J. Condensed Matter Nucl. Sci. 19 (2016) 29–45

Research Article

Observation of Macroscopic Current and Thermal Anomalies, at High Temperature, by Hetero-structures in Thin and Long Constantan Wires Under H_2 Gas

Francesco Celani*, †, A. Spallone‡, B. Ortenzi and S. Pella
INFN-LNF, Via E. Fermi 40, 00044 Frascati, Italy

E. Purchi, F. Santandrea, S. Fiorilla, A. Nuvoli, M. Nakamura, P. Cirilli and P. Boccanera
ISCMNS, Latium#1 Group, Via Cavour 26, 03013 Ferentino, Italy

L. Notargiacomo§
Dip. Chimica Università "La Sapienza", Pz. A. Moro 5, 00185 Roma, Italy

Abstract

Since 2011, we introduced into LENR field, the use of a Constantan (Cnst) alloy to absorb/adsorb proper amounts of H_2 or D_2 and to generate thermal anomalies even at low temperatures (>200°C). We developed a reactor with a core of sub-micrometric layered Cnst wires that produced measurable excess power (almost reproducible). Subsequently, we used fiberglass sheaths as electrical insulation and found out that this material actually improves reactor performance. In the most recent configuration, we studied the effects of adding Fe nanolayers to the Cnst wires and of including several small knots along their extension, actions that resulted in a larger excess power that grew with increasing wire temperature. We detected a new electric effect: the generation of spontaneous voltage between the ends of a floating wire in the reactor. We performed tests to study results in agreement with Inverse Rydberg Matter model by L. Holmlid.
 ISSN 2227-3123

Keywords: Constantan sub-micrometric surfaces, H_2 ad-/absorption, Iron, Rydberg Matter, Thermodynamic second law

*E-mail: Francesco.Celani@lnf.infn.it
†Also at: ISCMNS, Latium #1 Group, Via Cavour 26, 03013 Ferentino, Italy.
‡Also at: ISCMNS, Latium#1 Group, Via Cavour 26, 03013 Ferentino, Italy.
§Also at: ISCMNS, Latium#1 Group, Via Cavour 26, 03013 Ferentino, Italy.

 ISSN 2227-3123

1. Constantan alloys as H_2-Dissociation Catalyzers

Our investigations concerning the ability of metals such as palladium (Pd) and nickel (Ni) to absorb D_2 and H_2, and to generate anomalous heat at high temperatures, gained new momentum following the introduction of Constantan alloys to LENR research in 2011.

Our original idea was to create a low-cost material able to replace the very expensive (and mechanically weak) palladium in LENR experiments.

We focused our interest on the family of copper-nickel Constantan alloys as materials that fit our purposes because of their ability to dissociate molecular hydrogen [1]. In particular, we selected a low-cost commercial material called ISOTAN44, with atomic composition $Cu_{55}Ni_{44}Mn_1$ (Isabellenhütte Heusler, Germany). Together with a high H_2-diffusion coefficient at high temperature, this material offers good mechanical resistance against the aging effects of the thermal cycles and H_2 absorption/desorption. Moreover, it has very large values of (calculated) catalytic power with respect to hydrogen dissociation, as shown in Table 1.

We demonstrated experimentally that Constantan at nano-/micrometric size and at low temperatures ($T > 120°C$, in comparison with about $2000°C$ for tungsten) is able to catalyze the dissociation reaction $H_2 \rightarrow 2H$ and absorb/adsorb atomic hydrogen even inside the bulk of the lattice, as well as at the surface. The demonstration was reported in Ref. [1], chapter IV, points 18 and 19, as follows: 18) To get deloading we put the cell under a dynamic vacuum and increased the temperatures. 19) After several hours, we got the original starting value of $R/R_0 = 1$, meaning that the test was fully successful. The fact that H_2 decreases the resistivity of Constantan was first reported in Ref. [2].

Table 1. Catalytic power of different metals and alloys with respect to the reaction $H_2 \rightarrow 2H$, computed in Density Functional Theory [20].

	ΔE (eV)
Ni0.3750 – Cu0.6250	+3.16
Ni0.6250 – Cu0.3750	+2.86
Ni0.8125 – Cu0.1875	+2.10
Ni	+1.74
Ni0.1825 – Cu0.8175	+1.57
Ag0.8125 – Pd0.1875	+0.57
Ag0.625 – Pd0.375	+0.51
Ag0.1875 – Pd0.8125	+0.51
Pd	+0.42
Cu	–1.11
Ag	–1.42

In our experiment we employed Constantan wires of length 100 cm and diameter 0.1– 0.2 mm (Fig. 1). To increase their effective surface available for catalytic processes, wires were subjected to specific thermal/electric treatments that created sub-micrometric and multilayered structures at the surface and deeper in the bulk (Fig. 2). The sub-micrometric structures were simply created by oxidation, with a threshold temperature of $600°C$ in free air. Such structures are somewhat similar to hetero-structures.

The treatment includes electric high peak power pulses (20 kVA/g of material) with a rise time $T_r < 1\,\mu s$, corresponding to a current density $J > 50$ kA/cm^2, even neglecting skin effects. Such pulses induce extremely fast thermal treatments (warming→cooling) and shock waves. A rough evaluation by fast photo-camera of the color of light emitted from the wire revealed a surface temperature even larger than $1000°C$ in some tests. At the end of the process we observed glassy materials formed on the wire surface.

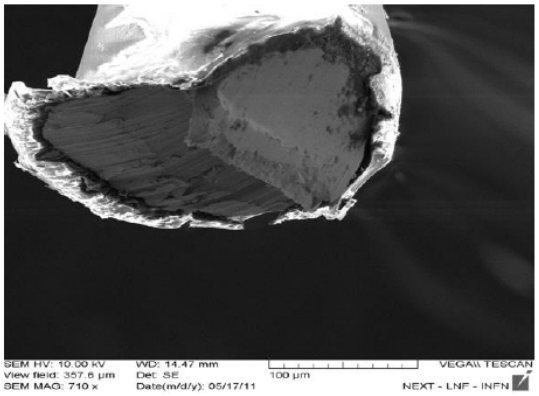

Figure 1. SEM image of the cross section of the Constantan wire as provided by Isabellenhütte Heusler. The plastic cover of the wire is visible as the light area rounding the wire.

This treatment produces sub-micrometric geometries, a sort of chaotic mixture of Ni, NiO, Cu, CuO, $Ni_xCu_yO_z$, reducing/avoiding, at the same time, the usual deleterious self-sintering processes due to high temperatures. SEM observations revealed that the wires so treated had a large number (up to 700 in some samples) of multilayered structures with thickness of 20–100 nm.

The number of layers was roughly characterized by preliminary experiments using 10, 20, 50 and 100 pulses, by SEM and "oblique" cross section of the wire. Among other parameters, we observed that the distance between layers decreases with an increase in the number of pulses. Sadly, the original documents (papers and CD) of this preliminary testing, located in another laboratory, were destroyed by a "third party" in February 2015, together with other materials and documents.

