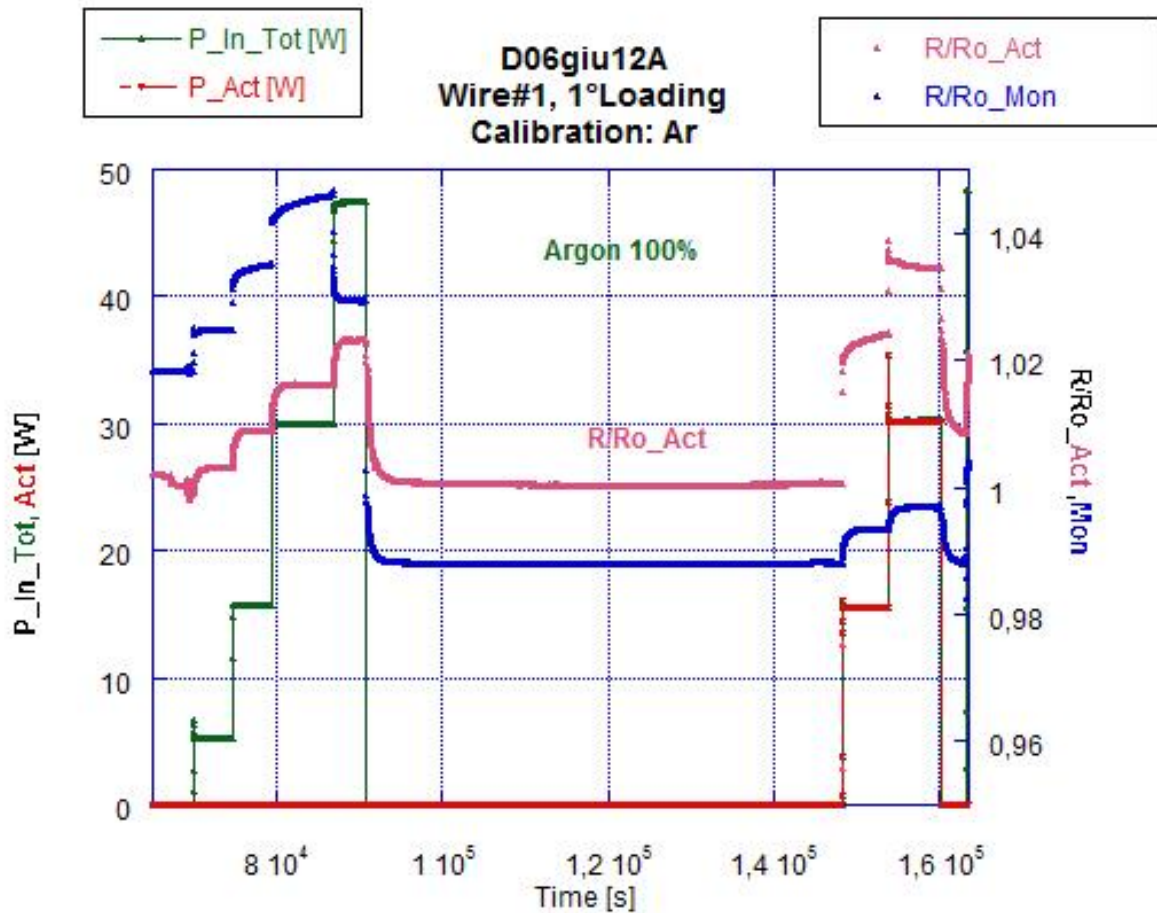
$$\mathbf{Cu \implies -1.11eV}$$

$$\mathbf{Ag \implies -1.42eV}$$

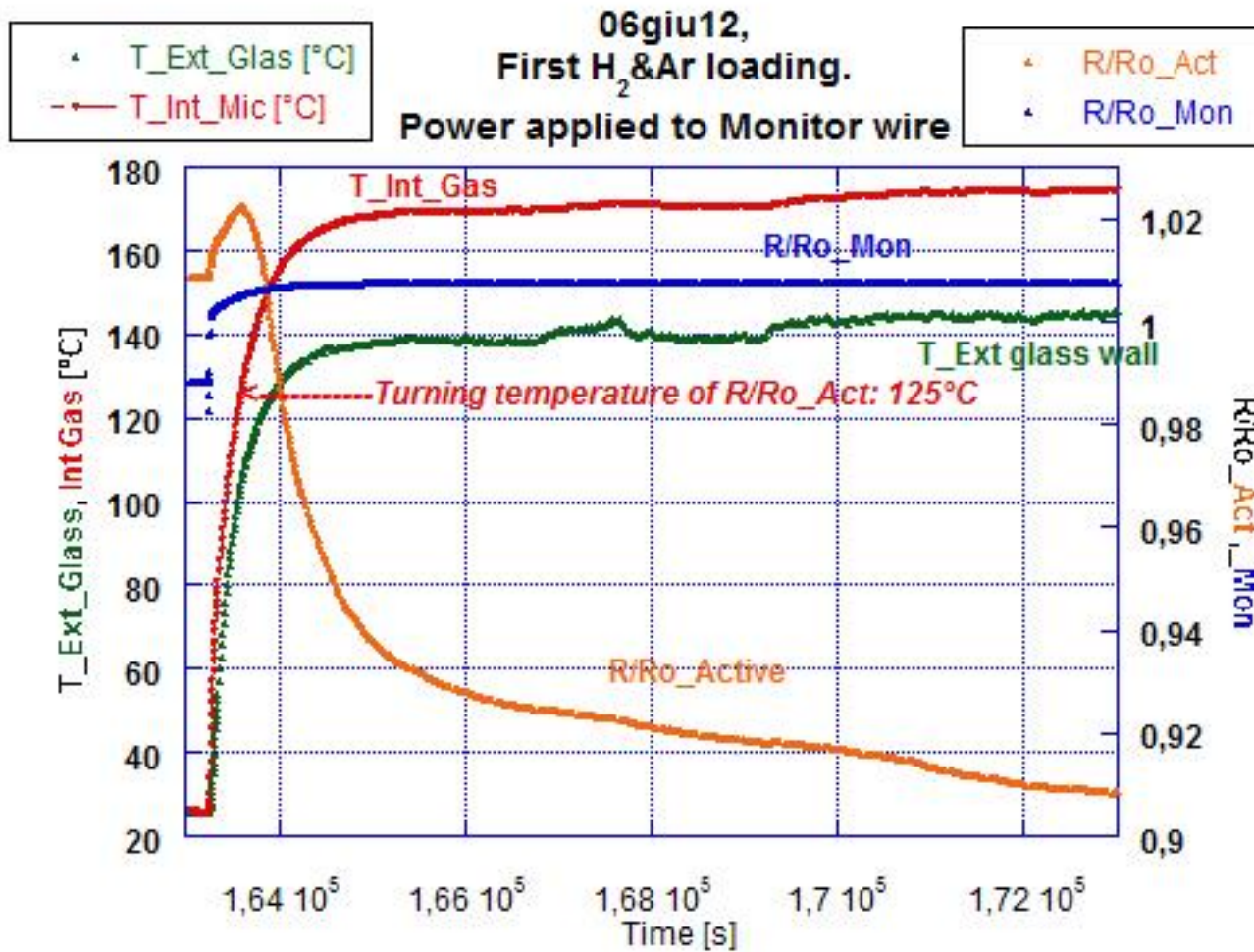


PHOTO OF THE SMALL, DISSIPATION TYPE, TRANSPARENT REACTOR OPERATING AT INFN-LNF. THE VOLUME IS ABOUT 250CC.

