

Research Article

Calorimetric Studies of the Destructive Stimulation of Palladium and Nickel Fine Wires

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Abstract

An experimental program was designed and performed to test three aspects of CMNS studies. A fourth objective was added in the light of reports from Rossi regarding large scale heat release from the nickel – natural hydrogen system, that prompted re-evaluation of earlier work on this system performed by Piantelli, and later claims by Defkalion.

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1. Background

- (1) The conditions causing the Fleischmann–Pons Heat Effect in Condensed Matter Nuclear Science (CMNS) experiments have been well established by empirical study. In a suitable lattice one needs to achieve (and maintain) a large D/Pd loading ratio and then stimulate a rapid disequilibrium condition causing a deuteron flux. In the experiments of Fleischmann and Pons the electrochemical process achieves both conditions. Of interest is whether the loading and stimulation conditions can be decoupled.
- (2) CMNS experiments have been demonstrated to produce over 20 keV of thermal energy per host Pd atom or interstitial D [1]. This is approximately 10,000 times larger than the largest possible chemical energy release. In experiments previously performed the rate of energy release has been limited by mechanisms unknown, to a few 10's or 100's of Watts per cm³ of Pd. We remain interested in evaluating potential limits on the rate of thermal energy release by optimizing then freezing lattice conditions and applying large and abrupt stimuli.
- (3) One reason for the slow development of the CMNS field is the unavailability of a robust experiment that can be performed rapidly and repeatedly to evaluate the influence of potentially relevant experimental parameters; the physical scientists equivalent of the biologists “lab rat”. The experiments described here were designed with

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the potential to play this role, allowing more rapid empirical exploration and rationalization of experiment with theory.

- (4) Initial and repeatable success with the Pd/D system and outside claims of success with Ni/H (or Ni natural H/D) systems, possibly involving structures having nano-dimensions, prompted an expansion of our study to include prefabricated, superficial, dendritic nano-structures, and the rapid stimulation of pre-loaded NiH and PdH wires with and without such nano-structures.

2. Introduction

Considerable progress has been made in elucidating the conditions necessary to produce the Fleischmann–Pons heat effect (FPHE or FPE) [2–7] in which heat is produced in amounts substantially larger than the sum of all possible chemical reactions by the prolonged and extensive electrolytic loading of deuterium into palladium. In such heat releases, energy densities have been measured more than 10,000 times larger than known chemistry [1]. An open question is, what imposes an upper limit on the rate of energy release? What, if anything, limits the power of the FPHE? In the history of the field going back now over 20 years several explosive incidents have been noted. Are there circumstances under which the energy release of the FPHE can be explosive? The experiments reported here were performed with very small samples, starting at low (liquid nitrogen) temperatures, in designed safety closures, to evaluate this possibility.

As reported previously [3, 4] the FPHE requires three conditions to be met^a simultaneously:

Loading. The cathode must achieve and maintain a D/Pd atom ratio greater than ~ 0.9 for times longer than ~ 10 times the deuterium diffusional time constant.

Flux. The heat effect appears to correlate closely, and approximately linearly [4], with the diffusive motion of deuterium atoms irrespective of direction.

Stimulation. The effect requires a trigger or stimulus to move the D/Pd system from its equilibrium or steady-state condition, or to populate appropriate energy modes in the lattice or on its surface [5].

In moving this experiment out of the laboratory and advancing towards utility application two practical questions are relevant:

- (1) (How) can we simultaneously achieve the *Loading* and *Flux* conditions? This problem is complicated by the severe degree of non-linearity in electrochemical kinetics and mass transport processes. In the attempt to obtain flux through the surface by partially loading and unloading the cathode, one generally achieves less loading than unloading with simple periodic functions and the cathode quickly falls below the threshold-loading requirement. Although not utilized heavily in the experimental set described here, the only waveform that we have found so far to be effective in creating simultaneously both loading and flux is the SuperWave developed and described by Dardik [1].
- (2) (How) can we decouple the *Loading* and *Stimulation* processes? In the electrochemical FPE experiments performed to date, both the loading and the stimulation were provided by the electrolytic current (density). Loading is a direct (although not inevitable) consequence of the net cathodic charge passed, but the current density of maximum loading is well below that needed to trigger the FPHE. Additional current is needed apparently for stimulation, possibly by means of an exchange flux in which areas of the cathode surface