Our treatment was inspired by the Melt Spinning and Quenching metallurgical process, extensively used by Prof. Yoshiaki Arata and his collaborators (Osaka and Tohoku Universities, Japan) to produce nanomaterials (palladium, or Pd_xNi_y, both dispersed into a matrix of ZrO_2 at 65(%) concentration) for his Solid State Fusion devices under

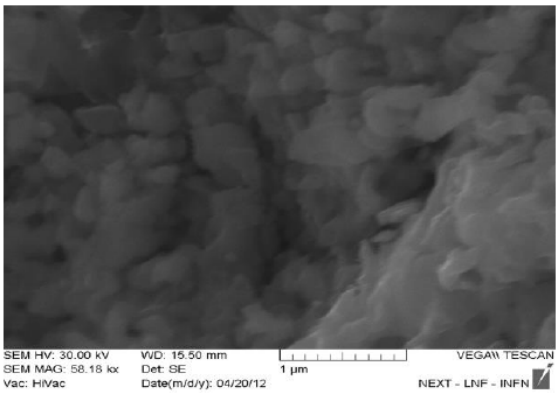

Figure 2. SEM image of the Constantan wire surface at micrometric scale after repeated high-power pulse treatments.

interaction with D_2/H_2 at 150–300°C, pressurized up to 60 atm [3]. In the quenching process their cooling rate was over 100,000 K/s. The important feature of Arata's technique was this "ultra-fast quenching" which yields glassy-like materials. Arata used fast rotating Cu disk where the mixture of palladium (35%) and zirconium (65%) was dropped in a melted state (about 1600°C). Instead of using this kind of disk, we employed ultra-fast powerful electric pulses with fall time <1μs. We needed only cooling from about 900°C down to 650°C. With very long and thin wires it is easy to perform this in a short time, just by natural cooling, because of the dependence of emitted power as T^4 (in Kelvin), i.e. the Stefan–Boltzmann law.

2. First Generation Experiments: the Introduction of Constantan wires

The dissipation reactor we designed to test the new generation Constantan wires consisted of mica sheets (of the type used in electrical heating elements) supported on a central stainless steel (SS) tube ensuring electrical insulation, on which two wires, one active (the surface-modified constantan wire) and the other inert (Ni–Cr control wire), arranged in parallel and helicoidally wound. Because the Ni–Cr wire is intrinsically stable against oxidation or other stresses, it was used to heat the reactor itself (via "indirect" resistive heating, i.e. by radiation and conduction by gas). The core of the reactor was contained inside a borosilicate Schott Duran glass tube with a wall thickness of 3 mm. Temperatures at the external glass wall and inside the reactor were detected by means of several Type K, SS-screened, MgO insulated, thermocouples (diameter 1.5 mm) [1].

Calibrations were made in noble gases (helium, argon) with different power levels applied to the inert wire. The first test was conducted in an atmosphere of H_2/Ar mixture in the ratio 75/25 at 7 bar of total pressure. The power input was 48 W. Figure 3 shows the behavior of the measured quantities over time. The green color line represents the temperature of the external borosilicate wall, while red shows the temperature close to the mica inside the reactor. The key monitor parameter is the ratio R/R_0 between the resistance of the wire at a given temperature T and at room

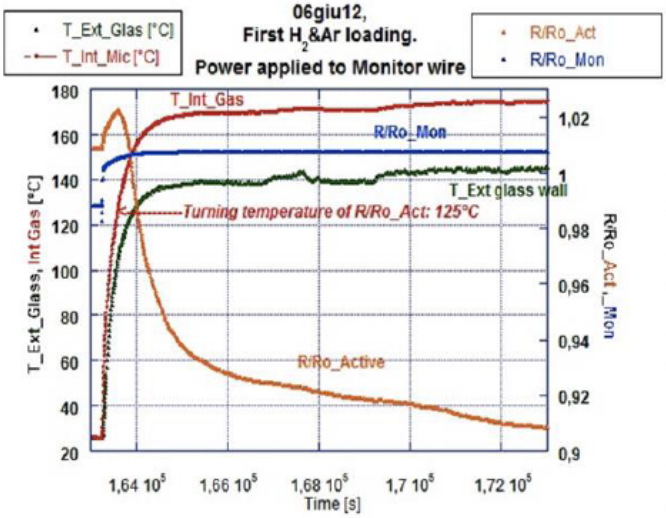

Figure 3. Time behavior of the measured quantities during the first loading by H_2/Ar mixture: temperature of the external glass (*green*), temperature of the internal mica support (*red*), R/R_0 of the inert wire (*blue*), R/R_0 of the active wire (*orange*). Ar inert gas introduced also to reduce H+H probability of uncontrolled recombination to H_2 in the reactor atmosphere.

temperature T_0. For Constantan, this ratio, because of hydrogen interaction, decreases with increasing temperature and time. In the blue line we indicate R/R_0 for the inert (Ni–Cr) wire and in the orange line R/R_0 for the active (Constantan) wire. Recall that one of the key characteristics of Constantan is its normally excellent resistivity stability ($\pm 1\%$) from –75 up to 500°C.

We observed that when the temperature inside the reactor reached 120°C, the R/R_0 of the active wire fell to 0.92 in about 2500 s and to 0.88 in 100,000 s. Correlated with this decrease in resistance, we also observed an increase in excess output power of the reactor. Coinciding with this, all temperatures in the reactor increased. The external glass temperature increased from about 140°C to 150°C; the SS tube temperature from 168°C to 190°C, and the gas temperature (close to the mica) from 170°C to 195°C (Fig. 4). These variations are unrelated to changes in room temperature. Instead, room temperature instabilities somehow helped the anomalous heat generation, perhaps by introducing non-equilibrium conditions. In fact, after a long time, room temperature went back to its initial value, while heat production continued to increase.

During several tests performed in Frascati with mainly Agilent instrumentation (in addition to many ancillary home-made instruments), the excess power ranged between 2 and 12 W (reaching 12 W a few times) at the reference input power value of 48 W. When excess heat was produced, it was typically in the range of 5–10 W. We found no difference in operating the reactor at constant current and constant voltage. Most of the time it was in the constant current regime.

After the National Instruments Annual Meeting (NI-Week, August 2012, Austin, TX, USA), the reactor at Frascati Laboratories, Italy, was disassembled, shipped and reassembled in the USA where it was operated in a public demo for three days. During this event, we observed the highest values of maximum excess power for this experimental set-up: about 21 W with indirect heating (power applied on the inert wire) and about 25 W with direct heating of the active wire with input power of 48 W. Just after NI Week, the reactor was again shipped to South Korea for our participation at the ICCF17 conference at Daejeon. Even there, after overcoming difficulties with the new strict safety rules and conditions of air travel from USA (no gas apart from air inside and no vacuum or pressure conditions allowed), the reactor functioned normally with reasonably reproducible results: 5–15 W of anomalous excess heat with 50 W of electric input power. The values seen were lower than in the test performed during NI-Week. Moreover, for safety reasons, the reactor was operated for most of the time in Constant Voltage regime, both at NI-Week and ICCF17.

