



Research Article

# Stimulation of Metal Deuteride Wires at Cryogenic Temperatures

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## Abstract

Several groups have reported anomalous effects (heat and nuclear products) in thin PdD<sub>x</sub> materials stimulated by different forms of electro-diffusion. Using our cryogenic calorimeter we have measured the energy released from destructive electro-diffusion of a highly loaded PdH(D)<sub>x</sub> wires, co-deposited PdH(D)<sub>x</sub> on highly loaded PdH(D)<sub>x</sub> wires, and NiH(D)<sub>x</sub> wires. Generally, the D loaded metals yielded greater and more reliable excess energy than seen with the H loaded metals. The co-deposited PdD<sub>x</sub> on highly loaded PdD<sub>x</sub> wires yielded greater excess energy than the bulk wire hydrides or PdD<sub>x</sub> co-deposited on Ag wires as predicted by the calculations of Hagelstein and DeChiaro. The addition of a partial monolayer of a recombination poison yields a highly loaded PdD<sub>x</sub> cathode. Electro-stimulation of NiH(D)<sub>x</sub> wires have also shown excess energy, suggesting that renewed interest in this system may be justified.

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## 1. Introduction

Several groups [1,2] have reported anomalous effects (heat and nuclear products) in thin PdD<sub>x</sub> materials stimulated by different forms of electro-diffusion. The ultimate extrapolation of this technology is the electrical heating of thin PdD<sub>x</sub> wires resulting in destructive high-speed melting—“exploding wires”. Exploding wire technology has been used for over 150 years to make fine metal particles [3]. Additionally, the nickel–hydrogen system has recently received renewed interest in its ability to yield anomalous effects.

Celani et al. [4–6] have reported loading thin Pd wires electrochemically up to high loading and sealing their surface electrochemically. Tripodi [6] reported that such sealed wires can be immersed in liquid nitrogen (LN) and analyzed for anomalous effects at those temperatures or soon after warming up. As such, electrically exploding such loaded wires while immersed in LN should release the deuterium and cause the evolution of gaseous N<sub>2</sub> equal to the electrical energy passed through the wire due to the heat capacity and enthalpy of vaporization of LN.

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One of the authors has proposed that if a vacancy-containing Pd lattice were formed and then deuterided by either exposure to  $D_2$  gas or  $D_2O$  electrolysis,  $D_2$  molecules would diffuse to re-form in these vacancy locations. Hagelstein has hypothesized that these sigma-bonded  $D_2$  molecules would allow interstitial  $D_2$  to be converted to  $^4He$  in the solid state. The creation of large numbers of vacancies using electron or ion beams is possible, but quenching of many of the vacancies occurs over hours, limiting the concentration to the 0.1% level. The vacancies are stabilized by H or D at high loading, but they do not diffuse near room temperature. Co-deposition of Pd (as in the Szpak protocol) when the D/Pd loading is above 0.95 will produce a large vacancy fraction. We have tested this hypothesis by examining the co-deposition of  $PdH(D)_x$  on  $PdH(D)_x$  and Ag, which does not form a hydride, wires. We also chose to examine the co-deposition of  $NiH(D)_x$  on Ni wires.