^aThese conditions are necessary but not sufficient. Further elucidation of a sufficient set of condition can be found in [2–4].

preferentially absorb, while others (perhaps grain boundaries) desorb. Of interest is whether we can use electrochemistry for the effect that it performs highly efficiently, loading, and provide stimulation by other means perhaps more energetically efficiently and more easily controlled.

Another concern is that “traditional” Fleischmann–Pons experiments take weeks or months to complete. Even if successful we have been faced frequently with the possibility and reality of learning only one new thing per experiment, per month. Fleischmann and Pons recognized this and attempted to offset this difficulty by performing large matrix experiments incorporating up to 32 cells operating simultaneously. At SRI we operated a matrix of 3×4 cells in a single thermostated enclosure connected electrically in series. This is an expensive approach, and still too slow. Of interest is an experimental scheme that allows us to learn faster and with lower expense. Basically we are looking for the physico-chemical equivalent of the biologists “lab rat” that allows us to perform experiments that are: relevant, repeatable, rapid and unambiguous.

Of final concern is the final answer to the following questions. What is the process that drives the FPHE? What is the detailed reaction mechanism and what are the products of presumably nuclear reactions that drive the non-chemical heat effect? What is the quantum-based, solid-state, nuclear physics model and theory for this process? One of us (PLH) has been concerned with finding rational and complete answers to these questions since it became evident that the Fleischmann Pons heat effect is both real and non-chemical in origin [7]. The hypothesis to be tested is the conjecture that a significant Pd vacancy^b (point defect) population is required to produce measurable excess heat generation. A final condition for our “lab rat” experiment is the requirement to fully interrogate the “metabolic” (in this case, presumably nuclear) products of any such reaction.

The experiments and protocol described below were designed to answer the various questions addressed above.

3. Experimental

Experiments were performed with fine wires pre-loaded with hydrogen or deuterium, and were designed to be performed in six steps:

- (1) *Loading.* When Pd wires were used as a substrate or as test objects these were pre-loaded electrolytically with either H or D in low molarity SrSO₄ electrolytes (50 μM) using procedures developed previously at SRI [8] and elsewhere [9].
- (2) *Sealing.* The atomic loading of H or D can be sealed inside the Pd lattice for extended periods (several hours or days) with the addition of very small concentrations of Hg₂SO₄ to the SrSO₄ electrolyte and continued cathodic electrolysis [8,9]. The deposited Hg at monolayer coverage is a highly effective poison for hydrogen atom recombination, effectively preventing desorption by inhibiting molecule formation.
- (3) *Co-deposition.* As first noted by Fukai [10], vacancies in FCC metals can be stabilized thermodynamically by high activities of hydrogen and its isotopes. Szpak and Boss [11] developed a co-deposition method to deposit Pd and H (or D) simultaneously onto a cathode surface under appropriate potential control. This provides a rapid and almost ideal way of both forming and stabilizing a high population of H or D-filled vacancies and was adapted for this purpose. Co-deposits were not used in all experiments, and were formed on Pd, Ni and Ag substrate wires. At the end of the codeposition process, Hg₂SO₄ was also added to stabilize the loading of the co-deposited layer.
- (4) *Transfer.* The wires were quickly transferred to a stainless steel dewar filled with liquid N₂ as a cryogenic calorimeter (see Fig. 1) for excess energy measurement. SEM characterization, EDX analysis, and optical

^bVacancies in the lattice provide a suitable host structure for diatomic molecular D₂ or H₂ states rather than atomic D or H. These states are required for the Hagelstein nuclear energy release mechanism [7].

microscope observations were generally carried out after the calorimeter testing to determine the quality of the deposited film as well as any possible relationship between the surface morphology and excess energy production.