THE 2 WIRES, REFERENCE AND ACTIVE, ARE ROUNDED ON A MICA SUPPORT. THE THERMOCOUPLES ARE TYPE K, SS SCREENED (DIAMETER 1.5MILLIMETER).

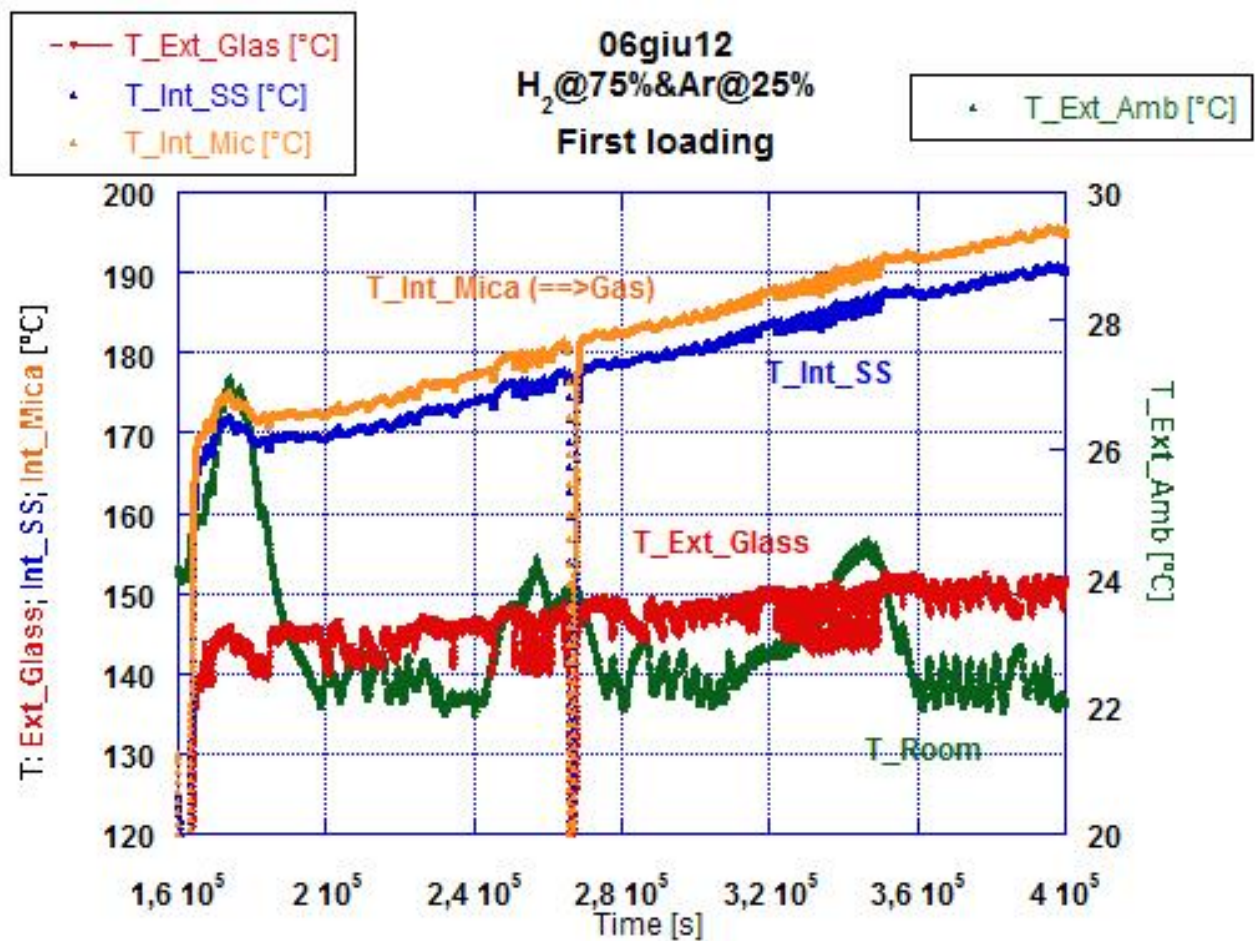


- Calibrations by Argon. Power, up to 48W, at Reference wire (Ni-Cr).
- Maximum power at sub-micrometric Constantan wire was limited to 30W: precaution against very deleterious sintering problems of nano-sized particles under pure noble gas.
- The R/Ro, of both wires, just slightly increased (as expected), increasing the temperatures.



