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FURTHER STUDIES, ABOUT NEW ELEMENTS PRODUCTION, BY ELECTROLYSIS OF CATHODIC PD THIN–LONG WIRES, IN ALCOHOL-WATER SOLUTIONS (H, D) AND TH-HG SALTS. NEW PROCEDURES TO PRODUCE PD NANO-STRUCTURES

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Abstract

They were continued, at National Institute of Nuclear Physics, Frascati National Laboratories-Italy, the systematic studies about detection of new elements, some even with isotopic composition different from natural one, after prolonged electrolysis of Pd wires.

The electrolytic solution adopted is the, unusual, used from our experimental group since 1999.

In short, it was a mixture of both heavy ethyl alcohol (C_2H_5OD at 90-95%) and water (D_2O, at 10-5%), with Th salts at micromolar concentration and Hg at even lower concentration (both of spectroscopic purity). The liquid solutions, before use, were carefully vacuum distilled (and on line 100nm filtered) at low temperatures (30-40°C) and analysed by ICP-MS. The pH was kept quite mild (acidic at about 3-4).

The cathode is Pd (99.9% purity) in the shape of long (60cm) and thin wires (diameter only 0.05mm). Before use, it is carefully cleaned and oxidised by Joule heating in air following a (complex) procedure from us continuously improved (since 1995). Before and after use, some pieces of it, about 50% of total length, are ICP-MS analysed.

The anode is a Pt wire (purity>99.99%), 0.250mm diameter.

The cell adopted is usually a borosilicate chemical glass (like SCHOTT-DURAN, Germany), filling volume about 750cc. Recently (since July 2004) an ultra-pure quartz cylinder (volume about 1050cc) was adopted in order to rule out possibilities of corrosion effects from the cell.

The sample older and details of cell are made only of PTFE, as detailed at ICCF10 and ICCF11.

In respect to previous experiments, we made the following progress:
* It was studied, for long time and at a current density about 2 times larger than usual adopted, a solution of light ethyl alcohol and water instead of heavy one. It was used the usual borosilicate glass cylinder.
* It was made a very long experiment (8 months) using the quartz cylinder, “heavy” solutions.
* It was developed an innovative circuitry (under patent procedures) aimed to produce nano-structures at Pd cathode surface during electrolysis. Experiment planned to “emulate” the Y. Arata procedure of Pd nano-particles. Experimentally proved, by D_2 gas, excess loading in respect to thermodynamic limit values.
* It was developed, very recently, a procedure to promote nano-structure since the beginning of experiment, even in a gas atmosphere.
* It was also experimentally demonstrated, for the first time in the world, the effect of “confinement” of D_2 gas (the so called ”Preparata effect”): increase of loading, over thermodynamic equilibrium, due to a voltage drop longitudinal to wire length. Work in progress.

** During the Workshop it was discussed, in details, only some of key results obtained.

Keywords: PdDx-Hx, electrolytic hydro-alcoholic solution, Pd thin-long wire, Th-Hg ‘transmutation’, colloidal silica stabilised nanostructures.

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1. INTRODUCTION

1.1. Heavy/light experiments, borosilicate/quart cells

In order to detect anomalies in Pd-Deuterium systems, and rule-out possible mistakes during measurements, they were performed (at Frascati National Laboratories of National Institute of Nuclear Physics), during the year 2004 two kinds of main experiments, one with almost "light Hydrogen" solution and another with "heavy Hydrogen".

In order to rule out some source of contaminant coming out from the beaker, the light experiment, used as reference one, was performed with the same borosilicate glass used by us from over 4 years. In total, were made over 8 experiments with deuteride solution (all the previous experimental results, analysed by ICP-MS instruments, were reported also at JCF4, JCF5, ICCF10, ICCF11; Ref. 1).

About the last heavy experiment, we used a new (virgin) ultra-pure quartz glass, properly aged/cleaned by pure, warm, aqua regia solution.

1.2. New interpretation of *all* positive experiments

Analysing (from a new specific point of view), several "Cold Fusion" experiments that give positive results, we were convinced that almost all worked "well" just because "spontaneous but uncontrolled" growing of nano-structures or fractal at surface.

For what we know, only Yoshiaki Arata (Osaka University, Ref. 2) make some specific experiments with nano-particles. Almost all of the other Researchers, starting even from M. Fleischmann-S. Pons, get such kind of geometry just because by chance. Among others, we considered some of the positive results obtained by: S. E. Jones, A. Takahashi, E. Storms, M. McKubre, F. Celani, A. B. Karabut, G. Preparata-E. Del Giudice-A. De Ninno, G. Miley, V. Violante, Y. Iwamura (Ref. 3), T. Mizuno.