- (5) *Calorimetry.* As a matter of safety and to preserve high loading, we chose to examine the energy release from PdD_x and other wires at 77 K in liquid nitrogen. For that reason we developed, calibrated, and utilized a cryogenic calorimeter for measuring the amount of heat released when a pulse of current is sent through a loaded wire (with and without co-deposit). In this way the loading (by electrochemistry) and the stimulation (by a sharp current pulse) are effectively decoupled. The calorimeter and its calibration are described below.
- (6) *Nuclear Product Analysis.* From previous experience [2,3,6] the anticipated products of FPE experiments are ³H, ³He and ⁴He, with only ⁴He expected to be present commensurate with the amount of released thermal energy. The experiment was designed to facilitate the search for ³He and ⁴He and boiling liquid N₂ provides an almost ideal medium in which to do this^c. Instrumental difficulties prevented us from completing this important step.

The means of calorimetry selected was to measure the output energy as the enthalpy of vaporization of liquid N₂. The heat of vaporization of liquid N₂ at 77 K is 5.56 kJ/mol so that 4.32 ml of N₂ gas evolves at STP per Joule of energy. With no other parameter needed, energy release can be measured directly from the mass flow of evolving gas. This was accomplished by sealing the sample to be tested in liquid N₂ inside a thermally isolated enclosure. Excess energy is the difference between the enthalpy of evolved N₂ gas and the measured electrical stimulation.

As shown in Fig. 1, the calorimeter is comprised of a stainless steel Dewar flask, a silicone rubber gasket, a DelrinTM adapter plate, a thick DelrinTM cap for good insulation, a 1/4" diameter tube for boiling off N₂ gas, and two copper current rods with blocks to fix the loaded Pd wire in place for the excess heat measurement. The gas outlet was sent to an Aalborg GFM-17 0–5 l/min calibrated mass flow meter with a 0–5 V analog output. The Dewar flask was filled with a fixed amount of liquid N₂. The copper rods and gas outlet were exposed to the environment to be connected to the electrical cables and gas mass flow meter. The parts exposed to the room temperature environment can transfer heat to the liquid nitrogen, especially through the copper, so that the N₂ evolves at a certain rate.

An integration of the mass flow rate gives the total amount of N₂ gas evolved. The whole system is placed inside a cylindrical acrylic shield to minimize the ambient environmental fluctuations.

After attaining a near constant^d N₂ evolution rate signaling thermal equilibrium, loaded and unloaded wires (for calibration) were stimulated and ruptured by passing current axially along the wires mounted between the copper blocks. The input energy is provided by a 50 V, 8 A, four-quadrant power supply (Kepco BOP 50-8, Flushing, New York) for all the 50- μ m wires. For thicker 250- μ m wires we used an 8 V, 125 A Sorenson DCS 8-125 power supply. The voltage and current were measured using a high-speed oscilloscope and transferred digitally to the computer. The analog output of the gas mass flow meter was also measured by the high-speed data acquisition systems. Further details of the calorimeter design and calibration verification can be found in [12].

4. Results and Discussion

Calorimeter calibrations were performed using a 50 W, 10 Ω resistor or a number of thin 50- μ m-diameter Pd wires. Figure 2 shows the measured N₂ gas evolved vs. input heat to the 10 Ω resistor. The data fall close to the straight line of expected slope of 4.32 ml/J, indicating that the calorimeter maintains its accuracy within a wide energy input range.

^cBecause boiling occurs in the liquid volume, liquid N₂ is self-sparging and the concentration of other dissolved gases rapidly falls to unmeasurably small values.

^dThe system does not reach a steady state because the N₂ is constantly evaporating, thus reducing level in the dewar. Analysis indicates that a quasi-steady state is attained when the variation of flow rate becomes negligible within the time period tested.