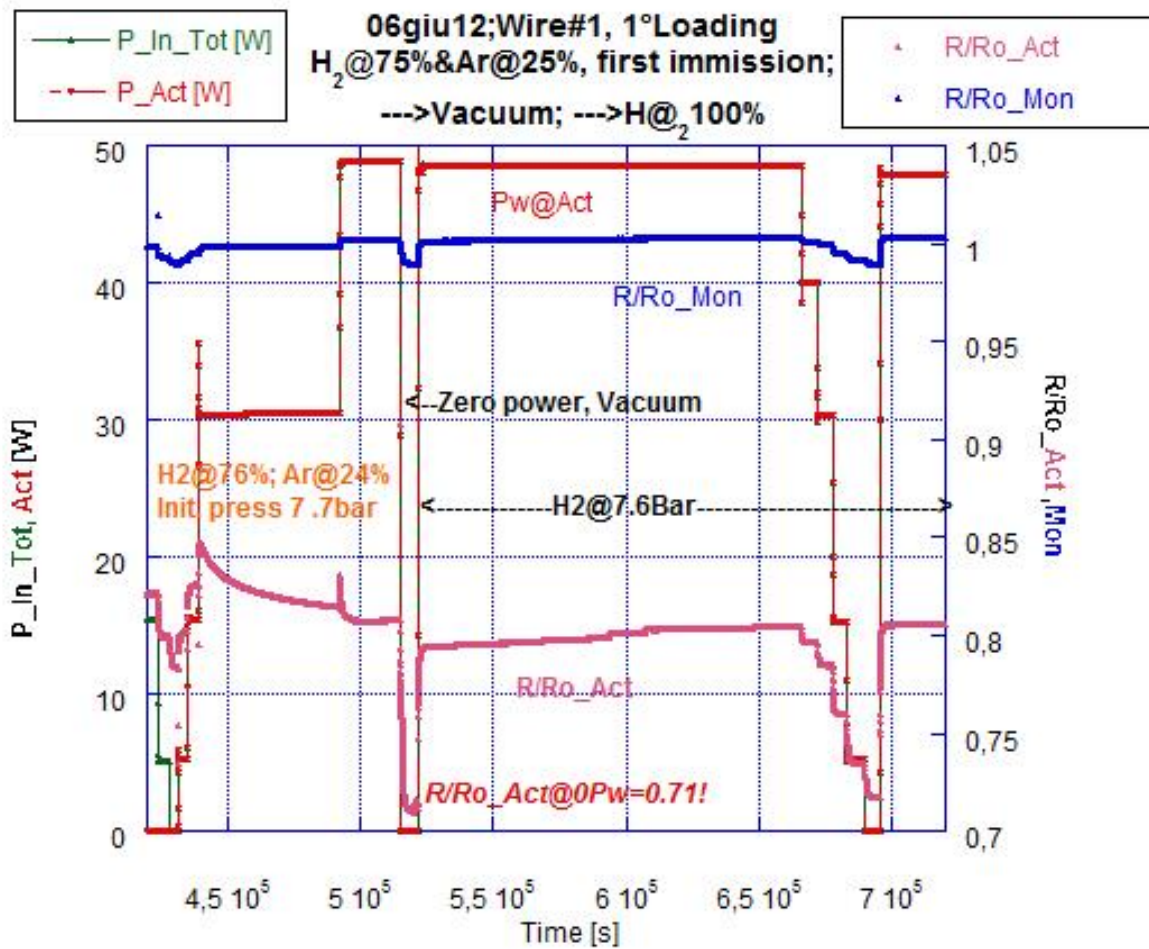
- Details of first loading by H₂-Ar mixture.

The **“trigger” temperature**, to get the large resistance decrease of sub-micrometric Constantan wire, was about **125°C**. Temperature measured by a type K thermocouple (SS sealed) inside the gas cell.



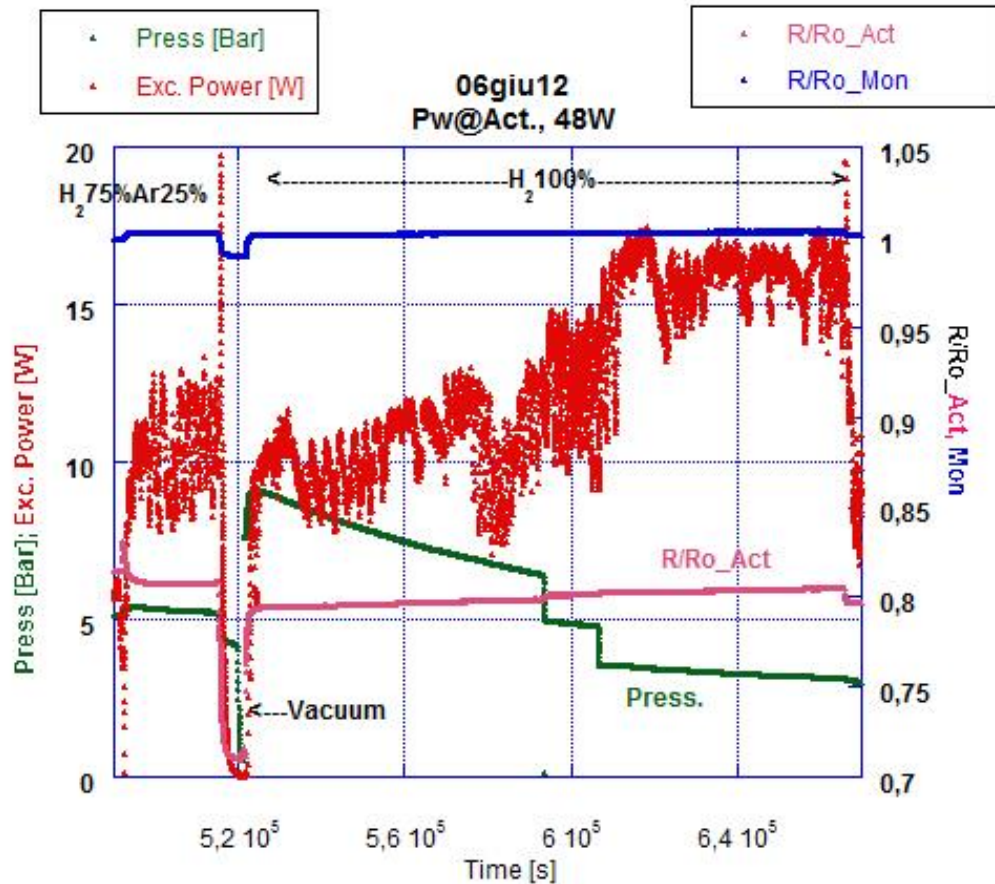
Behaviour of the temperatures of the reactor, at CONSTANT input power (48W at Mon. wire).

Flowing the time, **BOTH the external** glass temperature (140→150°C) and the **2 internal** (Gas, 170→195 °C; “Stainless Steel”, 168→190°C), **increased. The effect was not directly related to room temperature variations, although such temperature variation helped to get non-stationary conditions.**



Behaviours of R/Ro changing: a) power applied from Mon. to Act. (time 420→520ks); b) Vacuum and no power (515→521ks); c) Gas changed from $H_2&Ar$ to H_2 (at 100%) and power applied to Act.

After direct heating to Act., at the end of switch-off time (521ks), the R/Ro_Act dropped to only 0.71!