After returning to Frascati and performing several cross checks, we realized that the new NI system (the hardware and software set-up since August 2012) in our hands had underestimated the value of electric input power in the regime of Constant Voltage by 11.11% in the range of input power of 40–60 W, i.e. that used in the experiments. Considering this unexpected problem, the real values of AHE power would change to: 8–20 W at Ni-Week, 0–10 W at the ICCF17 Conference (assuming similar hardware arrangements).

We note that all the data were and are fully correct in the constant current regime. The reported lower values are however closer both to our starting values in Frascati and to the results of the subsequent experiments performed by the Martin Fleischmann Memorial Project group which used a batch of Constantan wire with a different starting composition from the old pre-1970s batch we used in the first series of experiments. See Section 3 for further details.

Regarding the overall better performance during NI-Week, in the absence of any systematic study, we can only suspect a positive effect from an accident that happened during the preparation of the set-up: some vapor of silicon oil from the rotary pump went inside the reactor chamber. We did try to remove the possible residual deposits by heating the wires. Anyway, we feel that such an accident was a further strong indication of the catalytic origin of the AHE effect, at least with our materials and operating parameters.

3. Second Generation Experiments: the Addition of Glass

The successive series of experiments exhibited unsatisfactory overall reproducibility. Using SEM/EDS/ICPMS analyses, we found out that the first batches of raw material we used in our experiments, which were produced before 1970, had a composition different from those we used later. Analyses revealed iron contamination in the order of 1000–5000 ppm, and locally up to 10,000 ppm.

Because of a severe budget cut in late 2013, we were forced to redesign and reschedule our experiments with the purpose to study again more deeply some of the most interesting effects obtained in the past and, if possible, to increase the AHE.

In the new experimental set-up we modified the geometrical arrangement of the wires inside the reactor [4]. We used three wires instead of two: a 500-layer Constantan wire, a 2-layer Constantan wire and a platinum wire for control and monitoring purposes. They were inserted inside fiberglass sheaths ($L = 100$ cm, $\Phi_{\text{ext}} = 1$ mm, produced by SIGI–Favier, Italy–France Company). Each fiber was porous, of 5 μm mean diameter, and closely braided together. The braid was then twisted around the central SS support that was likewise covered with a fiberglass sleeve with internal diameter of 12 mm. As before, the core was inserted into the thick-wall borosilicate glass tube previously used.

Since February 2013, all the sheaths were embedded in a $Sr(NO_3)_2$ diluted solution and further decomposed in SrO by thermal treatment. Strontium is a material with a low work function for electron emission ($W = 2.59$ eV), similar to the calcium oxide used by Yasuhiro Iwamura at Mitsubishi Heavy Industries Laboratories (Yokohama, Japan) since 1999. Electron emitter materials are empirically recognized to have "beneficial effects" on LENR reaction. We have studied the effects of calcium, barium, strontium and magnesium in electrolytic environment, since about 1995. Iwamura, independently, adopted CaO in his famous transmutation device (2002, JJAP) by flowing deuterium gas. Moreover, he showed that MgO is not effective, similarly to our electrolytic experiments (barium worked best, but it is toxic).

We calculated the emitted power using Stefan–Boltzmann law (emission proportional to T^4, in Kelvin) for the

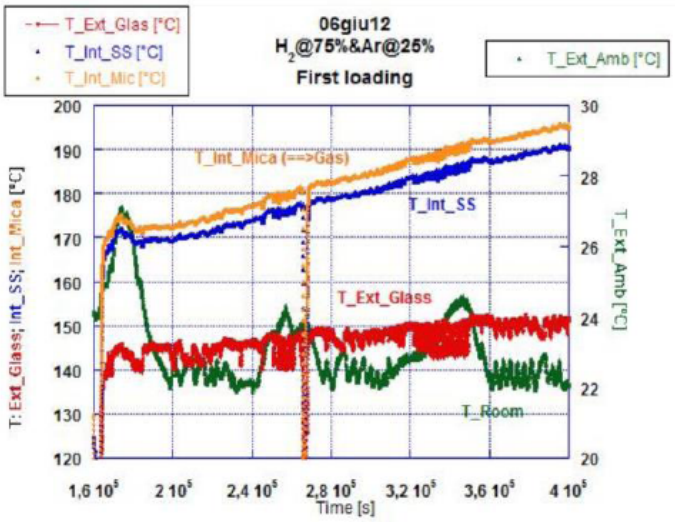

Figure 4. Temperature of the external glass wall (*red*), the internal SS tube (*blue*), the internal mica support (*orange*) and the ambient (*green*) as a function of time.

radiated energy from the glass wall and Newton's law (proportional to temperature) for the energy dissipated by convection.

During the tests several uncontrolled and unexpected phenomena occurred – including spontaneous overheating that damaged the 500-layer wire – making the results unclear. Therefore, we decided that the only way to clarify the role of the fiberglass in the process was to add a larger amount of glass. Even the SS-tube, where the glass-covered wires were twisted around, was inserted inside two more glass hoses.

To calculate excess heat, we decided that tests carried out with a smaller amount of glass would be considered the threshold, i.e. the blank test. Even with such a conservative constraint, the comparison between the two experiments showed that glass has intrinsic co-effects in the generation of anomalous heat. In Fig. 5 we compare the temperatures at the external wall and at the internal SS-tube in the two cases of a small and a large amount of glass. We note that, under the same conditions of pressure and input power, the temperature in the second case is clearly larger than the corresponding values for the experiments with lower glass content in the reactor.

4. Effect of Fiberglass on Hydrogen Storage

The experiments we carried out clarified that the borosilicate fiberglass (type E) we used as electrical insulator plays a role in the generation of excess heat. We signal out the mechanism responsible for this in the adsorption property of (borosilicate) glass, which was observed by Prof. Irving Langmuir since 1920 during his studies on hydrogen dissociation at high temperatures by Tungsten (W) wires (>2000°C, at H_2 low pressures). The hydrogen atoms,

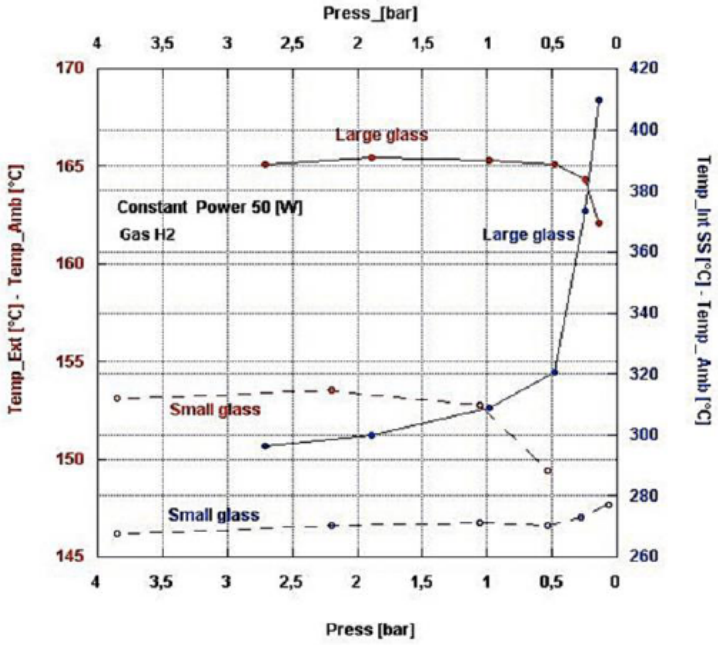

Figure 5. Data comparison between tests conducted with a small and a large amount of glass in the reactor. In red we display external glass temperature, in blue internal SS tube temperature after subtracting ambient temperature. Under the same conditions, temperature is higher when more glass is employed.