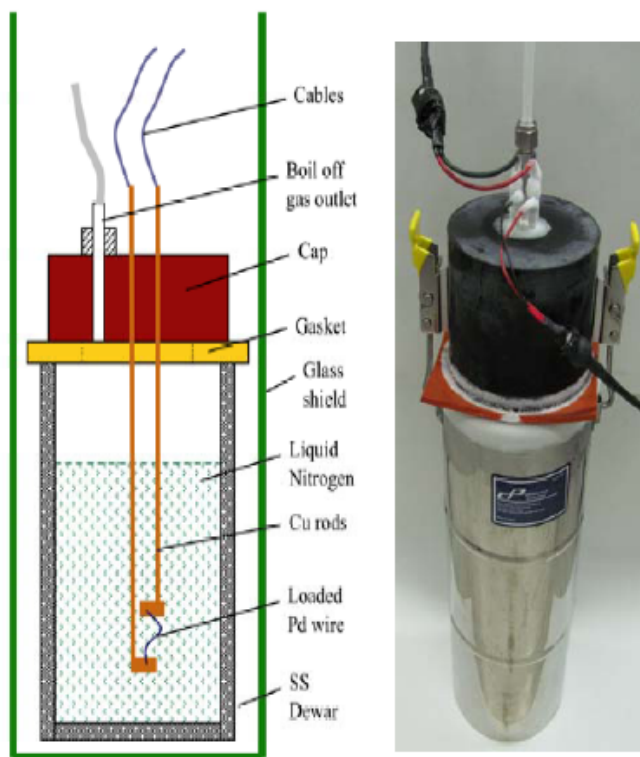


Figure 1. Schematic diagram and photograph of the cryogenic calorimeter.

Statistical analysis indicates that up to 0.25 ml of error could result due to sudden temperature fluctuations, either in excess or deficiency, when the base flow rate is below 1.8 l/min, which is equivalent to 0.06 J in energy. An upper bound and lower bound of 0.25 ml error range is also added to the plot. Figure 3 shows the calibration result with 10 unloaded 50 μm Pd wires. It is seen that all of the calculated evolved gas volumes match well with the input energy (except for one data point when the base flow rate was too high), and no excess energy is seen. The input energy for pulses that break the wires is usually between 0.4 and 0.8 J, and it usually breaks the wire in 3–6 ms.

Figure 4 plots the input vs. the measured output energy from all of the loaded wires studied. The different symbols represent the different materials tested. The results show clearly that excess energy is generated both from Pd and Ni wires loaded either with deuterium or natural hydrogen^e. However, data from Pd/D co-deposited onto highly loaded Pd wires (solid triangles) sit on top of the plot, indicating that this category of wires generates the most excess heat. Interestingly, the Ni co-deposited system also yields significant amounts of excess heat.

^eThe set of data Ni/NiH_x + Additive were generated by the addition of impurity species to the H₂O (natural) loading electrolyte. It is anticipated that these had poor H loading, and thus small or zero excess energy. This set provides good internal calibration of the calorimeter.