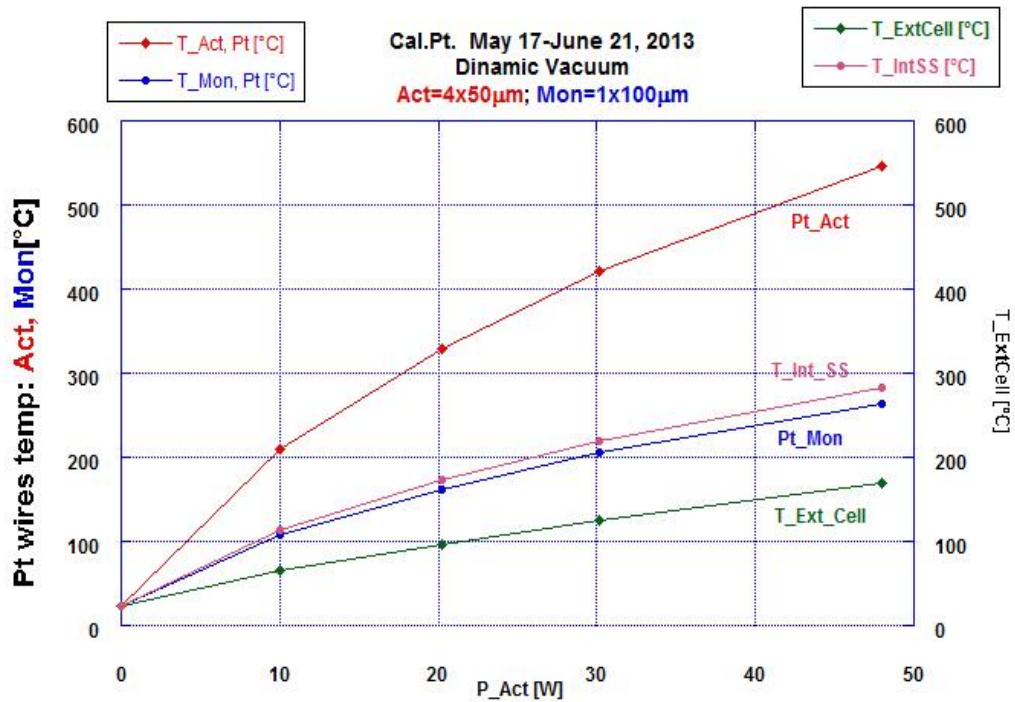


Experiment with power (48W) applied to Active wire. Up to time 518ks the gas mixture was H₂/Ar at 75/25 ratio. Later on, the power was reduced to zero and made vacuum: **R/Ro was as low as 0.71**. From time 522ks was added **pure H₂**: the excess power resumed the value before vacuum and, after controlled reduction of pressure, increased up to **16W**.

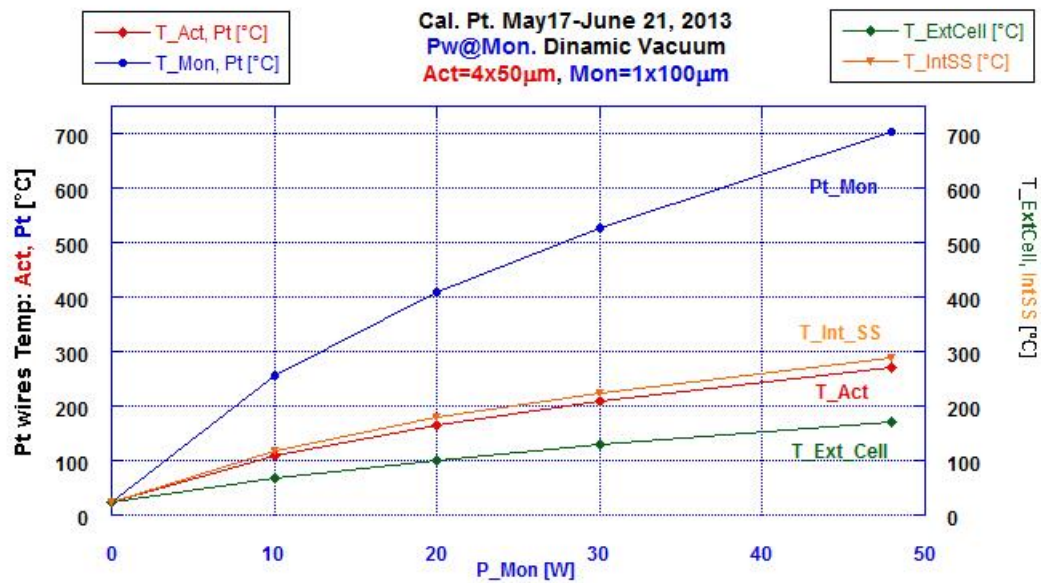
NB. The excess power increases with lowering the gas pressure.

Main results/comments on Pt wires measurements

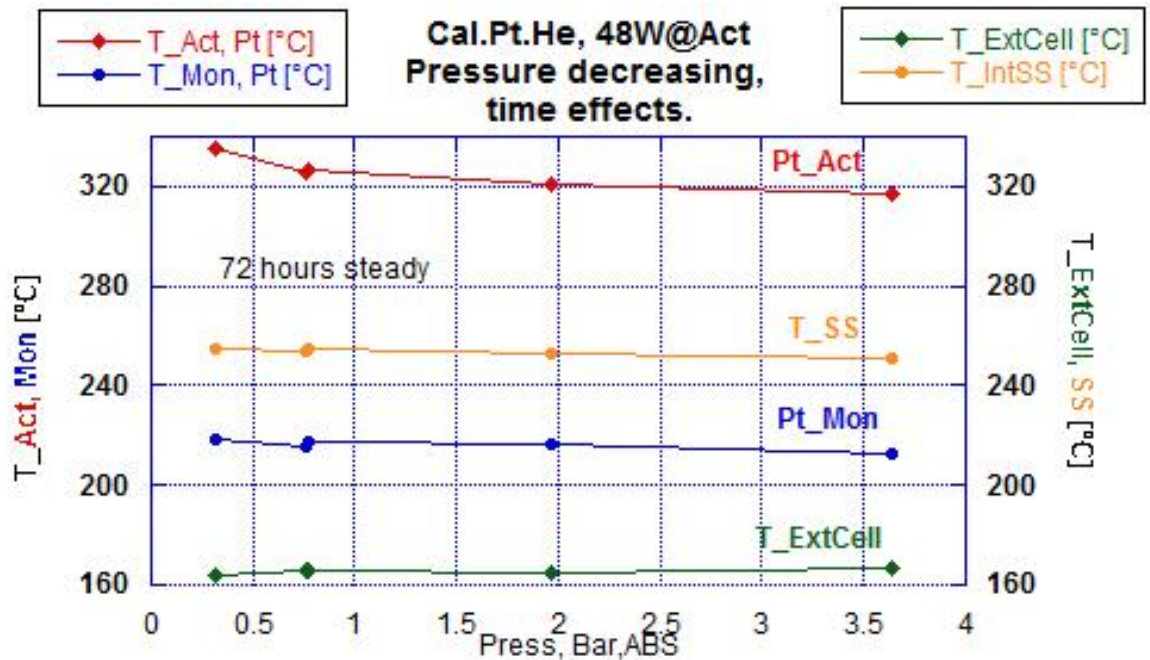
- a) Were used 2 wires, $l=100\text{cm}$: a1) made by assembling, in parallel, 4 wires with $\Phi=50\mu\text{m}$ (almost equivalent to $200\mu\text{m}$, called Active); a2) with a single wire of $\Phi=100\mu\text{m}$ (called Monitor). i.e., similar resistances.
- b) The behavior of mean local wire temperatures, changing the power applied, were **as expected** changing the wire diameters: higher temperatures on thinner wires.
- c) The behavior of local wire temperatures, changing the gas used (H_2 , He, Vacuum), were **as expected**: higher temp. into less conducting gas, i.e. vacuum (thermal conduction, apart local contacts with mica supports, mainly by irradiation).
- d) The effects on temperatures internal and external (used to calculate the anomalous excess power), if any, were **as expected changing the pressures**. I.E. reducing the pressure, under He, the internal chamber temperature increased and the external decreased. **Such result is the reply, fully experimental, to main critics on our previous experiments (June-December 2012) with Constantan and Hydrogen: in such specific conditions BOTH internal and external temperatures increased reducing H_2 pressures.** As a simple consequence, the experiments were right.