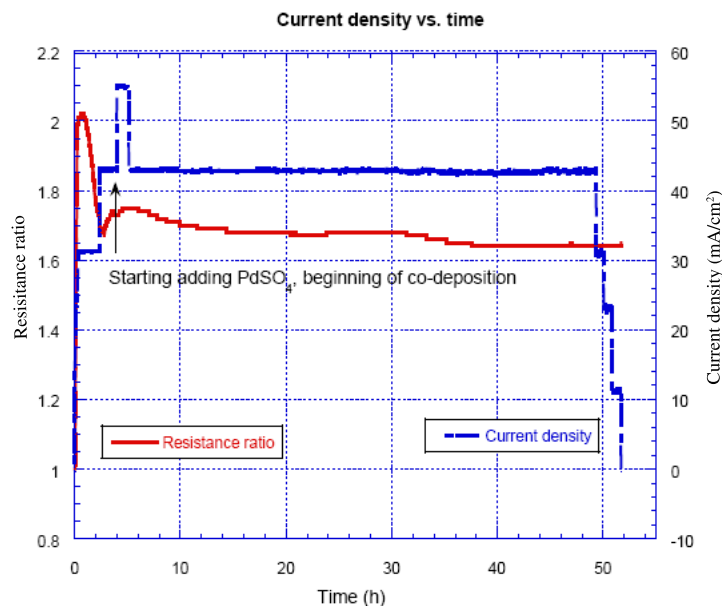
## 2. Experimental

The formation of highly loaded  $PdH(D)_x$  wires has been described elsewhere [7]. We have also carried out a series of co-deposition (codep) experiments by co-depositing metal + H/D on various substrates. The codep process generates a significant amount of Pd point vacancies in the co-deposited layer and these vacancies are immediately filled by co-deposited D(H) or  $D_2(H_2)$ . According to our hypothesis, these vacancies are able to host molecular  $D_2$ , and are necessary for excess heat generation in Fleischmann–Pons type experiments [8]. We first co-deposited  $PdD_x$  on 50  $\mu m$   $PdD_x$  wire substrate. The wire was first loaded to a high D:Pd ratio ( $>0.9$ ) in 50  $\mu M$   $SrSO_4$  solution using the previously referenced experimental protocol, then a few milliliters of 250  $\mu M$   $Hg_2SO_4$  was added to increase and stabilize the loading. After that, saturated (70–100  $\mu M$ )  $PdSO_4$  was added to the cell 1 ml at a time, each time allowing all of the  $Pd^{2+}$  to be fully reduced and deposited on the substrate surface. It is important is to co-deposit at high current density, so the Pd concentration in the electrolyte has to be relatively low in order for the Pd to co-deposit without flaking off. Figure 1 plots the variation of applied current density and resistance ratio of a typical wire during loading and co-deposition versus time. The current density is generally around 20–60 mA/cm<sup>2</sup>. High current density would probably raise the temperature of the thin wire and cause de-loading.

The resistance of the wire usually does not change significantly, indicating that the deuterium loading at the bulk wire is not changing significantly. Also, because the amount of  $Pd^{2+}$  added is limited due to the low solubility of  $PdSO_4$ , the codep layer does not grow by more than 1  $\mu m$  in most of the experiments. At the end of the codep process, Hg was added again to seal the loading, and the wire is transferred to the cryogenic calorimeter for testing. Note,  $PdCl_2$  has much higher solubility by forming  $[PdCl_4]^{2-}$  complex. However,  $PdCl_2$  was not used because in the presence of  $Hg_2SO_4$ , insoluble  $Hg_2Cl_2$  would quickly precipitate.

Similarly, Pd and D were also co-deposited on Ag wire substrates. No  $PdSO_4$  was added until a steady state Ag wire resistance was seen after the initial application of current. The axial resistance of the wire was measured and recorded over the time. No appreciable resistance change was observed during the codep process, since the  $PdSO_4$  concentration is very low, and the resulting the codep layer is usually less than 1  $\mu m$  thick. At the end of the co-deposition, Hg was also added to stabilize the loading of the codep layer. EDX analysis was used after the cryogenic calorimeter test to see if any measurable Pd was deposited on the Ag surface.

Since the Ni/H system has been in the spotlight recently, we also performed a series of codep experiments using Ni wire substrates. To remove the oxide at the surface, anodic stripping was used at the beginning of each codep. An anodic current of 1 mA was typically applied for about 5 min. Both concentrated  $NiSO_4$  (0.1–0.2 M) solutions and a mixture of  $SrSO_4$  and  $NiSO_4$  were used in forming the co-deposited layer. The morphology of the surface was examined. Pre-loading of the Ni wire is possible, but the process is painfully slow compared with that of Pd. Furthermore, hydride formation embrittles the Ni wire significantly and makes the process of transferring the loaded wire into the calorimeter very difficult. Therefore, in most of the experiments, the bulk Ni wire was not loaded. To complete the Ni system, we also tested the codep of Ni and D on Ni wires using the same experimental protocol.



**Figure 1.** Variation of current density and resistance ratio versus time during the loading/codep process.

After all the loading and codep processes were done, the wires were quickly transferred to the cryogenic calorimeter for excess energy testing as described above. SEM characterization and EDX analysis, and optical microscope observation were generally carried out after the calorimeter testing, to determine the quality of the deposited film, and any possible relationship between the surface morphology and the excess energy.