produced by the dissociation of molecular hydrogen by means of the catalytic action of our sub-micrometric structured Constantan wires on the reaction (at quite low temperatures, about 200°C), are largely adsorbed onto the surface of the micrometric glass fibers, forming a thin film. Moreover, according to one of our colleagues (Cesare Lorenzetti, private communication), a long-time expert in Fischer–Tropsch type catalysts, the oxides (in the specific case made by iron, potassium, strontium, boron) "locked" inside glassy materials (like fiberglass) are quite stable for long time (months) even in reducing environments and at high temperatures. The stability effect against the "evaporation" of light elements (like potassium) is further enhanced by manganese (present, in the type of Constantan that we used, at 1% concentration).

Langmuir measured the density of hydrogen atoms adsorbed onto the surface of a glass bulb (presumably of type borosilicate) kept at low temperature (about 90 K). The density is of the order of 10^{15} atoms/cm^2. In his experiments, the dissociation was obtained through a hot tungsten filament in H_2 atmosphere and the fraction of dissociated molecules depended on pressure and temperature: the lower the pressure and higher the temperature, the larger the fraction [5,6].

In our experiments the effective surface of each small sheath is larger than 1 m^2. The total surface of the used fibers could be larger than 50 m^2, corresponding at about $10^{20} - 10^{21}$ adsorbed atoms according to Langmuir's measurement. The hydrogen atoms concentrated onto the glass surface by adsorption are much closer to each other than the hydrogen atoms moving in the bulb as a gas, increasing so their probability of recombination in the molecular form. This reaction is largely exothermic with the release of 4.52 eV to the environment.

Moreover, the recombination time is in the time regime of so-called femtochemistry (some-several 10^{-15} s). The experimental demonstration that several chemical reactions have extremely short reaction time ($10^{-12} - 10^{-15}$ s) has been performed since 1980 by Prof. Ahmed H. Zewail using ultra-short laser pulses [7]. Obviously, with such short times, the peak power of recombination is extremely large, $10^{12} - 10^{13}$ times larger than the mean power at steady-state conditions.

With this new equipment configuration, the net effect of the introduction of glass in the reactor is the increase of the rate of the chemical reaction of hydrogen recombination. Therefore, the adsorption property of glass appears to be a co-factor in the generation of heat excess, in addition to the main unknown LENR process of non-chemical origin. We note that nearly all of the chemical reactions produce at most 4.5 eV of energy. In our experiment, the effect lasted for several weeks and its integrated value is very much higher than the product of chemical energy times the amount of material involved. We also suppose that adsorption may enhance absorption of atomic hydrogen in the Constantan lattice, supporting in this way the main LENR process of heat generation. Actually, the possibility that the presence of a hydrogen film closely surrounding the wire favors the diffusion of atomic hydrogen inside the metal should not be excluded. In conclusion, further investigation aimed at clarifying the effects and role of glass in such phenomena is necessary.

5. The Hypothesis of Energy Localization

In 1954 Enrico Fermi and his coworkers J. Pasta and S. Ulam with the help of M. Tsingou performed, at LANL-USA, the numerical simulation of a discrete nonlinear system using the computer MANIAC I [8]. The dynamic system they studied consisted of 64 one-dimensional oscillators coupled to the nearest-neighbors by nonlinear force terms. Fermi's expectation was that the excitation energy associated with a normal node would be distributed along all the normal modes after a sufficiently long time interval; that is to say, the system would have evolved toward a state of energy equipartition. Surprisingly, energy remained localized to few modes and showed a sort of periodicity, returning most of it to its initial mode.

Dr. Brian Ahern (previously at DARPA, USA) has recently revisited the Fermi–Pasta–Ulam problem/paradox, proposing it as a candidate to explain some of the complex phenomena occurring in LENR experiments [9]. While in

most solids the atoms reside in parabolic potential wells and therefore undergo simple harmonic motion, generally at high frequency and low amplitude, the atoms of some materials are subject to a non-parabolic potential corresponding to nonlinear force terms. This leads to nonlinear vibrational modes of large amplitude and low frequency. Hence, Ahern proposes that energy localization may take place in structures with a small number of atoms. Both properties – a relatively small number of atoms and nonlinear coupling – are possessed by nanoparticles of size 3–12 nm. This is the "right" dimension suggested by Y. Arata; experimentally reconfirmed by Takahashi–Kitamura, Univ. Osaka, Kobe, Japan, in experiments of LENR by interaction of D_2 and nanoparticles at high temperatures. In nanoparticles, a large fraction of atoms is located at the surface and is subject to nonlinear binding forces with the internal atoms.

The transition to the new regime would be triggered by a pulse of energy that the cluster can receive from thermo-mechanical oscillations of the surrounding medium, or from electrical pulses, even by radiations. As a consequence, a very small number of atoms in the cluster acquire a significantly greater amount of energy than they would in conditions of thermal equilibrium. Locally, the large oscillations manifest as hot regions. This is closely similar to the phenomenon of oscillons in granular media [10]. We note that, in our experimental conditions (i.e. especially the effect of glass fiber sheaths), the local pulse of energy could be provided by the $H + H \rightarrow H_2$ recombination reaction.

Energy localization could clarify the catalysis processes, usually associated to the lowering of the activation energy of a reaction. In this scenario, a few excited atoms, corresponding to a locally hot region, make their energy available for the activation of chemical reactions that could take place only at higher temperatures if the cluster was absent. Ahern sustains that energy localization could also explain the initiation of LENR reactions in H_2/D_2 saturated nanostructures. As a consequence, energy localization circumvents the second law of thermodynamics, since nanoparticles act as Maxwell's demons able to convert part of their thermal energy into valuable chemical energy potential.

The violation of the second law is apparent, because it is not applicable to ensembles with a small number of particles. We quote Maxwell's words [11]: "The truth of the second law is ... a statistical, not a mathematical, truth, for it depends on the fact that the bodies we deal with consist of millions of molecules ... Hence the second law of thermodynamics is continually being violated and that to a considerable extent, in any sufficiently small group of molecules belonging to a real body." Violations of the second law at nanoscales have also been observed experimentally as occasional short-time (less than 2 s) fluctuations around the thermal equilibrium state [12,13].