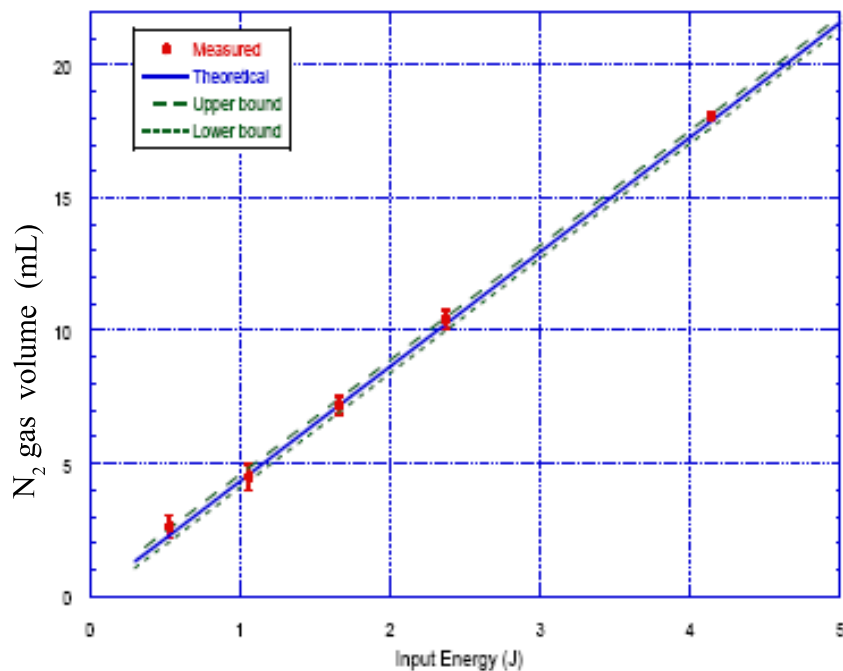


Figure 2. Wide range calibration of the cryogenic calorimeter with a 10 Ω resistor. Error range is ± 0.06 J.

5. Conclusions

A total of 30 experiments demonstrated output energy release in excess of input by amounts larger than can be accounted for by known chemical effects. Because Pd is a very dense material, the gravimetric energy density for these energy releases per gram of bulk Pd is quite low. That is, 2 joules released from ~ 1 mg of pure Pd ($50 \mu\text{m}$ diameter \times 5 cm long) only yields ~ 2 kJ/g^f. However we have reason to believe that the active region is primarily the co-deposited material, which is present at much lower quantities (mass) than the bulk supporting wire. Hence, the 5–8 ml of 7×10^{-5} M PdSO₄ that was deposited on the wire would correspond to 34–57 kJ/g of co-deposited Pd if all participated in the reaction.

Even this larger number is likely low for two reasons: (i) wires generally ruptured at a single point consuming only a small fraction of the total length; (ii) the amount of energy input stimulation used was likely much greater than that needed to trigger the effect. Clearly this is an experimental method that shows considerable promise in evaluating nuclear heat release from solid-state hydrides and deuterides, and should be further explored.

The purpose of the experimental program was not just to seek a tool to evaluate potential heat-producing systems, we were hoping for a means to elucidate the underlying mechanism. On a theoretical basis we have identified what we believe to be the key to the new effects, which is a novel and fundamental coupling mechanism that allows for coherent energy exchange between vibrational excitation and nuclear excitation (see Ref. [7] and Appendix A of Ref. [12]). A key detail of the experimental protocol was left incomplete, the evaluation of product gases and residual metal mass for

^fFor reference 1 g of TNT yields ~ 4.6 kJ.