Because the previous reason, we specifically investigated the possible rule of fractal surface (and/or nano-structure at Palladium surface) by the use of an innovative electronic circuitry (developed by our Group) able to induce continuously, ***fresh*** specific geometry during the electrolysis.

2. Cell description and experimental results

The cell geometry and experimental set-up was detailed in our previous reports, especially at ICCF10 one.

2.1 ICP-MS result

The results about main new elements, detected by a high resolution ICP-MS, are reported in Tab. 1. The composition of solutions, refillings included during the long experiments, were the following:

a) Light experiment: main solution 750cc (C_2H_5OH 95%, H_2O 5%); $Th(NO_3)_4$ =5cc; Hg_2SO_4 = 7cc.

b) Heavy experiment: Main solution: C_2H_5OD=1005cc, D_2O=89cc; $Th(NO_3)_4$=6cc; Hg_2SO_4=8cc; NH_4OD (0.16M), in D_2O=6cc.

Tab. 1. Main new elements detected in light alcohol-water (Pyrex type) and heavy alcohol-water (quartz) cell; all reagents $Th(NO_3)_4$ *(at 1mg/ml concentration) and* Hg_2SO_4 *(10^{-3}M) are in* D_2O*. BKG and reagents subtracted. 1 Count = about 5E10 Atoms.*

Element	Light Exp. Counts	Heavy Exp. Counts	Comments
P	0	**6.4E6**	BKG=4E3
^{39}K	0	1.8E7	BKG=1E6
Cu	2.3E6 63/65=2.20	**2.5E7** **63/65=2.11**	Nat. 63/65 =2.25
Zn	6.2E6	**4.9E7**	
Rb	3.1E4	8.2E4	
^{108}Pd (26.5%)	Normal	**Depleted of 5%**	
Ag	6.5E4	2.6E5	
^{140}Ce(88.5%)	1.86E4	1.31E5	
W	1.16E4	4.42E4	
Tl	80	**900**	
Pb	4.5E5	**1.38E7**	
U	1.1E3	**1.0E4**	
^{195}Pt(33.8%)	4.3E7	10.8E7	Marker Anode dissolution

2.2. Deuterium self-loading after electrolysis and SEM analysis

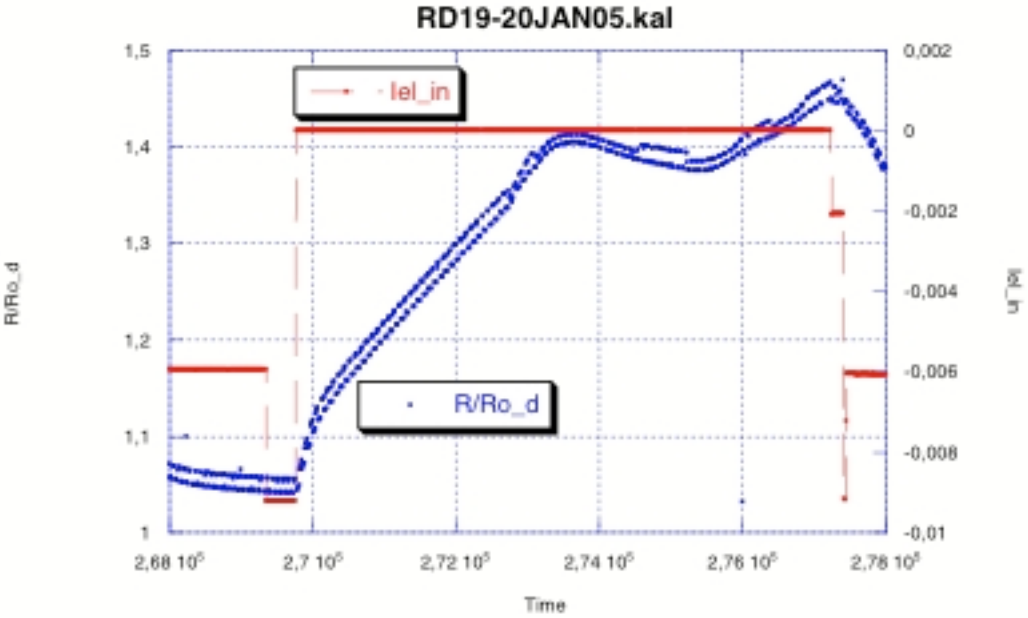
In previous electrolytic experiments we get, several times, evidence (although not fully reproducible) of spontaneous deuterium self-loading, in liquid solution, without applied electrolytic current. The deuterium was absorbed from the gas dissolved in the solution due to previous electrolysis.

The effect was increased, and made almost reproducible, after prolonged “specially cycled” electrolysis.

The gaseous loading-unloading can be controlled just changing the kind of gas (D_2-->Ar-->D_2-->Ar) dissolved in the solution (Fig.1).