The catalytic action of nanostructures at the surface of our surface-modified Constantan wires can partially explain the thermal anomalies we found in our experiments, as they enhance H_2 dissociation even at temperatures $T \ll 800°C$. If further confirmed, the energy localization would be the mechanism for coordinating the normal thermal motion of particles in nanometric regions of matter into localized high-energy oscillations.

6. Spontaneous Voltage Generation

In our experimental set-up, we can control only two wires at the same time. For this reason one of the Constantan wires is not connected to the Data Acquisition System (PIXIe, NI) and left unconnected ("floating"). However, we measure periodically its resistance by means of a high sensitivity multimeter (Fluke 187) to evaluate the amount of adsorbed hydrogen. When the wire is heated in the presence of hydrogen, its resistance ratio can decrease up to 0.7. Anyway, from what we know from "open literature", any systematic study on the relationship between the amount of hydrogen absorbed and the decrease of constant resistance is not available. We have just qualitative data about the correlation of the two quantities.

On June 25, 2014, we noted, just by chance, that the floating Constantan wire generated by itself a macroscopic voltage of the order of hundreds of microvolts that resulted as a function of many parameters: temperature, type of gas, pressure, resistance ratio. The highest measured values were about 1400 μV for the voltage and 120 μA for the current with duration of only few hours, while stable outputs were about half. We note that the spontaneous tension cannot be ascribed to the usual Seebeck effect, because we considered only one single wire and not a junction of two

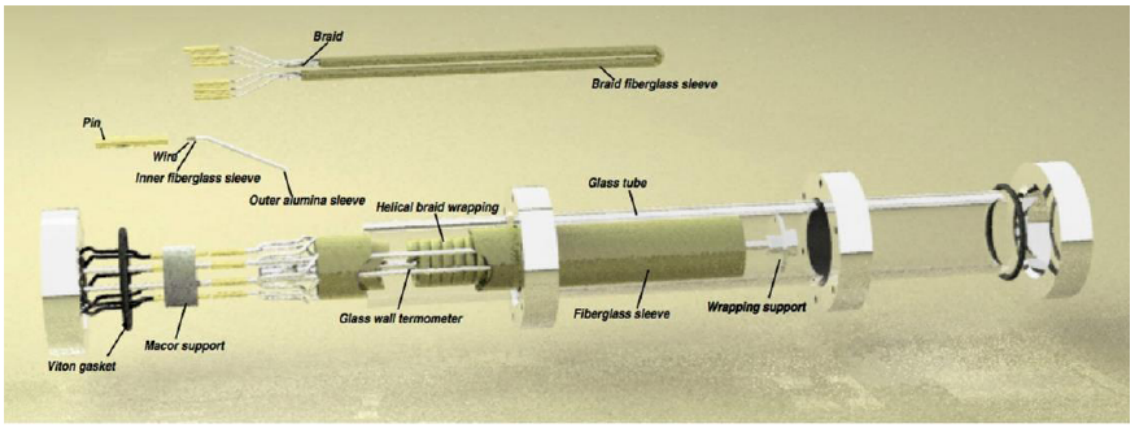

Figure 6. Schematic of the third generation experimental set-up.

different materials as in the thermocouples.

7. New Third Generation Experiments: the Effect of Iron

In previous experiments we discovered that iron contamination in the wires had a positive influence in terms of stability and excess power of the reaction. Hence, we decided to develop a procedure to add iron of nanometric sizes to the surface of Constantan wires and even some microns deep into the bulk during our thermal/electric treatments for the preparation of the nanolayers. From a chemical point of view, iron is characterized by a solubility of hydrogen

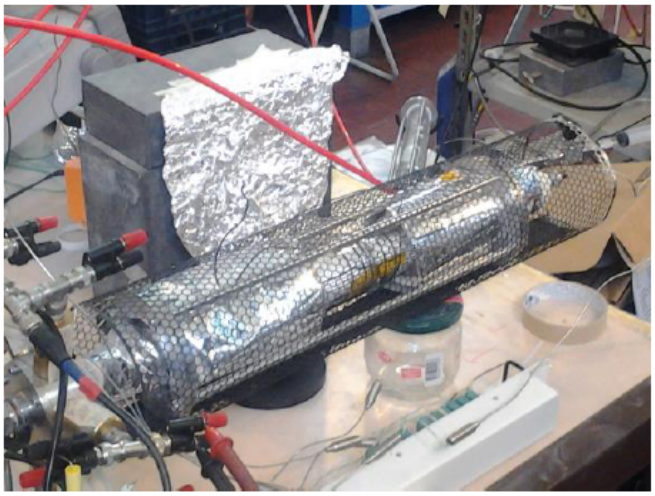

Figure 7. Photo of the third generation reactor.

into the lattice that increases largely with temperature: in 100 g of material, from 0.37 cm^3 at 400°C to 7 cm^3 at about 1000°C. To fully exploit this property of iron, the reactor had to reach higher temperatures than we previously obtained. For this reason, we added another sheath over the usual borosilicate glass one, made of alumina (Al_2O_3), with a higher melting temperature ($T_{max} = 1200$°C). Figure 6 shows a complete schematic of the reactor and in Fig. 7 we show a photograph of it, taken during the execution of one of the several experiments we conducted. To increase wire temperature at constant input power, we used a mixture of H_2 with low thermal conductivity noble gases (argon, xenon). The effectiveness of such mixtures was verified by comparing the corresponding excess heat results.

With the new preparation procedure, fully developed at INFN-LNF, we produced 20–40 iron thin layers, similar to multiple hetero-structures, at the wire surface. Moreover, we introduced further non-equilibrium conditions in the wire by making several (up to 20) knots with hole diameter 0.3–2 mm. These knots represent local geometrical variations of the path of the current flowing in the wire and are crossed by the lines of the magnetic field they generate. Because of the large currents (up to 2.3 A) we inject in the wire, they become the locus of large thermal non-homogeneities. The tests we carried out with all different combinations of elements (wire with/without iron/knots) showed that the new configuration (iron plus knots) offers measurable advantages in terms of hydrogen absorption and AHE amount.

As usual, we calculated very conservative estimations of the excess power, using as a blank the corresponding result obtained with the configuration with no iron in the wire. The best result (with Xe/H_2 mixture) was 15 W against an input power of 100 W. The local temperature of the wire was estimated, through the platinum wire, at around 800°C. In Fig. 8, we show the results of the tests carried out in hydrogen atmosphere. $T_{ext} - T_{amb}$ is plotted as a function of the input power in the case of standard Constantan wire (*blue*) and Fe-added Constantan wire (*red*). In green we indicate the excess power of the configuration with iron compared to that without it. Clearly, excess power increases with temperature. This behavior was confirmed by the experiments with Xe/H_2 atmosphere, where larger wire temperatures were reached (Fig. 9). Wire temperature was estimated through SS-support temperature measured by the thermocouples (Fig. 10). For comparison, while at an input power of 90 W, excess power is about 7.5 W in a pure H_2 atmosphere, this raises up to 15 W in a gas mixture.