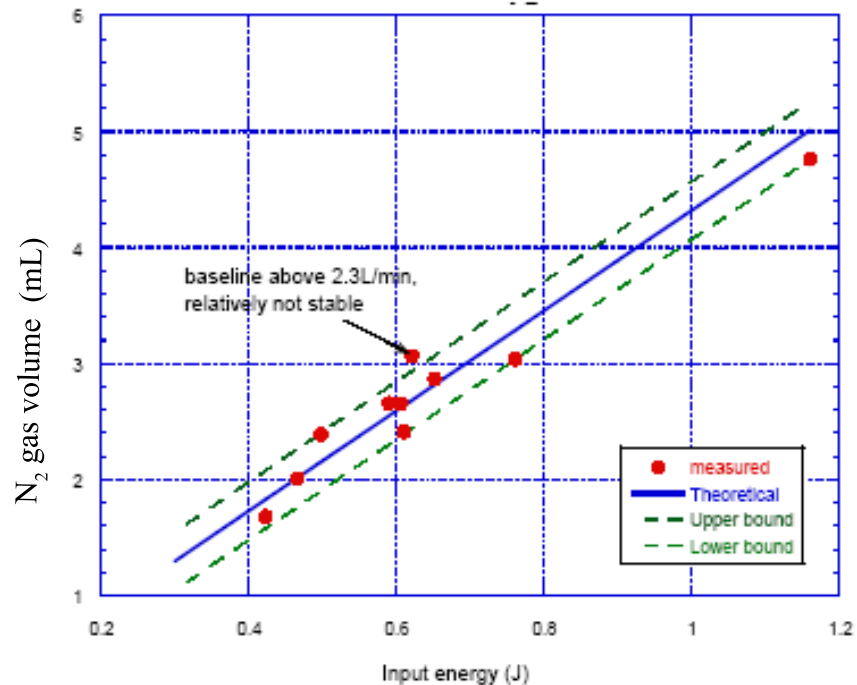


Figure 3. Calibration of the cryogenic calorimeter with thin Pd wires.

^3H , ^3He and ^4He . It is hoped that in future experimentation this task can be completed, allowing for full rationalization of theory with experiment.

Observation of excess energy from Pd wires heavily loaded with D, and particularly those with PdD co-deposits is consistent with our previous experimental experience and with theoretical conjecture. As such these results provide support and comfort, and also validation that this new experimental method may play a useful role in progressing the field forward. Although not the major focus of the present activity, one interesting observation was the evidence of excess energy from Ni wires coated with co-deposited Ni and H from normal water electrolytes (in two out of three experiments).

Although supported by theory as resulting from lattice-vacancy mediated interaction between H and the minor component D in natural water, in no previous experiments at SRI has excess heat been measured either for systems with Ni electrodes or in electrolytes or gas systems containing only natural hydrogen. This suggests that the nickel/deuteride or mixed nickel deuteride/hydride systems may be appropriate materials to produce excess energy, in potentially useful amounts.

Results of these preliminary studies suggest that very high rates of energy release signaling high explosive powers do not normally or necessarily result from extreme electrical stimulation of metal wires highly loaded with hydrogen and/or deuterium. Experimental support is given for the claims of nuclear level excess heat both from Pd wires loaded with isotopically enriched D, and Ni wires loaded with H at natural isotope levels. The excess heat effect was larger for PdD, and largest for PdD with dendritic PdD surface structure, but was nevertheless clear and present for Ni wires

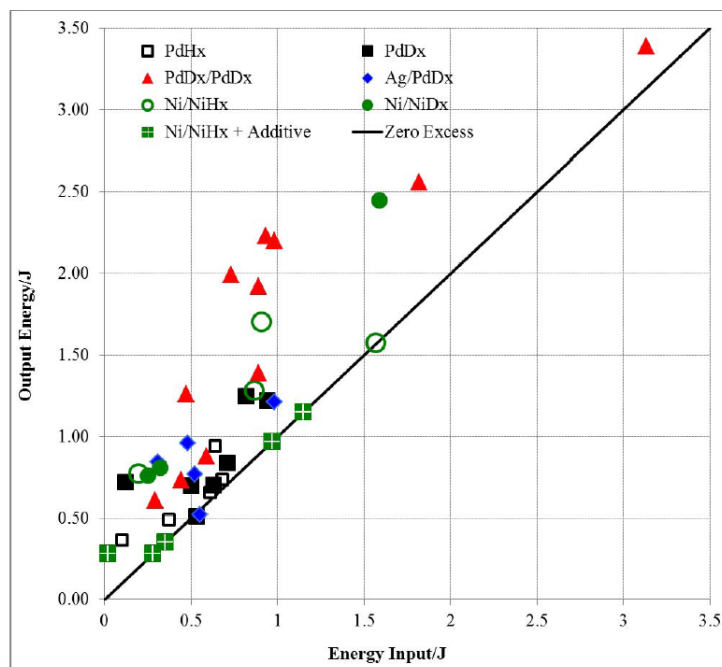


Figure 4. Summary of excess heat from all wires tested.

loaded in “normal” H_2O containing natural isotopic D concentrations providing further experimental support for the work and claims of Piantelli, Rossi, Defkalion and Brillouin.

Acknowledgment

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