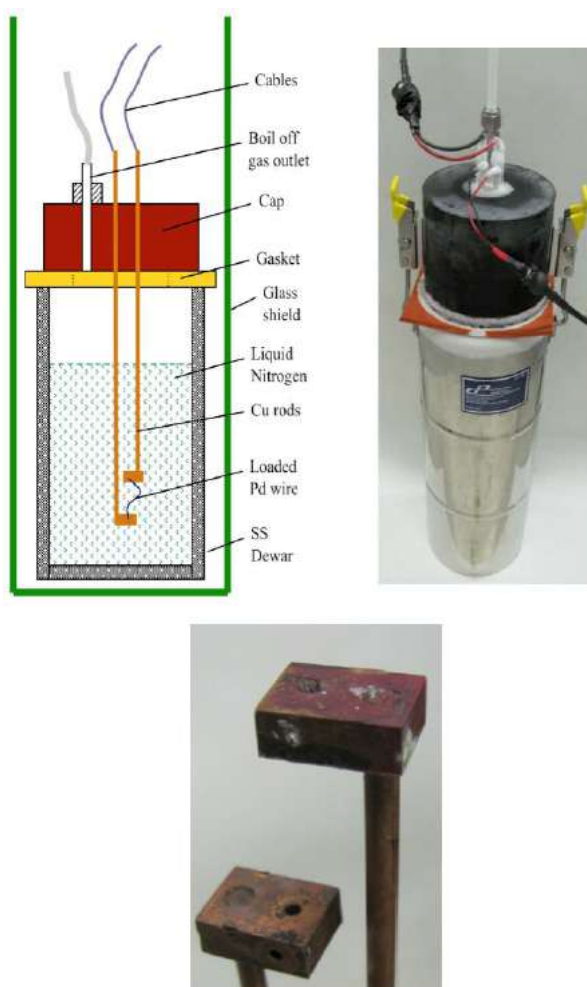
The wires are then immersed in liquid nitrogen in a cryogenic nitrogen boil-off calorimeter, shown in Fig. 2, which also shows the cathode connection blocks to be immersed in the LN. The copper probes hold the sample via a set-screw in each probe. This probe is then immersed in the LN, sealed with a low temperature O-ring, and held tight with two clamps.

The measured input energy from the pulse boils off a known amount of nitrogen, which is measured by a calibrated thermal mass flow meter (MFM). By using different length pulses into a 50 W  $1 \Omega$  current shunt immersed in the LN calorimeter, we calibrated the volume of  $N_2$  evolved at different input energies. In the case of  $PdD_x$ , the energy from the input pulse will boil off a known volume of nitrogen. The voltage, current, and time were measured using a high-speed data acquisition system and transferred digitally to the computer. The analog output of the MFM is also measured by the high-speed data acquisition systems.

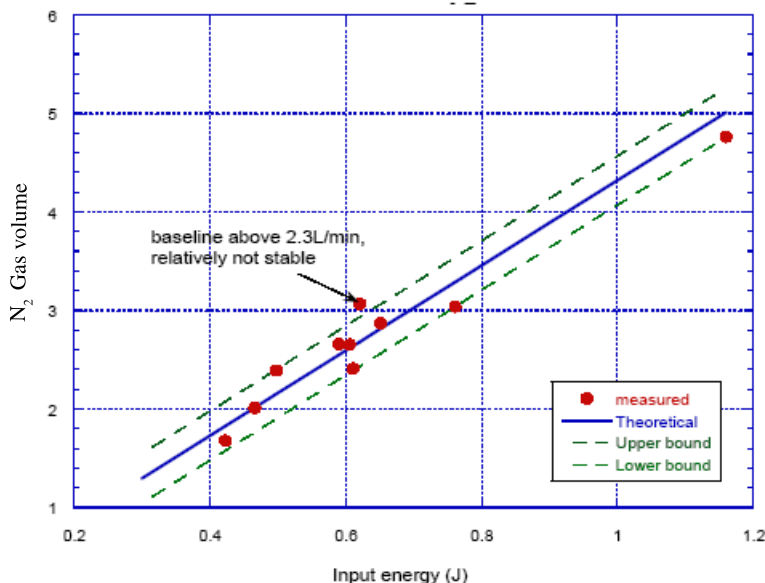
We also used nine  $50 \mu\text{m}$  pure Pd wires to calibrate the calorimeter. The results are shown in Fig. 3 and indicate an error range for this calorimeter to be  $\pm 0.25$  ml. This error was obtained by analyzing a large amount of base flow rate fluctuation data over the time. This error is due to a systematic variation caused by environmental temperature fluctuations. From the heat of vaporization of LN at 77 K we calculate that a temperature change of 1 K should result in a flow rate change of 8 ml/min for a typical test setting.