We also verified the presence of a spontaneous voltage in the non-powered wire in the reactor. In wires having several knots with hole diameter smaller than 1 mm and filled with iron at nanometric size, we observed in gas mixture atmosphere currents up to 150 μA and voltages up to 1900 μV, stable over long times. We compared current generation for different wires with the same number of knots and measured values about 2.2 times larger with the addition of iron. In particular, we ascertained that the local presence of iron in knots was extremely important for maximizing the effect.

8. Discussion on the Indetermination of Temperature Measurements

With regard to the thermometric experiments and the relative indeterminate results, we used three different approaches/typologies/analyses:

(A) Experiments performed in 2012–2013, i.e. the so-called first series.
(B) Experiments performed during 2014, in which we studied in some detail the effect of fiberglass addition, as presented at MIT March 21–23, 2014 Colloquium on Cold Fusion effects.
(C) Experiments concerning the effect of iron addition together with a wire geometry with several knots (main results at ICCF19, April 2015.

First of all, we note that the AHE are considered real by us if, and only if, there are simultaneous increases of both the internal and external temperatures of the reactor, at a given constant input power used as reference. For the experiments of type A we adopted the approach of performing calibrations in inert gases, mainly helium or argon before H_2 addition. Helium has a thermal conductivity similar to H_2. Argon has about seven times lower thermal conductivity than H_2.

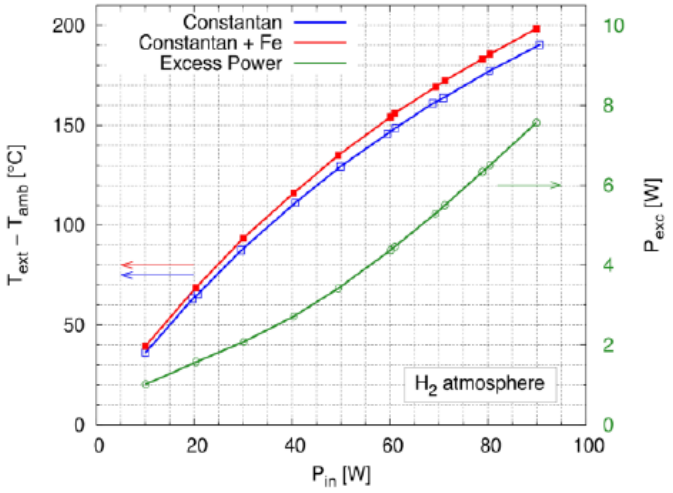

Figure 8. Tests performed in H_2 atmosphere for the configurations with knots with (*red*) and without (*blue*) iron addition. The difference of power between the two configurations is displayed in green.

The improvement of the overall performance using a low thermal conductivity gas, i.e. increasing the wire temperature at constant input power, was discovered by us after 2010, employing both palladium and/or nickel wires. At that time we used flow-calorimetry and the effects were no longer in doubt. The main drawback was the low response time of the system: meaning we could do only two tests per day at most. With isoperibolic-type measurements we can do up to 5–6 experiments/day.

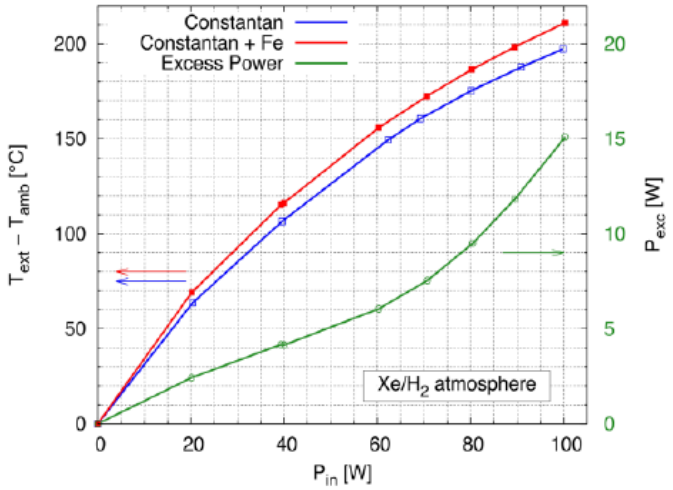

Figure 9. Tests performed in gas mixture atmosphere of Xe (1.4 bar) and H_2 (1.7 bar). The meaning of the colored curves is the same of Fig. 8.

Because we used a mixture of H_2 and argon in the actual experiments (as opposed to the control experiments), we carried out the same procedure for He/Ar mixtures. Furthermore, in the old experiments, we realized that one of the reference "good working points" was at an electric input power of 48 W. As a consequence, the results made public are mainly at the input power of 48 W (plus a few tests at 50 W). All the work performed at different input powers were not shown or discussed in public, and was only used for internal discussions in the working group.

The main disadvantage of this approach is the large indetermination, usually quantified in ± 1 W and in some specific conditions up to ± 2 W. The typical excess power when the system showed "useful" effects was in the range of 5–10 W during the test performed at Frascati Laboratories using the Agilent DAQ. In conclusion, the detected excess power, even in the worst situation, is real beyond any doubt.

As regards to the experiments of type B, they were actually a comparison of two different experiments. The two were at the same power level of 50 W, but with varying pressure of H_2 inside the chamber, from 3.8 down to 0.5 bar at low glass content and from 2.7 down to 0.1 bar for a large amount of glass. This was accomplished by dismantling the internal set up in order to add additional glass fibers. In this case the comparison is more difficult. Anyway, the difference on both the external (about 16°C, from 149 to 165°C) and highest internal temperatures (over 50°C, from 270 to 320°C) at 0.5 bar of pressure, is so large that one can hardly infer that the results are meaningless or invalid. In short, adopting for the calculation of the true effective area of the reactor just a value of length = 10 cm, diameter = 4 cm and for the (convective) Newton component a value of 15, we conservatively assumed that the experiment with a low amount of glass is the blank, i.e. equal to the input power of 50 W. In such conditions, the excess power of the configuration with large amount of glass seems to reach a value as large as 11.7 W.