We would like to remember that in almost our experiments, since 2003, we introduced an innovative procedure that allows evaluating, together with R/Ro value, the Resistive Thermal Coefficient of Palladium versus the Hydrogen or Deuterium content. Such procedure is based on cyclically injecting, along the wire, a current of low (typically 15mA) and high intensity (typically 120mA). This is the reason because we observe 2 parallel lines in R/Ro measurements.

Moreover, we get experimental evidence of spontaneous self-loading **over the thermodynamic**, well-known, **limit**. In other words, we expected a R/Ro ratio less than 1.8 but we observed a value much larger, close to 1.95—2.0. Such value is equivalent to a deuterium pressure of about 8—10 times larger then 1bar (Fig. 2).



In Fig 1, at time about 269500s, the anodic stripping was ended (the current, from –9mA returned to 0mA). The wire, almost immediately, started to absorb the deuterium dissolved in the solution and the R/Ro increased from about 1.05 to about 1.405. At time 273500s was introduced large amount of Argon gas, by bubbling it inside the solution. Immediately, the R/Ro started to decrease. At time 275500, after the R/Ro decreasing (because Argon effect) from 1.405 to 1.375, it was added again D_2 gas by external bottle. The R/Ro value again increased, showing reversible and controllable effects. At time 277300, when the R/Ro increased to 1.45, was stopped the intake of D_2 and added again Argon. At the least, was made again anodic stripping (at –6mA) in order to deload fully the wire.

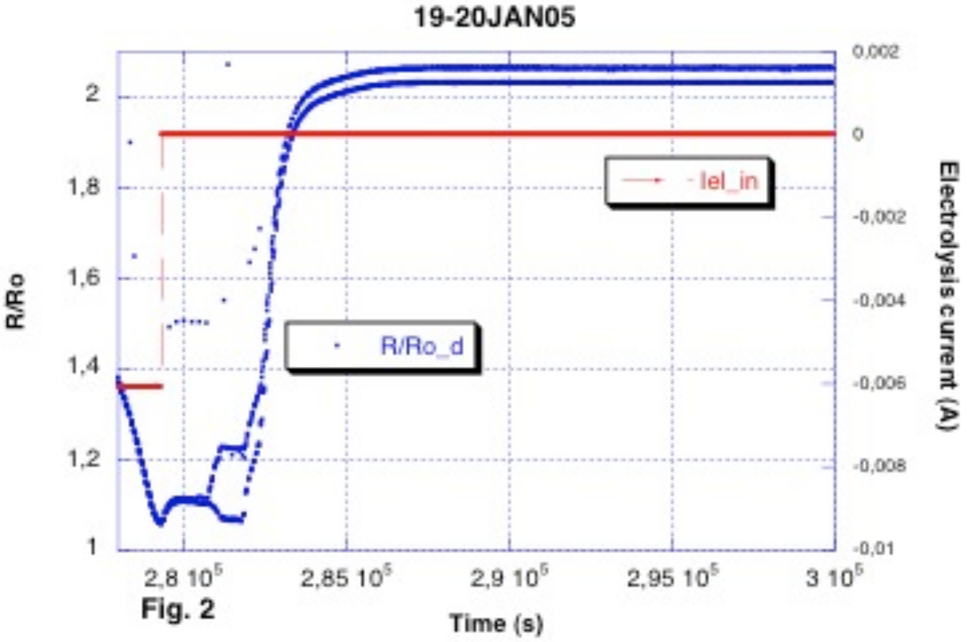


Fig. 2

In Fig. 2 it is shown the spontaneous loading by deuterium gas dissolved in solution (time

282000s →over 300000s). At time 279000s was ended the anodic stripping in Argon atmosphere. At the end of anodic stripping was observed a weak self-loading. Later (time 281000s) was added again Argon, because calibration purposes. At time 282000s was finally added Deuterium gas and self-loading started immediately.

The R/Ro values are >2.0 (time 290000) because effect of residual stress (R/Ro at D/Pd=0 is increased to about 1.05 in respect to 1.00 at time 0 of beginning the experiment). In other words, the wire was deloaded (at time 282000) and intentionally we didn't correct (by mathematic calculation) the value in such experiment because we would like to "monitor" the value of residual stress over time.

In Fig.3, 4, 5, are shown some pictures, by SEM microphotography, of Pd wire before (Fig. 3) and after (Fig.4, Fig. 5) heavy solution electrolysis.

Elemental analysis (by microprobe) of some «white» area of Fig 5 are shown in Fig. 6.

The wire analysed was about 10cm long in respect to 60cm total. The new elements are concentrated at about 15% of total length, in a random like distribution.