In Fig. 3 the resistor calibrations all fell directly on the calculated line. It is seen that all the calculated evolved gas volumes match well with the input energy and no excess energy has been seen. The input energy for pulses that break the wires is usually between 0.4 and 0.8 J, and the wire usually breaks in 3–6 ms. Using the heat capacity and heat of

fusion (melting) data provided by the computer program HSC<sup>®</sup> (Outokumpu), 0.75–0.9 J is needed to melt a 5–6 cm long Pd wire of 50  $\mu\text{m}$  diameter in LN, neglecting the thermal conduction between the wire and the LN. However, the wire usually breaks at a weak point in around 1 ms, and the input energy is generally less than 0.1 J. The average response time for blank wires with diameter of 50  $\mu\text{m}$  was 1.22 s, with a standard deviation of 0.035 s. Therefore, for the ease of calculation and minimal error, a response time of 1.2 s was used in calculating the volume of gas evolved after pulse input. All of the wires discussed here were stimulated using either a 50 V, 8 A, four-quadrant power supply (Kepco BOP 50-8, Flushing, New York) or a 20 V, 20 A, four-quadrant power supply (Kepco BOP 20-20, Flushing, New York).



**Figure 2.** Photographs of the cryogenic calorimeter and its cathode connection blocks.



**Figure 3.** Calibration of the cryogenic calorimeter with thin Pd wires. Error range is  $\pm 0.25$  ml.

### 3. Results

Loading of H into 50  $\mu\text{m}$  Pd wire is relatively easy. The ratio of resistance for the wire being loaded to that of the original wire usually passes through the maximum (indicating the formation of  $\text{PdH}_{0.75}$ ) within an hour and then starts dropping. The final ratio H:Pd is generally near or greater than 1. High loading of D into 50  $\mu\text{m}$  Pd wire ( $\text{D:Pd} > 0.9$ ) is difficult to achieve. Adding Hg could partially suppress the deuterium recombination process and increase the loading into the bulk, up to 0.97–0.98. After water ( $\text{D}_2\text{O}$ ) splits into H(D) and oxygen at the surface of the cathode and anode, respectively, loading of H(D) is a result of competition between the surface recombination of H-H or D-D and the diffusion into the bulk as Pd is both a good catalyst and allows for fast diffusion of H(D). Initial surface condition and impurities in the system could significantly affect the loading. Table 1 lists the wire number, its final resistance ratio and the loading level for H or D, in the case of 50  $\mu\text{m}$  Pd wires.

The development of a large number of Pd vacancies is the key issue [9] here for excess heat production, since molecular  $\text{D}_2$  can form in one of the octahedral sites around a vacancy in PdD. The electron density is too high in bulk PdD, so that occupation of anti-bonding orbitals occurs, and the deuterium atoms are pushed apart. Co-deposition at high loading ( $\text{D/Pd} > 0.95$ ) can produce the vacancies, and high loading ( $\text{D/Pd} > 0.85$ ) causes the other octahedral-sites near the vacancy to be occupied which is required to stabilize the  $\text{D}_2$ .

We first tested the vacancy hypothesis by co-depositing various amount of Pd and D on highly loaded 50  $\mu\text{m}$   $\text{PdD}_x$  wires. The substrate wire was usually loaded to  $x > 0.92$  in pure 0.05 M  $\text{SrSO}_4$  solution, then partially sealed by a few monolayers of Hg.  $\text{PdSO}_4$  solution was then added 1ml at a time. After adding Pd, the resistance could either go up or go down, with the former indicating that the de-loading of the substrate wire may be the dominating process and the later indicating that the codep process is the most dominating. Table 2 lists the Pd wires that were first loaded and then subjected to the co-deposition of various amount of Pd and D. Scanning electron micrographs shows that these co-deposited Pd films are composed of nano-particles and dendrites. The size of nano-particles is usually less than

200 nm.

Since our hypothesis is that the codep layer is key in contributing to the generation of excess heat, we need to differentiate its contribution from the bulk-loaded wire, and demonstrate its role in the generation of excess heat. We carried out the co-deposition of Pd and D on Ag wire substrate, since Ag does not load H(D), and therefore does not participate in the process of excess energy generation. If excess heat is still seen without a highly loaded Pd bulk, it could indicate the importance of the codep layer, and meanwhile, indicate to which degree, the codep layer contributes to the overall process in a highly loaded Pd wire.

Electrolysis was first carried out on an Ag wire in pure SrSO<sub>4</sub> electrolyte where no resistance change was seen and the wire remained intact. After that, PdSO<sub>4</sub> solution was added usually 1 ml at a time. Only small variations of resistance were seen, since the amount of Pd deposited (within 1 μm) was negligible compared to the diameter of the Ag wire (50 μm). Therefore, the loading level in the codep layer was also not clear. Table 3 summarizes the experimental conditions for all the codep experiments on Ag wire substrate. Generally, a nice film could be seen using an optical microscope.