Pt wire, Pw applied to Act wire. Measurement of mean Pt wire temperature by resistive thermal coefficient values. Cross-check by visual observation, color, at higher powers: only limited wire sections “started” light-red colors.



Pt wire, Pw applied to Mon wire. Measurement of mean Pt wire temperature by resistive thermal coefficient values. Cross-check by visual observation, color, at higher powers: “started” red color almost uniform.



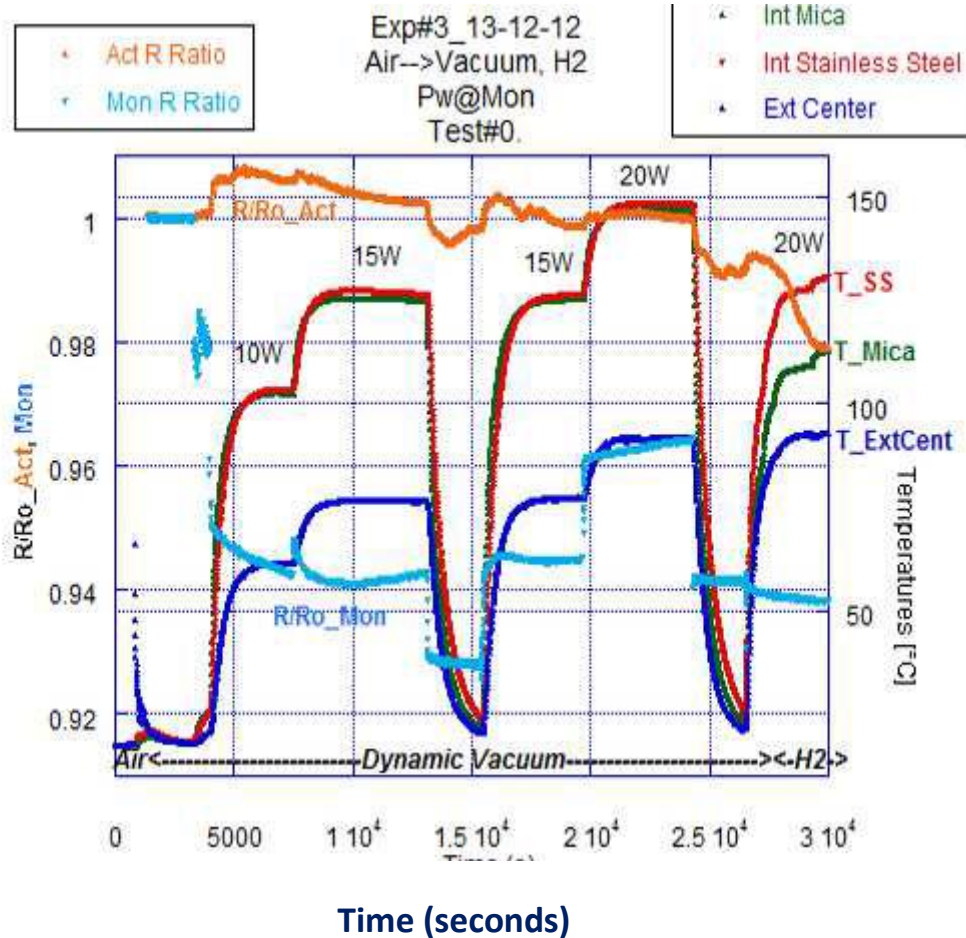
Pw at Pt_Act., 48W. He atmosphere. Effect of pressure variation on Pt_Act and Pt_Mon. temperatures: they increase as the pressure decreases. Also The internal cell temperature (T_SS) increases. **Only the External Cell (ExtCell) temperature (green color) decreases.**

Such value is used to evaluate the power produced inside the cell, both by the Stefan-Boltzmann law (proportional to T^4) and by simple linear calculation:

$$(T_{\text{extCell}} - T_{\text{Room}}) / P_{\text{in}} \text{ [}^\circ\text{C/W]}.$$

The calibration curves were made at different, constant, input powers (W).

Both the calculations method adopted gave similar results.



First experiment with 2 Constant wires, one with 2 Layers (pale blue color), the second with 360 Layers (brown color).

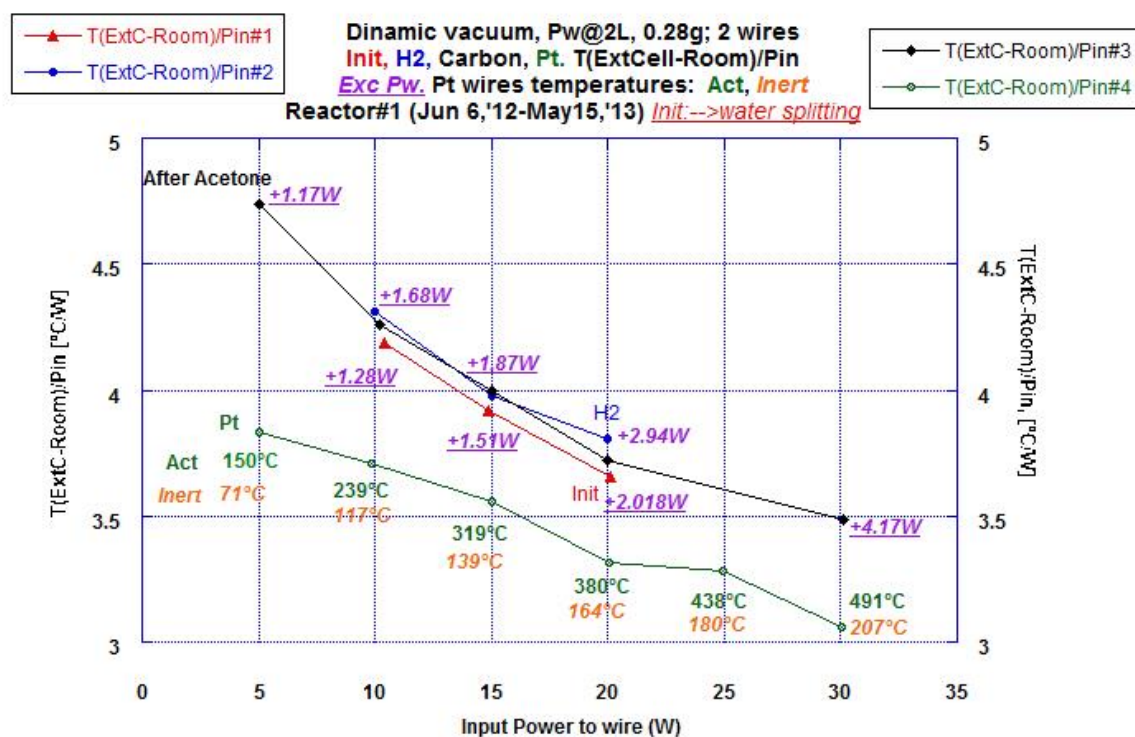
Observation of possible water splitting phenomena during vacuum degassing of the reactor and power applied at 2L wire.