It is clearly shown the problem coming out from anode dissolution and its deposit at Pd cathode surface. Such deleterious effect, in respect to H, D absorption in Pd, is not yet solved (despite our deep efforts). We recall that, unfortunatelly, the overvoltage of H,D at Pt surface is close to zero. We are convinced that one of most important reasons of poor Deuterium loading into Palladium, as reprted from several Researchers, is just the Platinum coating (from the anode) at Palladium cathode surface.

It is interesting to note that, apart sensitivity, the some elements are detected from both SEM and ICP-MS. In other words, the ICP-MS results are "safe" and aren't instrumental fakes.

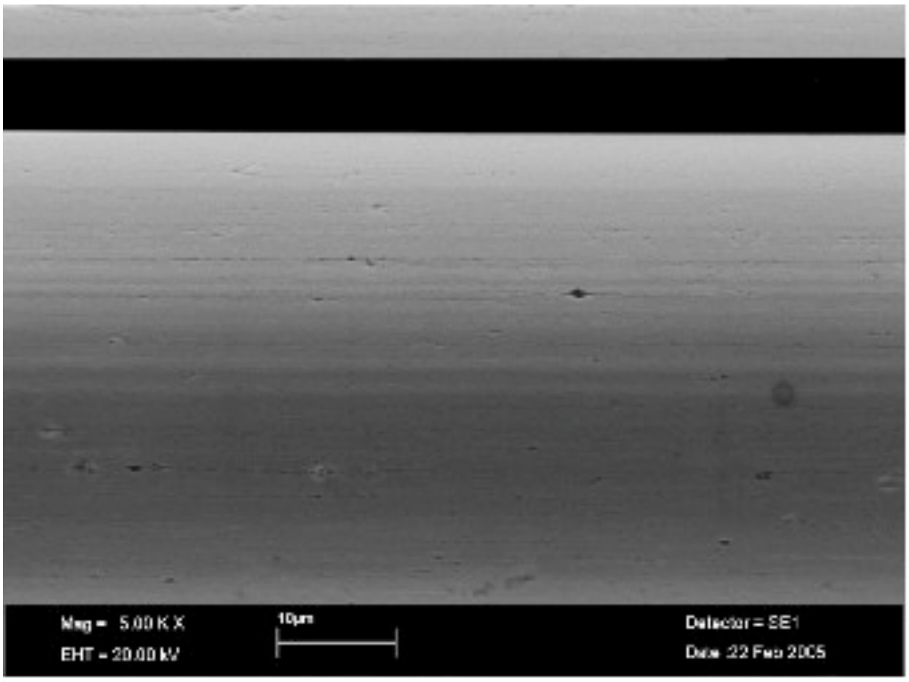


Fig. 3. SEM picture of Pd virgin wire, before electrolysis. The wire is contiguous to used one of Fig. 4.

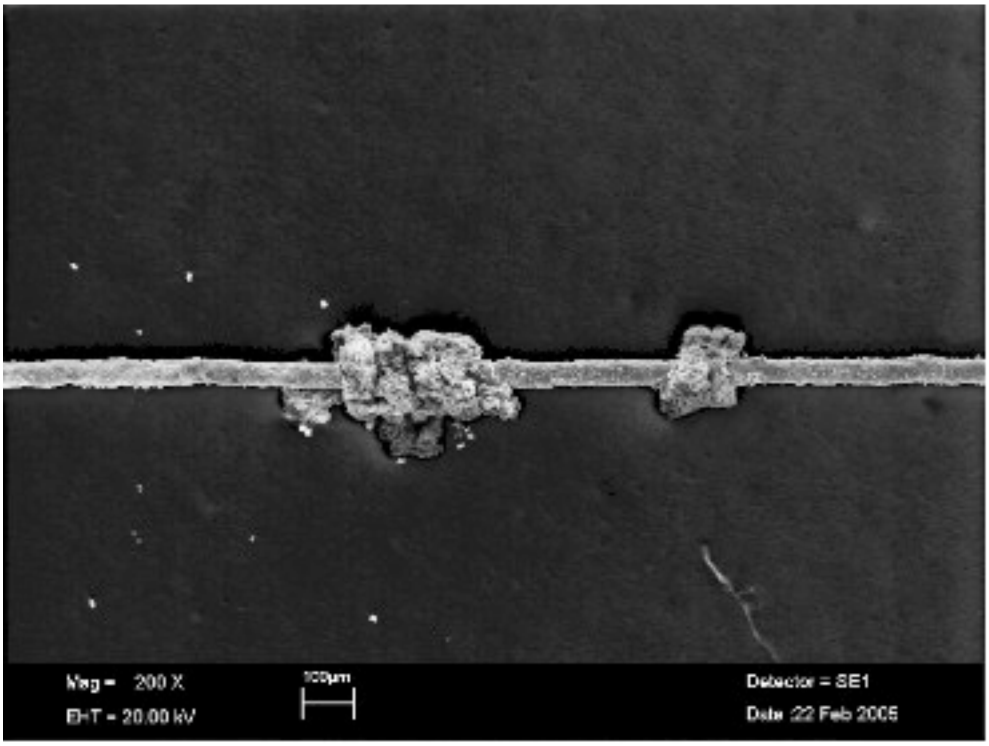


Fig. 4 SEM picture of a used wire, heavy solution electrolysis. The “new” elements and Pt deposit (from anode) are concentrated in few spot area (about 15% of wire length).