In conclusion, even supposing a margin of error of ± 3 W, the effect seems to be real. About the experiment of type C, the comparison is performed in a very conservative way. We have two Constantan wires, with the same length and diameter, both with several knots, where the only difference is the addition of at most a few milligrams of iron inside the knots of the "active" wire. Iron is added through a very dilute solution of $Fe(NO_3)_2$ in HNO_3 (at about 5% concentration), 18 times, for 14 knots. In such a way iron is deposited in sub-micrometric layers. After such

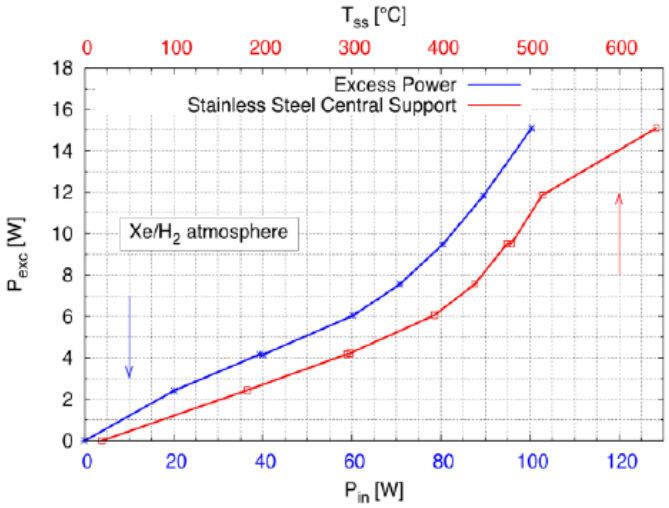

Figure 10. Tests performed in gas mixture atmosphere of xenon (1.4 bar) and H_2 (1.7 bar). The temperature of the SS internal support is showed in red. The difference in power between the configuration with iron and without iron is in blue.

treatments, the knots show strong ferromagnetic behaviors. Each wire is put inside the usual glass sheath and again inserted in an Al_2O_3 sheath ($T_{max} = 1200°C$). The sheaths are twisted around each other about every 2 cm. Moreover, they are inserted in another, more large diameter sheath. In such a geometrical configuration it is very difficult that temperature differences arise because of some geometric effect: only internally generated energy can be their source. For such kind of set-up power indetermination can be easily kept at less than 1 W.

9. Conclusions

The observation of single-wire spontaneous voltage generation in our experiment, in addition to achieving the aim of increasing AHE (using iron in the most recent specific case), represents one of the unexpected results of our recent research activity. The phenomenon shows itself as the generation of a voltage between the extremities of the non-powered wire in the reactor. The effect was first revealed serendipitously in the second-generation reactor with a large amount of glass. Furthermore, the successive addition of iron nanolayers and small knots in the wire (third generation reactor) increased and stabilized the magnitude of the generated voltage (up to 1900 μV) and current (up to 150 μA).

As concerns the anomalous heat production, iron has a beneficial effect because of its solubility of H_2 in the lattice largely increasing with temperature, while the knots are meant to create further non-equilibrium conditions inside the reactor. With such new wire features, we obtained larger excess power. From our observations and experiences we deduce that anomalous heat excess and spontaneous voltage generation are somehow related to the following conditions, or at least to some of them:

- Temperature as large as possible, obviously avoiding material sintering.
- Large hydrogen absorption/adsorption by means of catalytic materials, i.e. nanomaterials.
- Hydrogen flux as large as possible from regions at high concentration to regions at lower concentration.
- Presence of elements with hydrogen concentration increasing with temperature, such as iron.
- Presence of non-equilibrium conditions as large as possible: this is the main condition for getting any type of thermal or electrical anomaly.

We highlight that wires with good performances in terms of excess heat showed remarkable values of spontaneous voltage. One key aspect to be clarified is the role of strontium (Sr) in the generation of the spontaneous voltage. Supposing that the effect is due to some motion of electrons from the powered-wire toward the non-powered one, i.e. a thermionic emission or a process similar to it, an electron-emitting material like strontium (due to its low work function) might give a large contribution to it. Unfortunately, we performed no measurement of wire voltage for the old set-up with no strontium deposited on the glass sheaths, therefore, targeted tests are needed. Regarding iron, we found out that the fiberglass sheaths (SIGI Inc.) that we used may contain measurable amounts of iron (<2%) and iron oxide (<1%). Hence, a certain amount of iron was already present in the second-generation experiments. In this article we have also formulated some hypotheses about the mechanisms leading to thermal excesses in our experiments. We have focused on $H_2 \rightarrow 2H \rightarrow H_2$ reactions, individuating three combined processes:

- The catalytic properties of Constantan help molecular hydrogen dissociation.
- The hydrogen produced is partly adsorbed at fiberglass surface. Adsorption favors hydrogen recombination (an exothermic chemical reaction) but could also promote hydrogen absorption into the metallic lattice.
- If demonstrated, energy localization at nanoscales would enhance H_2 dissociation by converting thermal mechanical energy into a valuable chemical energy potential.

The next step of our activity is aimed at investigating in detail spontaneous voltage generation and possibly identify its nature and the variables that are related to this anomalous effect as well as to get its maximization. As concerns the better performance of the reactor after the accident with vapors of silicon oil, we think it is somehow related to the

recent "Breakdown of Richardson's law ..." found in the electron emission from heated carbon nanotubes [14]. In this study, the authors measured an emission density at large temperature (1800–2000 K) more than one order of magnitude higher than that expected with the normal thermionic emission at macroscopic levels. We hypothesize that the heating of the wires in presence of silicon oil vapor may have led to the formation of meta-stable carbon nanostructures at the surface, acting as enhancers of the anomalous effects produced in our reactor. Further inspired by the experimental design of such an important paper, we observe that the pointed shape of the nanotube is also found in some of the nanostructures present at the surface of our Constantan wires after the thermal/electric treatments. As a consequence of the supplied power or even of the energy localization mechanism if real, hot pointed-shaped nanostructures could be also responsible for an electron emission whose current manifests even at temperatures (averaged on macroscopic extensions of the wire, as measured by the thermocouples) lower than 600°C, the threshold of the known thermionic emission (i.e. Richardson law). We note that also in Iwamura's experiments, the anomalous effects, specifically in the case of "transmutations", disappear if the size of the nanoparticles is too large or the Low Work Function material used (CaO) is changed to another with higher values of Work Function (MgO) [15].

Addendum

After the ICCF19 Conference, in May 2015, we became aware that Prof. Leif Holmlid (Göteborg University, Sweden) suggested the use of nanosized iron, as a cofactor in its deuterium catalyzer (the so-called "hydrogen transfer catalyst"), to increase the amount of the so-called, ultra-dense Rydberg matter in its specific reactor by Inertial Confinement Fusion (ICF) processes. He aimed, and demonstrated experimentally possible by high quality and sophisticated charge particle measurements, to produce very large excess power (energy gain over 1000) just using Deuterium gas (made ultra-dense by an appropriate catalyst, based on Fe–K) as initial fuel and a table-top laser as stimulator for the fusion processes. His main ideas are summarized in the recent patent application EP 2680271A1 [16].

Moreover, Prof. Friedwardt Winterberg (Germany–USA, Nevada Univ., USA), the well-known expert in ICF at the international level, suggested the use of a magnetic field to increase the amount of Rydberg matter in Holmlid's experiments [17]. We observe that our knots (carrying a sufficiently large current), filled with iron and/or iron oxides at nanosize, can represent a simple/first step, experimental set-up, to match some of these requirements. We guess that the ultra-short time of recombination reaction with a range of hundreds of femtoseconds could help the stimulation of LENR effects (extremely high peak power), especially in our set-up where we have at the same time:

- Sub-micrometric structured Constantan (large production of hydrogen);
- Large amount of fiber glass where to "store" and recombine hydrogen;
- Large electron emission as a consequence of the use of low work function materials and of the increased field emission due to the low dimensionality (the trigger of the system).