**Table 1.** Final resistance ratio and corresponding loading levels for 50 μm Pd wires.

Wire No.	Diameter (μm)	Composition	Final ratio	Loading (x)
9	50	PdH <sub>x</sub>	1.27	~ 1
10	50	PdH <sub>x</sub>	1.16	> 1
11	50	PdH <sub>x</sub>	1.18	> 1
19	50	PdH <sub>x</sub>	1.28	~ 1
20	50	PdH <sub>x</sub>	1.31	~ 1
8	50	PdD <sub>x</sub>	1.77	0.88
12	50	PdD <sub>x</sub>	1.58	0.98
13	50	PdD <sub>x</sub>	1.7	0.93
14	50	PdD <sub>x</sub>	1.65	0.95
15	50	PdD <sub>x</sub>	1.62	0.96
16	50	PdD <sub>x</sub>	1.6	0.97
17	50	PdD <sub>x</sub>	1.61	0.97
18	50	PdD <sub>x</sub>	1.79	0.90

**Table 2.** Summary of PdD(H)<sub>x</sub> co-deposited on PdD(H)<sub>x</sub> wires.

Wire No.	Diameter (μm)	Composition	PdSO <sub>4</sub> (ml)	Final ratio	Loading x**
23	50	PdD <sub>x</sub> /PdD <sub>x</sub>	1*	1.94	0.85
24	50	PdD <sub>x</sub> /PdD <sub>x</sub>	3.5	1.74	0.92
25	50	PdH <sub>x</sub> /PdH <sub>x</sub>	10	1.44	0.92
26	50	PdD <sub>x</sub> /PdD <sub>x</sub>	5.5	1.66	0.95
29	50	PdD <sub>x</sub> /PdD <sub>x</sub>	3	1.75	0.91
30	50	PdD <sub>x</sub> /PdD <sub>x</sub>	6	1.65	0.94
31	50	PdD <sub>x</sub> /PdD <sub>x</sub>	9	1.65	0.94
32	50	PdD <sub>x</sub> /PdD <sub>x</sub>	8	1.62	0.96
37	50	PdD <sub>x</sub> /PdD <sub>x</sub>	12	1.72	0.93
38	250	PdD <sub>x</sub> /PdD <sub>x</sub>	3	1.85	0.88
39	250	PdD <sub>x</sub> /PdD <sub>x</sub>	13	1.84	0.89
40	250	PdD <sub>x</sub> /PdD <sub>x</sub>	10	1.74	0.92
42	250	PdD <sub>x</sub> /PdD <sub>x</sub>	5	2.00	0.76
43	250	PdD <sub>x</sub> /PdD <sub>x</sub>	10	1.95	0.84

\*1 ml of 0.05 M PdCl<sub>2</sub> was added, which caused the precipitation of Hg<sub>2</sub>Cl<sub>2</sub> when HgSO<sub>4</sub> was added.

\*\*Loading of the bulk wire.

The nickel–hydrogen system has been of great interest in this field for a long time. Various results have been reported including transmutation products and radiation emission, besides excess heat [10]. In this work, we have also carried out Ni/natural water electrolysis experiments. Since codep generally gave us more excess heat in the PdD<sub>x</sub> system, codep of Ni and H/D was subjected to a similar experimental protocol. The morphology of electrodeposited Ni film can vary significantly from a nice crystalline film to poorly adhered dendrites, depending on the solution used and current density applied. Our experimental results confirmed those variations, as will be discussed below.

Several solution combinations were used to test our hypothesis and determine the morphological changes of the codep layer and its effect on the excess heat generation: pure 0.1 and 0.2 M NiSO<sub>4</sub>, mixtures of NiSO<sub>4</sub> and SrSO<sub>4</sub> solutions. Currents from 2 to 5 mA were applied, corresponding to ~250–600 mA/cm<sup>2</sup> for 50 μm diameter, 5 cm long wires. Pre-loading of Ni with H was tried at the beginning. It was found that loading was very slow with resistance increase similar to that of Pd wires. However, as noted above, the hydrided Ni wires became extremely brittle making the transfer process very difficult. Therefore, it was later preferred not to load the Ni wire before codep (it is likely that loading and codep could occur at the same time when a high over-potential is seen at the surface). The local loading at the surface only needs to be H/Ni > 0.7 for vacancies to form, which seems probable at high codep current density.