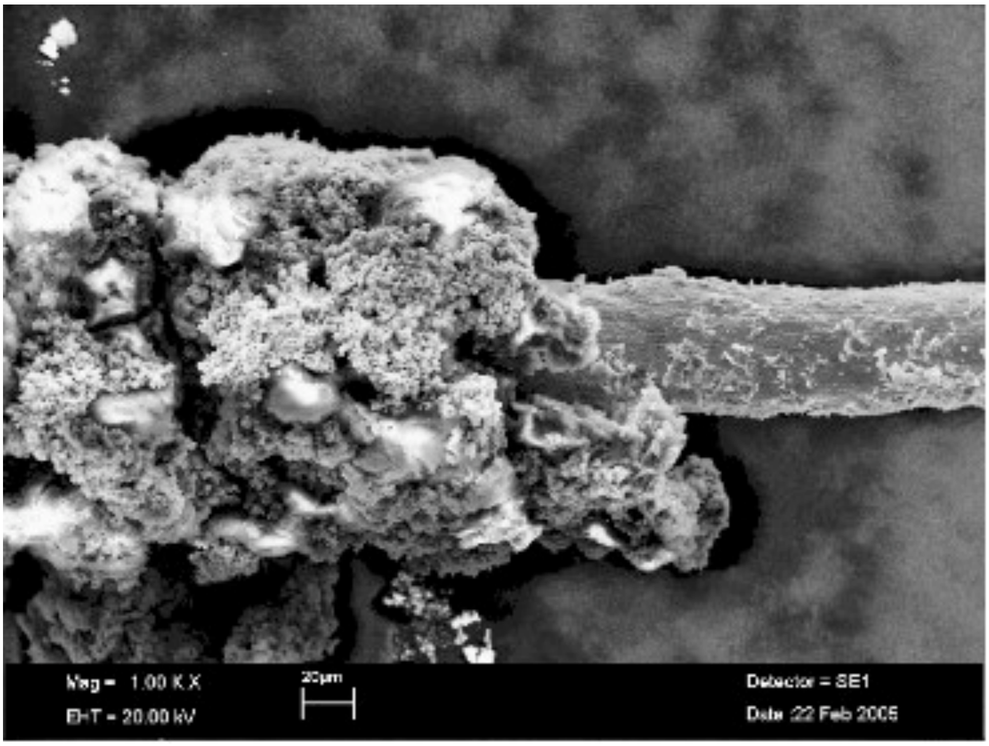


Fig. 5. Details of deposits as reported in Fig. 4.

Fig. 6. SEM elemental analysis of one of “white” area has shown in Fig. 5. The, unwanted, large deposition of Pt at Pd surface is clearly detected. Moreover, also Zn and Cu, detected by ICP-MS analysis, are re-confirmed.

3. Four experiments to understand the effect nanostructure on deuterium absorption

The key points and experimental steps/drawbacks of nanostructure growing can be resumed as following.

3.1. Wire just after electrolysis

The first experiment started using the wire used for over 6 months in electrolysis which ICP-MS results are reported in tab 1. We emphasise that previous long lasting electrolysis was performed using a new special circuitry to enhance nano-structures (under patent procedure). Electrolysis was performed at low current intensity (5-20mA/cm^2). The operation sequence was as following:

a) Wire overloaded in liquid solution (C_2H_5OD 90%, D_2O 10%) with very few amounts of salt dissolved (about 10mg/liter) was left without electrolysis for few hours.
b) After about 2 hours, the wire was still loaded. In order to unload we applied proper anodic stripping (up to complete unloading, R/Ro=1). When anodic current was removed, we observed that R/Ro increased spontaneously up to about 2.0 in about 10,000s (note that usual gas loading up to D/Pd=0.75, i.e. R/Ro=2, requires 10atm).
c) The stability was poor: R/Ro decreased from 2.0 to 1.8 (i.e. D/Pd=0.55, equivalent to a gas loading at 1atm) in about 10h.
d) The wire was completely deloaded, in solution, by usual anodic stripping (j=2mA/cm^2).
e) Liquid solution was removed from the cell and the cell was filled by D_2 gas (p=1030mbar).
f) The wire spontaneously loaded up to maximum (R/Ro=2) in 3,000s. See Fig. 2 for further details about.

g) The stability, in respect to point c) improved: R/Ro=2, was maintained stable more than 20h.