In the final analysis, we conclude that in some tests where we used pure D_2 and/or Xe/D_2 mixtures (ratio 10/1) at mild pressures, we observed a certain increase of gamma radiation by a NaI(Tl) gamma detector (model LB125 by Berthold), in the energy range of 25–2000 keV. This increase happened mainly during the fluctuations of operating temperatures of the system, i.e. increasing or decreasing input power. The effect lasted for several hundreds of seconds. Again, this effect appears to be due to non-equilibrium conditions. The first detection of this phenomenon occurred on June 2012; it was reported in a meeting on LENR held at the Italian Parliament (July 2, 2012) and shortly after that discussed at both the NI Meeting and at the ICCF17 Conference (Daejeon, South Korea) in August 2012.

Considering the fact that such effects happened mainly using D_2, we suppose that even in our experimental set-up there are places where Rydberg Matter, as described by Leif Holmlid, might produce a low intensity signal in our experiment during non-equilibrium conditions. Further systematic work has been planned in the next experiments to explore this possibility.

Finally, some of the authors of this report, considering the experimental evidence that in several LENR experiments (performed worldwide since 1989) there is no consistency between the AHE detected and the usual nuclear particles emitted, have the feeling that some LENR are related, in some aspects, to the so-called Dark Matter (which is theoretically or experimentally necessary to explain the universe, although its existence has not yet been clearly demonstrated) and emission of new type/exotic particles like the WIMP (Weakly Interacting Massive Particles). Even studies devoted to explain the large discrepancies in observations involving heat and helium released from the earth – such as the finding that heat measured when compared to helium too large by a factor of 20 – indicate the existence of new types of particles and related reactions [18].

Acknowledgements

This work was partially supported, since 2011, by a high-tech metallurgical company in north-east Italy. We are indebted to Prof. Giorgio Vassallo (Univ. Palermo, Italy) for very stimulating suggestions/discussions/critics and Dr. Cesare Lorenzetti for in-deep analysis about catalysis problematics. Additional editing for English clarity undertaken by Robert W. Greenyer B.Eng. Volunteer, MFMP.

References

[1] F. Celani et al., Cu–Ni–Mn alloy wires, with improved submicrometric surfaces, used as LENR device by new transparent, dissipation-type, calorimeter, in *ICCF17*, Daejeon, South Korea, published in *J. Condensed Matter Nucl. Sci.* **13** (2014) 56–67, ISBN: 978-1-63439-142-9, ISSN: 2227–3123.

[2] W. Bruckner et al., Oxidation behaviour of Cu–Ni(Mn) (Constantan) films, *Thin Solid Films* **258** (1995) 252–259.

[3] Y. Arata and Y.C. Zhang, Development of "DS-Reactor" as the practical reactor of "Cold Fusion" based on the "DS-cell" with "DS-Cathode", in *ICCF12*, Yokohama, Japan, published in *Condensed Matter Nucl. Sci.*, 2006, pp. 44–54, World Scientific, Singapore, ISBN: 978-981-256-901-1. http://www.worldscientific.com/doi/abs/10.1142/9789812772985_0004.

[4] F. Celani et al., Are specific glass surfaces co-factors for generation of anomalous effects, by catalytic materials, under H_2 gas at high temperatures? in 2014 MIT Colloquium on Cold Fusion effects, March 21–23, 2014, http://www.coldfusionnow.org/wp-content/uploads/2014/03/Celani-2014-CF-LANR-MIT.pdf.

[5] I. Langmuir, Flames of atomic hydrogen, *Ind. Eng. Chem.* **19**(6) (1927) 667–674.

[6] F. Celani et al., Further progress/developments, on surface/bulk treated Constantan wires, for anomalous heat generation by H_2/D_2 interaction, in *ICCF18*, Columbia, MO, USA, 2013, http://hdl.handle.net/10355/37367.

[7] The Nobel Prize in Chemistry 1999, http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1999/press.html.

[8] E. Fermi, J. Pasta and S. Ulam, Studies of Nonlinear Problems, Document LA-1940, 1955.

[9] B. Ahern, Energy Localization: The key to Understanding Energy in Nanotechnology and Nature, http://lenr-canr.org/acrobat/AhernBSenergyloca.pdf.

[10] P.B. Umbahnhowar, F. Melo and H.L. Swinney, Localized excitations in a vertically vibrated granular layer, *Nature* **382** (1996) 793–796.

[11] Ed Gerstner, Second law broken, *Nature* (2002, July), http://www.nature.com/news/2002/020722/full/news020722-2.html.

[12] G.M. Wang, E.M. Sevick, E. Mittag, D.J. Searles and D.J. Evans, Experimental demonstration of violations of the second law of thermodynamics for small systems and short time scales, *Phys. Rev. Lett.* **89**(5) (2002) 050601. doi:10.1103/PhysRevLett.89.050601.

[13] J. Gieseler, R. Quidant, C. Dellago and L. Novotny, Dynamic relaxation of a levitated nanoparticle from a non-equilibrium steady state, *Nature Nanotechnology AOP* **9** (2014) 358–364.

[14] X. Wei, S. Wang, Q. Chen and L. Peng, Breakdown of Richardson's law in electron emission from individual self-Joule-heated carbon nanotubes, *Scientific Reports* **4** (2014) 5102. http://www.nature.com/srep/2014/140529/srep05102/full/srep05102.html.

[15] Y. Iwamura, S. Tsuruga and T. Itoh, Deuterium permeation induced transmutation experiments using nano-

structured Pd/CaO/Pd multilayer thin film, in *2014* MIT Colloquium on Cold Fusion effects, March 21–23, 2014, http://newenergytimes.com/v2/conferences/2014/MIT/Iwamura-MIT-2014.pdf.

[16] L. Holmlid, Method and apparatus for generating energy through inertial confinement fusion, EP2680271A1, Jan. 01, 2014, https://data.epo.org/publication-server/pdf-document?pn=2680271(&)tabki=A1(&)cc=EP.

[17] F. Winterberg, Ultra-dense deuterium and cold fusion claims, *Phys. Lett.* A **374** (2010) 2766–2771.

[18] F.J. Mayer and J.R. Reitz, Thermal energy generation in the earth, *Nonlin. Processes Geophys.* **21** (2014) 367–78.

[19] F. Celani et al., Experimental results on sub-micro structured Cu–Ni alloys under high temperatures hydrogen/deuterium interaction, in *Tenth Int. Workshop on Anomalies in Hydrogen–Metal Systems*, Pontignano, Italy, 2012, published in *Chem. Materials Res.* **3**(3) (2013) 27–56, ISSN 2224–3224 (Print), ISSN 2225-0956 (Online).

[20] S. Romanowski et al., Density functional calculations of the hydrogen adsorption on transition metals and their alloys. An application to catalysis, *Langmuir* **15**(18) (1999) 5773–5780.