When the codep started after adding NiSO<sub>4</sub> to SrSO<sub>4</sub>, the wire was observed to be surrounded by a layer of green solution. After a while, the green layer dispersed, and the wire resistance started to decrease continuously. When the green NiSO<sub>4</sub> was depleted, the resistance stopped decreasing and more NiSO<sub>4</sub> was added. If pure NiSO<sub>4</sub> was used to begin with, the wire resistance kept dropping quickly (though the resistance drop gradually leveled off as the current density continued to decrease with increasing surface area). The experiment was stopped at a certain resistance ratio and a few milliliters of Hg<sub>2</sub>SO<sub>4</sub> were added before turning down the current in order to stabilize the loading in the codep layer. The amount of Ni deposited could be calculated from the final resistance of the wire, assuming a homogeneous film growth and that the resistance of the codep layer is similar to that of the bulk. Table 4 summarizes the codep experimental conditions of the Ni wires that have been tested. The calculated final wire diameter and film thickness are also shown. Generally, a nice, smooth metallic finish was obtained, with 10 μm grain size, when the applied current density was low and the cell thoroughly cleaned. Dendrites are usually formed in the presence of additives.

Table 5 summarizes the calorimetric results for loaded wires: PdH<sub>x</sub> and PdD<sub>x</sub>. It is interesting to note that after a large amount of testing with thin Pd wires, it seems that whether the wire disintegrates into fine powders or simply breaks is determined by the nature and pre-history of the wire itself, and possibly has nothing to do with loading and generation of excess energy. If the wire has defects, it would break at the weakest point(s). Otherwise, the wire will completely disintegrate, whether it is loaded or blank. If the defect is very weak, then the input pulse energy is also very low, as the input energy is an indication of the energy to break the wire. It is also interesting to note that the wire with the highest deuterium loading was very brittle. When transferring it to the calorimeter, it broke several times near the point fixed to the calorimeter, and finally became too short to measure. Whether it is due to the high loading or an intrinsic defect within the wire is unknown since it happened only on one occasion.

**Table 3.** Summary of the experimental conditions for codep on Ag wires.

Wire No.	Diameter ( μm)	Material	PdSO <sub>4</sub> (ml)
33	50	Ag/PdD <sub>x</sub>	8
34	50	Ag/PdD <sub>x</sub>	14
36	50	Ag/PdD <sub>x</sub>	16
41	50	Ag/PdD <sub>x</sub>	15
44	250	Ag/PdD <sub>x</sub>	15
45	250	Ag/PdD <sub>x</sub>	15
46	50	Ag/PdD <sub>x</sub>	12

**Table 4.** Summary of codep experimental conditions for Ni wires and the thickness of deposited film.

Wire No.	Composition	Electrolyte	Final ratio	Final diameter ( $\mu\text{m}$ )	Film thickness ( $\mu\text{m}$ )
47	Ni/NiH <sub>x</sub>	0.2 M NiSO <sub>4</sub>	0.062	201	75.5
48	Ni/NiH <sub>x</sub>	0.1 M NiSO <sub>4</sub>	0.074	184	67
49	Ni/NiH <sub>x</sub>	0.2 M NiSO <sub>4</sub>	0.083	174	62
50	Ni/NiH <sub>x</sub>	1.5 ml	0.300	91	20.5
51	Ni/NiH <sub>x</sub>	1.5 ml with Ag, D <sub>2</sub> O*	0.961	–	–
52	Ni/NiH <sub>x</sub>	1 ml with Ag, D <sub>2</sub> O*	0.992	–	–
53	Ni/NiH <sub>x</sub>	0.5 ml with Ag, D <sub>2</sub> O*	0.986	–	–
54	Ni/NiH <sub>x</sub>	4 ml NiSO <sub>4</sub> + 2 ml Ag + 1 ml D <sub>2</sub> O	0.183	117	33
55	Ni/NiH <sub>x</sub>	2 ml NiSO <sub>4</sub> + 1 ml Ag + 0.3 ml D <sub>2</sub> O	0.143	132	41
56	Ni/NiH <sub>x</sub>	2.5 ml NiSO <sub>4</sub> + 0.8 ml Ag + 0.8 ml D <sub>2</sub> O	0.322	88	19
59	Ni/NiD <sub>x</sub>	0.1 M NiSO <sub>4</sub>	0.165	123	36.5
60	Ni/NiD <sub>x</sub>	0.1 M NiSO <sub>4</sub>	0.186	116	33
61	Ni/NiD <sub>x</sub>	0.1 M NiSO <sub>4</sub>	0.216	108	29

\* The amount of Ag and D<sub>2</sub>O is about 1–2% of the mass (or volume?) of Ni.