* About the self-loading effect described at point b), it is easy to evaluate that the Deuterium dissolved into the solution is enough large to refill the wire after deloading. Although we can't find specific data about deuterided solutions, we can estimate that the reported values on hydrogenated liquids are similar each other between a 20% indetermination.

* The Pd wire used (diameter 0.05mm, length 60cm, density 12g/cm^3, atomic mass about 106g) is equivalent to about 133 microM (Moles=volume*density/atomic mass).

* The solubility in H_2O (at 293K and 1013mbar) of O_2 and H_2, are respectively 31ml/l and 18ml/l (when divided by Avogadro number i.e. 1 Mole=22.4l, such values are equivalent to 1384 and 800 microMole/l). The values in C_2H_5OH are respectively 143ml/l and 80ml/l (equivalent to 6384 and 3571 microMole/l), i.e. over 4 times larger.

* Considering that at the end of experiment, because selective evaporation of alcohol in respect to water, we will have about 950ml of C_2H_5OD and 109ml of D_2O, we can estimate the total amount of D_2 dissolved as following:

- in D_2O, 800 microMole*0.109=87.2 microMole;
- in C_2H_5OD, 3571 microMole*0.950=3392 microMole.

* In conclusion, even supposing that some of the Deuterium dissolved is recombined with Oxygen to heavy water because catalytic effects of Pt anode and Pd itself, the amounts of D_2 dissolved is over a factor 50 larger (i.e. (3392+87)*2/133=52.3) of what necessary to load the Pd wire at a value of D/Pd as large as 1.

3.2. Three other experiments without previous electrolysis.

In order to elucidate the phenomena of large self loading after the end of electrolysis, three different experiments were performed using three different virgin wires never electrolysed.

The samples were coming from the same batch used for our previous electrolytic experiments, i.e. wires with a diameter of 0.05mm and length of 60cm.

Aims of such systematic studies were the promotion of stable (>24h) nano-structures at Pd surface in a way as simple as possible.

There will be shown results about R/Ro loading behaviour versus time.

We anticipate that we obtained both a very large diffusion speed (about 0.5 micron/s) and deuterium concentration over thermodynamic limit. The **improvements** were, respectively, over **1,000** times and about **8** times in comparison to reference one.

3.3. The second experiment

The second experiment started using a virgin wire. Several different tests performed on this wire are detailed in the following:

a) Virgin Pd wire, no acetone washing, only distilled water washing and drying. Loading in D_2 gas at 1030mbar.

b) Time to reach maximum loading (R/Ro=1.82) about 230,000s. Such time doesn’t include the “activation time” of virgin Pd (about 60,000s). These values are in agreement with literature results. The results are shown in Fig. 7.
c) Stability (at R/Ro=1.82), is obviously very good: (over 100h) at the thermodynamic limit.
d) Wire deloaded by Joule heating in ^{4}He atmosphere.
e) **Colloidal silica was hand-painted ex-situ on the wire surface** (silica characteristic: diameter 3-4nm, normalised surface 500m^2/g, low sodium content. Specially developed (patenting) for our purposes: fabrication tests started since year 2000.
f) Time to reach maximum loading (R/Ro=1.78) about 80,000s. The loading ratio was a little bit worse than the experiment a), Fig. 7, but loading time was about 3 time shorter than a).
g) Please note that applying DC electro-migration current (100mA), after other 20,000s, R/Ro reached 1.86 and was stable (demonstration of ***“Preparata effect”***, although “weak”). Removing electro-migration, after about 20h, R/Ro slowly decreased to 1.82 (usual thermodynamic value). In other words the Preparata effect improved the resistance ratio from 1.82 to 1.86.
h) **Joule heating, i.e. oxidation, of wire in situ** (600°C, 60s, 3 times) in dry ultrafiltered air atmosphere.
i) Time to reach maximum loading (R/Ro=1.95), 600s.
j) Stability over 2h. The wire was again deloaled, without checking long-time stability, in order to check reproducibility of the fast loading.
k) **Another Joule heating, i.e. oxidation, of wire in situ** (600°C, 60s, 3 times) in dry ultrafiltered air atmosphere.
l) Time to reach maximum (R/Ro=1.95), 700s.
m) Stability: at R/Ro=1.95 for about 12h; later, after 15h, R/Ro decreased to 1.93. Please, note that the combined effect of colloidal silica and later oxidation improved largely the loading ratio and the loading time.