The temperature where phenomena started was 240°C.

A possible processes step can be:



Absorption of H inside Constantan lattice. The H absorption is inferred by resistance decreasing of 2L constantan (-6%), stable even coming back to Room Temperature.



Dynamic vacuum measurements. Reactor #1 (June 2012; May 15, 2013).

Used linear relationship between temperatures differences ($T_{\text{External Cell}} - T_{\text{Room}}$) over the input powers [$^{\circ}\text{C}/\text{W}$].

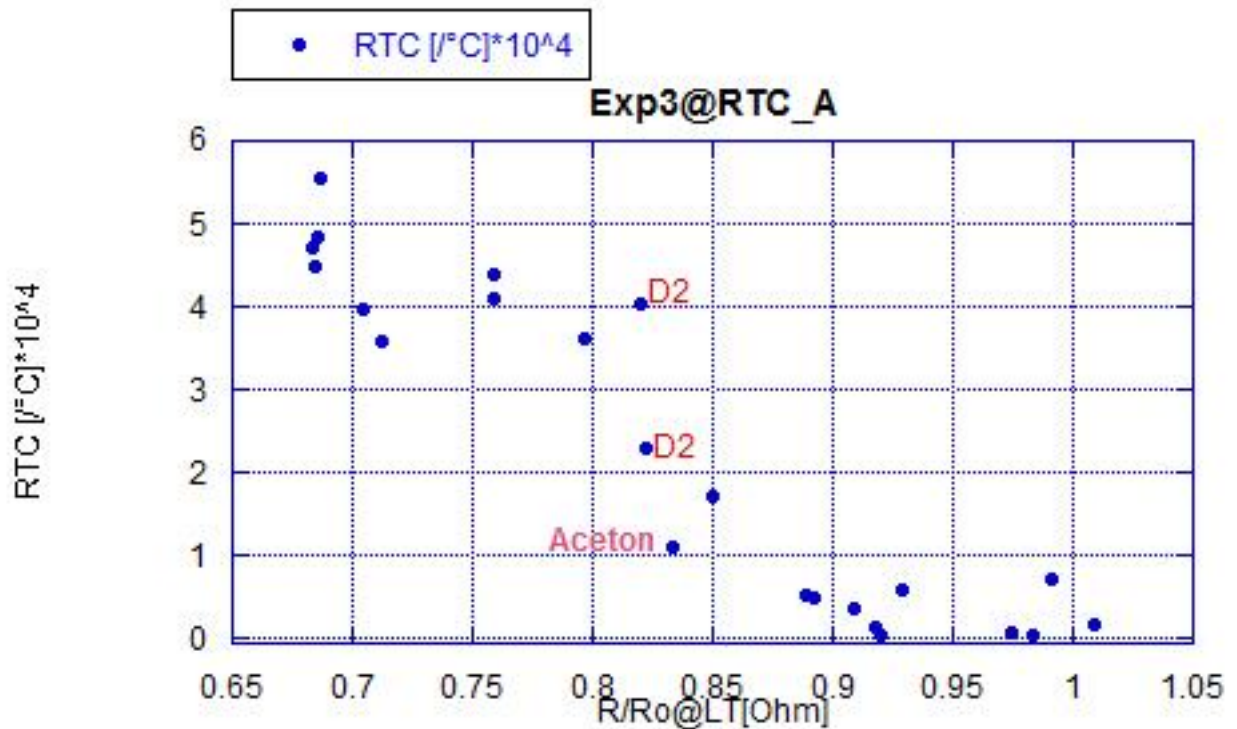
Cross-calibrations using Pt wire (4x50 μm in parallel, called Act) of the same diameter of Constantan wire (200 μm).

It is supposed that the values of $^{\circ}\text{C}/\text{W}$ of Platinum is the reference value, i.e. zero excess power. **Excess power is shown in violet color.**

Are reported behaviors of Constantan wire with power applied to wire type 2 Layers (so-called nano-diamondoids type).

Init is after “water splitting” event; **H₂** is after several loading cycles with **H₂**; **Acetone** is after injection of small amounts of acetone and air (1cc, 11cc) inside the cell (static vacuum) and subsequent high temperature decomposition (followed by vacuum \rightarrow H₂ \rightarrow vacuum cycles).

The anomalous power increases at higher local wire temperatures.



Experiment #3, Constantan wire (360L): RTC vs R/Ro.