**Table 5.** Summary of the cryogenic calorimeter test results for loaded PdD<sub>x</sub> and PdH<sub>x</sub> wires.

WireNo.	Composition	Final ratio	$x$	Input energy (J)	Output energy (J)	Excess energy (J)	Excess%
8	PdD <sub>x</sub>	1.77	0.88	0.12 ± 0.01	0.7 ± 0.12	0.6 ± 0.13	500 ± 100
9	PdH <sub>x</sub>	1.27	~ 1	0.68 ± 0.01	0.7 ± 0.12	0.1 ± 0.13	8 ± 18
10	PdH <sub>x</sub>	1.16	> 1	0.64 ± 0.01	1.0 ± 0.12	0.3 ± 0.13	50 ± 19
11	PdH <sub>x</sub>	1.18	> 1	0.37 ± 0.01	0.49 ± 0.06	0.12 ± 0.07	32 ± 16
12	PdD <sub>x</sub>	1.58	0.98	0.71 ± 0.01	0.84 ± 0.06	0.13 ± 0.07	18 ± 8
13	PdD <sub>x</sub>	1.7	0.93	0.94 ± 0.01	1.22 ± 0.06	0.28 ± 0.07	30 ± 6
14	PdD <sub>x</sub>	1.65	0.95	0.63 ± 0.01	0.70 ± 0.06	0.07 ± 0.07	10 ± 10
15	PdD <sub>x</sub>	1.62	0.96	0.53 ± 0.01	0.51 ± 0.06	–	–4 ± 11
						0.02 ± 0.07	
17	PdD <sub>x</sub>	1.61	0.97	0.50 ± 0.01	0.70 ± 0.06	0.20 ± 0.07	40 ± 12
18	PdD <sub>x</sub>	1.79	0.9	0.82 ± 0.01	1.25 ± 0.06	0.43 ± 0.07	52 ± 7
19	PdH <sub>x</sub>	1.28	~ 1	0.10 ± 0.01	0.37 ± 0.06	0.27 ± 0.07	270 ± 60
20	PdH <sub>x</sub>	1.31	~ 1	0.61 ± 0.01	0.66 ± 0.06	0.05 ± 0.07	8 ± 10

\*Note: The error percentage is calculated by dividing the inherit system error range 0.06J by the input energy of that specific wire.

Among the listed wires, eight wires were loaded with deuterium and five showed the generation of excess energy significantly higher than the error range. The amount of excess energy varies from 18 ± 8% to 52 ± 7% (excluding wire No. 8, which has an excess percent of 500 ± 100%, but the N<sub>2</sub> flow rate baseline was unstable). One wire showed no significant amount of excess energy, one wire showed slight deficient energy, and one wire was not measured. No obvious correlation can be made between excess energy production and bulk loading level. Of the five wires loaded with hydrogen, three showed the generation of excess energy significantly higher than the error (note, wires Nos.9 and 10 were measured when the base flow rate was above 2 l/min or 1.9 l/min, and thus had relatively higher error). In one case, wire No.19, 270 ± 60% of excess energy was generated while the wire probably broke at a very weak point with the input pulse energy only at 0.1 J.

Wire No.18 is particular interesting. This wire generated the most excess energy, at 0.43 J. The wire broke at only one spot, and the remainder of the wire seems intact. However, two metal beads were seen at both of the broken ends.



**Table 6.** Summary of the calorimetric test results for co-deposited Pd wires.

WireNo.	Diameter ( $\mu\text{m}$ )	Composition	PdSO <sub>4</sub> added (ml)	$x$	Input en-ergy (J) $\pm 0.01$	Measured en-ergy (J) $\pm 0.06$	Excess en-ergy (J) $\pm 0.07$	Excess %
25	50	PdH <sub>x</sub> /PdH <sub>x</sub>	10	0.92	0.74	0.99	0.25	34 $\pm$ 9
23	50	PdD <sub>x</sub> /PdD <sub>x</sub>	1	0.85	0.44	0.73	0.29	66 $\pm$ 16
24	50	PdD <sub>x</sub> /PdD <sub>x</sub>	3.5	0.92	0.29	0.61	0.32	110 $\pm$ 24
26	50	PdD <sub>x</sub> /PdD <sub>x</sub>	5.5	0.95	0.47	1.26	0.79	168 $\pm$ 16
29	50	PdD <sub>x</sub> /PdD <sub>x</sub>	3	0.91	0.59	0.88	0.29	49 $\pm$ 12
30	50	PdD <sub>x</sub> /PdD <sub>x</sub>	6	0.94	0.73	1.99	1.26	173 $\pm$ 10
31	50	PdD <sub>x</sub> /PdD <sub>x</sub>	9	0.94	0.89	1.92	1.03	116 $\pm$ 8
32	50	PdD <sub>x</sub> /PdD <sub>x</sub>	8	0.96	0.93	2.23	1.30	140 $\pm$ 8
38	250	PdD <sub>x</sub> /PdD <sub>x</sub>	3	0.88	0.98	2.20	1.22	124 $\pm$ 7
39	250	PdD <sub>x</sub> /PdD <sub>x</sub>	13	0.89	0.89	1.39	0.50	56 $\pm$ 8
40	250	PdD <sub>x</sub> /PdD <sub>x</sub>	10	0.92	3.13	3.51	0.38	12 $\pm$ 2
42	250	PdD <sub>x</sub> /PdD <sub>x</sub>	5	0.76	5.08	8.98	3.90	77 $\pm$ 1
43	250	PdD <sub>x</sub> /PdD <sub>x</sub>	10	0.84	1.82	2.56	0.74	41 $\pm$ 9