3.4. Third wire experiment

The effect of Joule heating oxidation was studied using a new virgin wire. The operations were the following.

a) Virgin Pd wire, acetone washed.
b) **Joule heating, i.e. oxidation, of wire in situ** (600°C, 60s, 3 times) in dry ultrafiltered air atmosphere.
c) Time to reach R/Ro=1.90: 200s.
d) Time to reach R/Ro=1.95: 1,000s.
e) Stability was not excellent at long time: after 20h, R/Ro decreased from 1.95 to 1.93; after 100h, R/Ro decreased to 1.87.
f) No further data allowable: wire broke during operation of D_2 gas refilling (pressure gauge damaged).

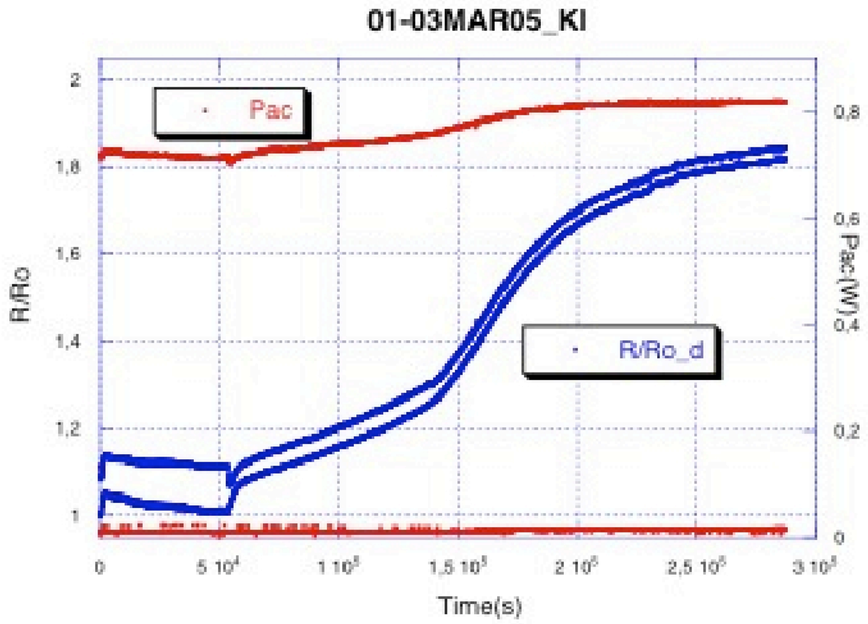


Fig. 7. Loading characteristic of a virgin Palladium wire: loaded at room temperature with 1bar of Deuterium gas. In order to “activate” the Pd surface, it was made a preloading cycle (from time 0 to about 60000s) with D2 gas, 293K, 1 bar and later allowed to decrease, very slowly, the Deuterium content in the cell. Even neglecting the activation time, the time needed to reach the thermodynamic limit of R/Ro=1.82 is as large as 220000s. Such values (i.e. R/Ro and time) are in agreement with data usually reported in the literature. As standard in our procedure from about 2 years, we cyclically inject electromigration ac current (square wave, 10KHz) with low (about 10-15mW) and high power (700-800mW) in order to calculate the Resistive Thermal Coefficient versus D/Pd ratio.