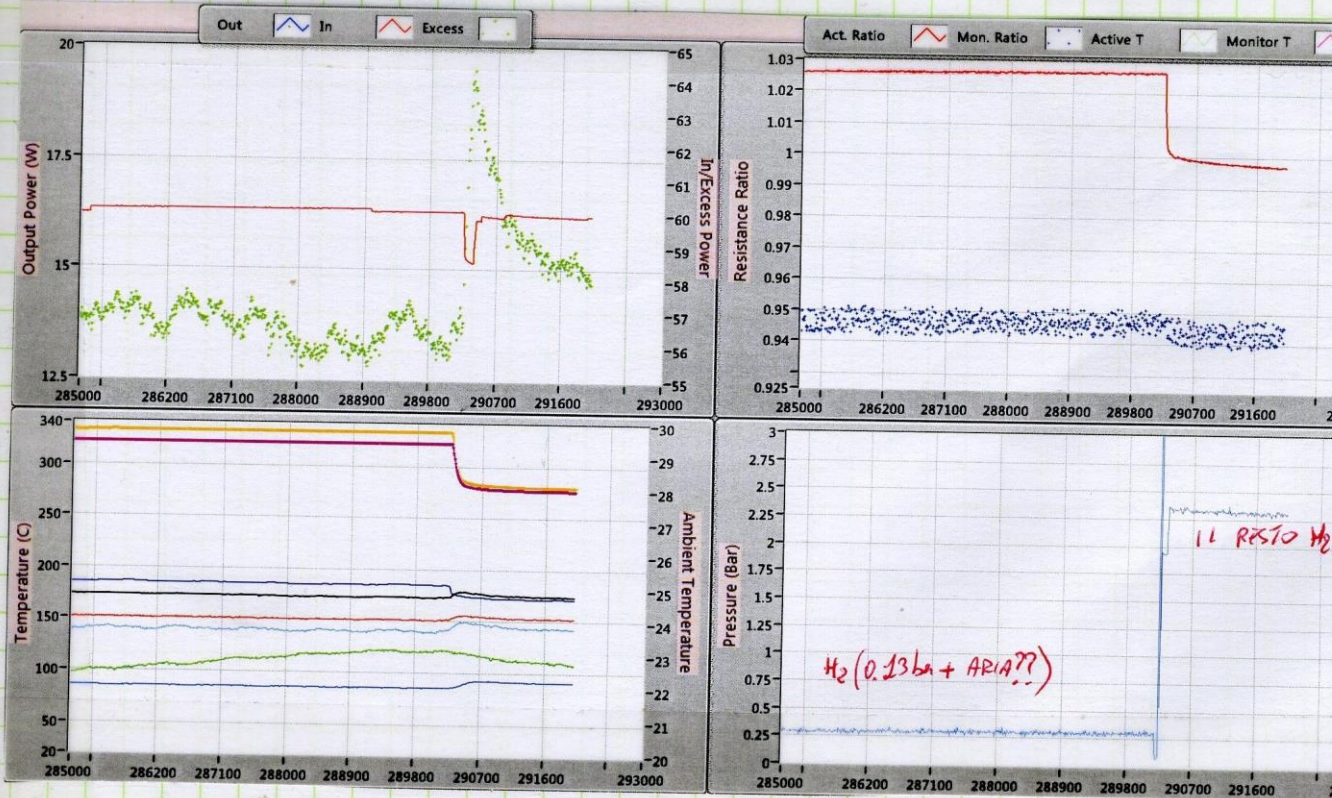
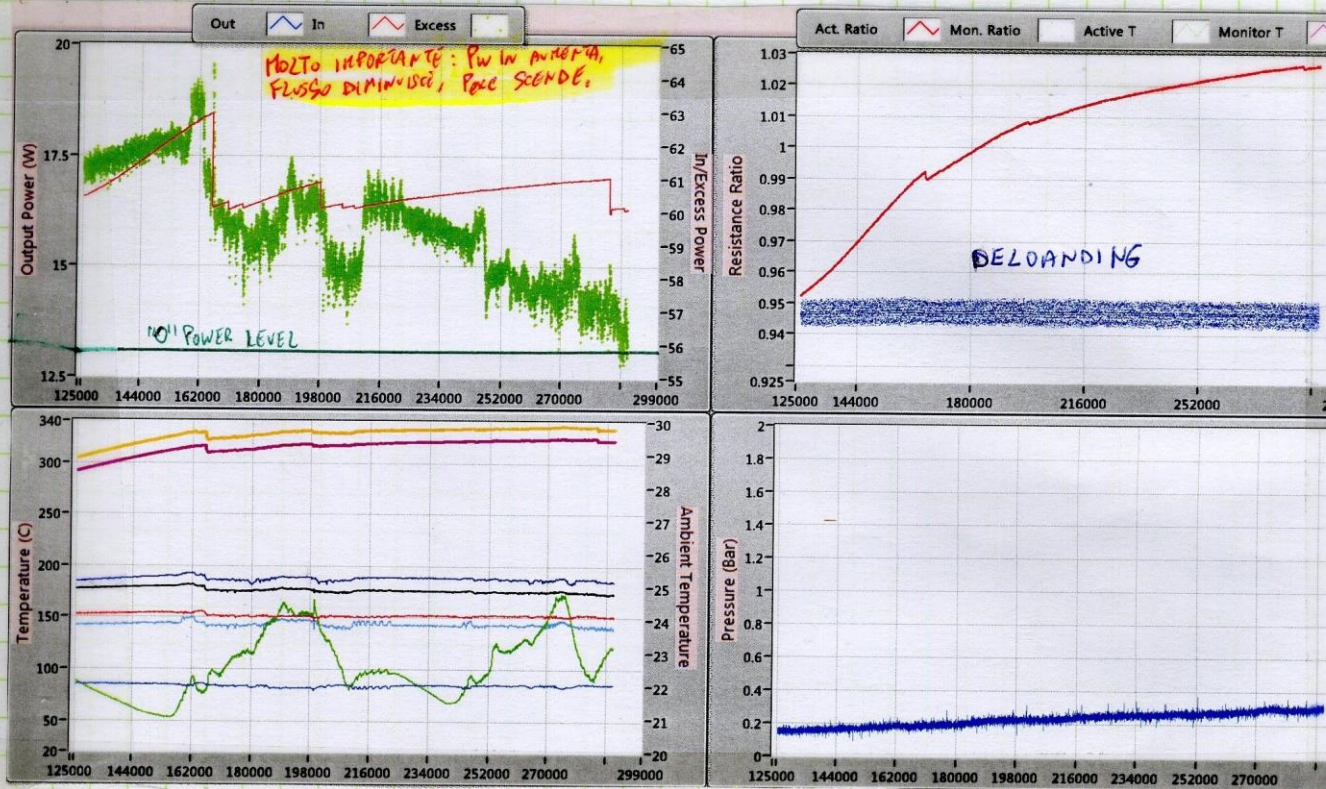
The results reported are made collecting the whole data from High to RT regime, indirect heating, “fast” cooling (about 15m to RT). The typical temperature were 180-280°C (High) and about 23°C for RT.

Other experiments were performed dropping the same cell, with some residual H₂ gas inside (pressure>1.2bar) to avoid fortuitous incoming of liquid nitrogen, from Room Temperature to 77K (liquid nitrogen) and then measured again at RT (usually 293K). The values of RTC were sometimes quite high ($>3 \cdot 10^{-3}$) for situations at the lower values of R/Ro (0.68-0.72). Anyway such values, very intriguing, were of poor reproducibility.

It was detected a nice correlation between the amount of Hydrogen absorbed inside the Constantan lattice (because value of R/Ro) and the RTC.

The overall changing of RTC (temperature range 180-280 → 20°C) was as large as 60 and increased with the increasing of Hydrogen loading.

Further studies are needed, in particular at low temperatures (<100K).



During degassing cycle the P_w , applied to Active wire, was kept almost constant.

The de-loading is due to the concomitant effects of high temperatures inside the wire and very low Hydrogen pressure ($<0.2\text{Bar ABS}$) inside the chamber. Moreover, the hydrogen pressure is probably further reduced by the slow inlet of external air ($N_{80\%}$, $O_{20\%}$) that increases the pressure of the chamber. The Oxygen can recombine with Hydrogen, at the high catalytic constant surface, and forms water that can condensate as liquid at the colder area of the tube (at the ends).

The overall effect is a “fast” degassing of Hydrogen from the wire until the flux vanished (R/R_o close to 1). At this time also the AHE vanished.

Similar effects were observed, same times, in previous experiments. This time we decided to verify if the mechanism was correct with a dedicated experiment.

The forced de-loading procedure, by low pressure, although didn't give large values of AHE in respect to optimal conditions, anyway is simple proof of the flux-related heat, even at poor values of loading ($R/R_o > 0.95$).

Conclusions

- 1) The Anomalous Heat Effect (AHE), according to our results, seems strongly related to the “flux” of H₂ (and/or D₂, but only few experiments performed) through the “sponge” (at sub-micrometric size and quite different local composition) of the “**material**” (Cu₅₅Ni₄₄Mn₁). We have indications, mainly by experiments at STMicronics, that even the bulk, after repeated low-high temperature and H₂-vacuum cycles, sometimes could be “activated”.
- 2) The original observation by G. Fralick (and co-workers) at NASA on December 1989 (made public to “general people” on 2004) about the un-explicable Anomalous Heat Effect during **BOTH** the **loading** and **de-loading** of Pd tube with D₂ at high temperatures (about 320°C), using H₂ as reference, are still valid. Such **KEY experiment** was replicated by NASA itself on 2009 and went in public only on August 2011 (by chance). *Recently, the NASA management decided to share almost immediately their results/projects on the LENR field.*

- 3) The results obtained on Pd-D system both in electrolytic and gaseous experiments about flux effect (M.M. Kubre, X.Z. Li, J.P. Biberian, Y. Arata, F.C.,) are all, among them, qualitatively consistent. Perhaps the original “formula”, developed on about 1994 by M.M. Kubre in Pd-D system and electrolytic environments (relationship between the (loading value)*(flux²) and excess heat amount, i.e.: $AHE = k*(X-X_0)*flux^2$), is still-now valid, at least qualitatively.
- 4) As a general observation (rule??) the AHE amount increases with increasing of temperature (up to 700°C in Cu-Ni-H??) until the concomitant self-sintering phenomena will damage the material, more or less permanently.
- 5) In other words, because of the key role of flux, the AHE is a **dynamic effect** (macroscopic and/or microscopic), **not static**. Even local “oscillations” (e.g. time about 10 minutes as detected in our experiments on July 2012) are important. Any kind of not-equilibrium conditions (external) could help to increase the effect, once the “proper” conditions of the material were fulfilled. Obviously the current pulsing at very large current density (up to 200kA/cm²) and short duration (0.5-2μs), as we introduced since 1993, could help. Anyway, at this stage of research, we decided to have DC current in order to better identify the other, still un-known and/or uncontrolled, parameters

- 6) The extremely large efforts of *Martin Fleischmann Memorial Project* (worldwide collaboration), and their habit to show (in real time) the results of the experiments, without any kind of “filtering”, was a source of scientific stimulations and deeper understanding of the quite complex phenomena and their cross-relationships. BTW, it is really peaty that their “transparency” was used, by some bad people, to dismiss the realty of any kind of LENR phenomena, not just thermal.
- 7) *We are now completely confident, thanks to long and tedious blanks with 2 Platinum wires (even 2 different glass reactors and mica supports), instead of Constantan, that our previous results, since June 2012, were real and not bona-fide mistakes, as we worried/commented several times in the past (even in public).*

- 8) More and more work, of high quality, will be necessary to grow the “*child*” from baby-time (now) to “*adult age*” when, everybody in the world, will be able to switch-on the AHE “immediately” and reduce significantly the pollution due to green-house effects related to hydrocarbons combustion. The role of lattice geometry and local composition are, still now, the most problematic and scientifically appealing aspects. The preparation procedures, included the original composition of bulk material and its covering layer/mechanical stability (e.g. de-foiling problem), isn’t, still now, under full control: giant, systematic and “creative” work, is needed (ASAP!!!).
- 9) Last but not least, the nice experimental results of Technova-Kobe University Collaboration (A. **Takahashi**, A. **Kitamura** and Co-workers), using an alloy of nanometric $\text{Ni}_{80}\text{-Cu}_{20}$, dispersed in meso-porous silica, show, again and again, the general trend of “Constantan family” (cfr. Pg. 3) as good candidates to get AHE at low cost (in comparison with the precious metal Palladium, previously used from almost everybody in this field of Research).
- 10) *It is reconfirmed that the intuitions of Prof. Yoshiaki Arata (Osaka University, since 1993 with Pd-black and further key progress on 2002 with nano-Pd dispersed in Zirconia) about the specific role and characteristic of materials at nanometric sizes, were fully correct.*

- 11) The progress in these last years, about the key role of nano-dimensionality, were so large and wide-spread that, if the LENR community will get enough large resources, could be realistic to “made” some working devices, based on low-cost material, in few years since now.

- 12) We are indebted with Dr. James J. **Truchard**, CEO of National Instruments (Austin, TX, USA) and his Colleagues (Stefano Concezzi, Brian Glass, Wenzel Lothar, ...) because providing us (since July 2012) the PIXie system for data collection and on-line analysis. More important, their supports and moral encouragements were for us basilar to help to overcome the numerous and un-expected difficulties in such pioneering field of Science.

- 13) We would like to thank, from deep of our heart, all the **brave Researcher worldwide** (obviously included the MFMP group) that spent time and own money in the efforts to replicate our results. Now we understood more details, and weak points, of our fabrication procedures and experimental set-up, thanks to their long and wonderful work. In the next steps of experimentations we will provide them with materials having more controlled or specific characteristics, at the best of our ability. Moreover, even the “geometry” of assembling the wires and measurement procedures are quite important because the key requirements of Hydrogen “flux”, i.e. ***non-equilibrium***.

14) We would like to anticipate that is under final construction a new type of reactor with geometries optimized to keep enough far-away the area where the Hydrogen is dissociated (by sub-micrometric Constantan, kept at temperatures $\gg 300^\circ\text{C}$), from H_2 to $\text{H}+\text{H}$, and where is located the recombination area ($\text{H}+\text{H} \rightarrow \text{H}_2 + 4.5\text{eV}$). Considering several external constraints, we are planning to use the W because of: enough good catalytic properties (the best material is Pt, followed by Pd, both precious metals), its low cost, ability to withstand very high temperatures. About the average lifespan of hydrogen atoms, it is relatively long (about 0.5s at a pressure of 0.7Pa), so the distance between the two sections isn't a real problem, considering the high temperatures involved. We are confident the results of such specific experiment will help to clarify/identify the kind of complex/several phenomena involved in LENR anomalies.