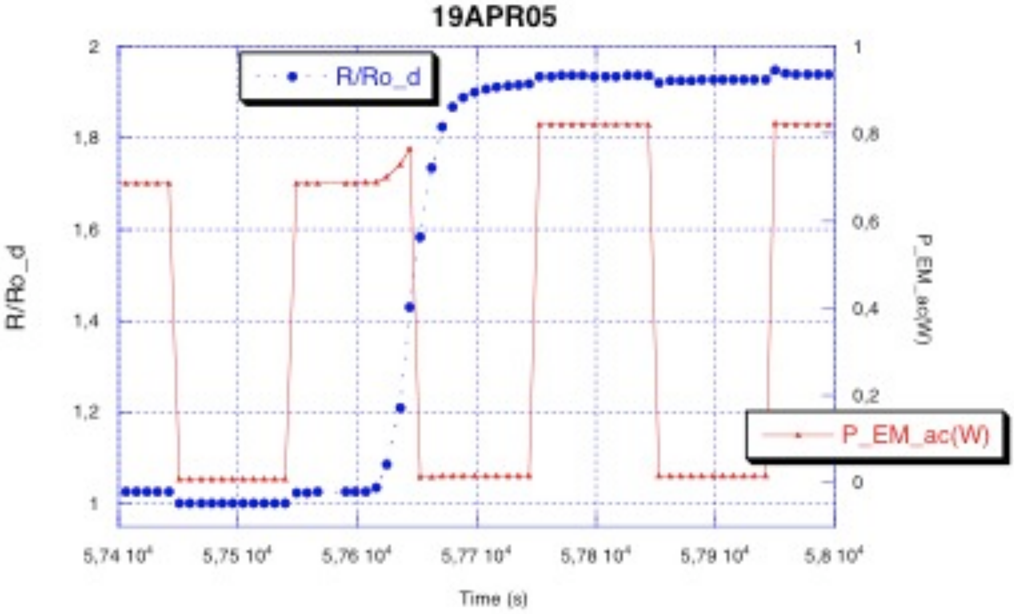


Fig. 8. Behaviour of R/Ro and electromigration AC power in the wire oxidised and painted by colloidal silica, experiment # 4.The time to reach R/Ro=1.90, from beginning of experiment, was as low as (less than) **100 seconds**.

3.5. Fourth wire experiment

A new virgin wire was used to check the sequential combined effects of oxidation and silica stabilisation as following:

a) Virgin Pd wire, acetone washed, outside cell:
b) **Joule heating in free air** (600°C, 60s, 3 times).
c) **Painting with colloidal silica in free air.**
d) **Joule heating in free air** (600°C, 60s, 3 times).
e) **Painting with colloidal silica in free air.**
f) **Joule heating in free air** (600°C, 60s, 3 times).
g) **Operation b-c-d-e-f were performed sequentially in about 30 minute taking care of cleanness.**
h) Wire inserted in the cell.
i) Short time Joule heating in dry ultrafiltered air (600°C, 30s, 1 time) in order to burn possible uncontrolled contaminants affecting the wire during the set-up of the experiment.
j) **Time to reach R/Ro=1.90: 50s.** See Fig. 8.
k) Time to reach R/Ro=1.95: 300s
l) Stability, at R/Ro=1.95, over 3h.
m) No further data allowable: wire broke during operation of D_2 gas refilling (due to pressure gauge damaged, same problem of experiment 3.4.f).

Please note the "giant" diffusion speed, Calculations give diffusion speed about 0.5 micron/s

4. CONCLUSIONS

It was found that the anomalous effects, about the amount of new elements detected by ICP-MS analysis, are over one order of magnitude larger in deuteride solution in respect to hydrogenated one.

Moreover, we argued that surface condition of cathode, especially at nanometric size, make a key rule in the production of anomalous effects.

It was exsperimentally proved that it is possible to improve both the diffusion speed of deuterium inside palladium and value of the thermodynamic limit, just providing the surface of a stabilised nano-metric geometry. The method that we developed (before, oxidation of Pd surface by Joule heating and immediately later, stabilisation by colloidal silica of nanometric dimension) looks quite simple and reliable.

The results we found are, obviously, in agreement with the (very impressive) experimental results obtained by Prof. Yoshiaki Arata at Osaka University (deuterisation of PdO-ZrO powders of nanometric size: subsequent fusion induced by proper triggers like laser or ultrasounds).

About theoretical models, we think that the “Tetrahedral Symmetric Condensation” model developed by Prof. Akito Takahashi (Osaka University, Ref. 4) is a good tool to explain several of our results.

Further, systematic, work is obviously necessary to study the long-term stability of the procedure adopted and the effects due to the increasing the pressure and/or changing the temperature.

Finally, can be very interesting to make some experiments were before the “special” Pd wire (prepared according to such new procedure) is gas loaded and just after the cell is filled with some proper liquid to perform electrolysis.

As a general comment, we are almost optimistic about the fate of Researches named “Condensed Matter Nuclear Science”. We feel that some application in real life (like remediation of some radioactive fission products coming out from nuclear power plant) is quite near. Perhaps, a proper “mixing’ of the very elegant methods introduced by Dr Yasuhiro Iwamura (at Mitsubishi Heavy Industries) about transmutation of natural Strontium and Caesium and “nanometric point of view” will be the winner in the field of long waited “application” of “Cold Fusion” effects.

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REFERENCES

1) F. Celani, A Spallone et al. Proc. of ICCF10, 24-29 August 2003:**http://www.lenr-canr.org**; and JCF4, JCF5 at **http://wwwcf.elc.iwate-u.ac.jp/jcf/**
2) Y.Arata, Y.Chang Proc. of ICCF10, 24-29 August 2003: **http://www.lenr-canr.org**
3) Y. Iwamura et al Proc. of ICCF10, 24-29 August 2003: **http://www.lenr-canr.org** ; and JCF4, JCF5 at **http://wwwcf.elc.iwate-u.ac.jp/jcf/**
4) A, Takahashi Proc. of ICCF10, 24-29 August 2003: **http://www.lenr-canr.org** ; and JCF4 , JCF5 at **http://wwwcf.elc.iwate-u.ac.jp/jcf/**