One of the beads is about 250  $\mu\text{m}$  in diameter, and the other is smaller. Two other melted but unbroken spots are also seen in other regions of the wire. These two melts are relatively smaller in size. Since the wire was immersed in liquid nitrogen at 77 K, and the melting point for Pd is 1827 K, the melting of the wire indicates that at least some of the regions were heated up to at least 1827 K and melted to liquid. Melting a 250- $\mu\text{m}$ -diameter ball of Pd from 77 K would require approximately only 0.02 J, which can be ignored in this analysis, given that the excess energy is estimated to be 0.43 J. The calculation is based on the density of Pd (12g/cm<sup>3</sup>), the enthalpy of melt (157 J/g), and the temperature-dependent heat capacity provided by HSC<sup>®</sup> by Outokumpu.

Table 6 summarizes the calorimetric test result for codep experiments on highly loaded Pd wires. It is important to note that the H(D) loading at the surface is expected to be higher than the bulk loading reported in this table, such that many of the substrate wires will have surface loadings of 0.95 or greater.

Table 7 summarizes the calorimetric test result for all the codep experiments on Ag wires. It is seen that when a similar amount of PdSO<sub>4</sub> is deposited on a Ag wire, the amount of excess heat generated is much less than that generated from the PdD<sub>x</sub> codep on highly loaded PdD<sub>x</sub> wires. In fact, the level of excess energy generated for all of these Ag wires is around 0.5 J or below, similar to the loaded Pd wires.

**Table 7.** Summary of the calorimetric test results for Pd/D<sub>x</sub> co-deposited Ag wires.

Wire No.	Diameter ( $\mu\text{m}$ )	Material	PdSO <sub>4</sub> added (ml)	Input en-ergy (J) $\pm 0.01$	Measured en-ergy (J) $\pm 0.06$	Excess en-ergy (J) $\pm 0.07$	Excess %
33	50	Ag/PdD <sub>x</sub>	8	0.31	0.84	0.53	170 $\pm$ 23
34	50	Ag/PdD <sub>x</sub>	14	0.98	1.21	0.23	23 $\pm$ 7
36	50	Ag/PdD <sub>x</sub>	16	0.48	0.96	0.48	100 $\pm$ 15
41	50	Ag/PdD <sub>x</sub>	15	0.55	0.52	-0.03	-5 $\pm$ 13
46	50	Ag/PdD <sub>x</sub>	12	0.52	0.77	0.25	48 $\pm$ 13

Both the Ni/H<sub>2</sub>O (natural) and Ni/D<sub>2</sub>O systems were studied, using 0.1 M or 0.2 M NiSO<sub>4</sub> solution, or by adding 0.1 M NiSO<sub>4</sub> to the dilute SrSO<sub>4</sub> solution. A summary of the calorimetric test results for all the Ni codep wires is

**Table 8.** Calorimetry results summary for co-deposited NiH(D)<sub>x</sub> wires.

Wire No.	Composition	Codep film thickness (μm)	Input energy (J)	Measured energy (J)	Excess energy (J)	Excess %
47	Ni/NiH <sub>x</sub>	75.5	0.91 ± 0.01	1.7 ± 0.06	0.79 ± 0.07	87 ± 8
48	Ni/NiH <sub>x</sub>	67	1.57 ± 0.01	1.55 ± 0.06	– 0.02 ± 0.07	–1 ± 4
49	Ni/NiH <sub>x</sub>	62	4.53 ± 0.01	5.56 ± 0.06	1.03 ± 0.07	23 ± 2
50	Ni/NiH <sub>x</sub>	20.5	0.87 ± 0.01	1.28 ± 0.06	0.41 ± 0.07	47 ± 8
59	Ni/NiD <sub>x</sub>	36.5	0.25 ± 0.01	0.76 ± 0.06	0.51 ± 0.07	204 ± 28
60	Ni/NiD <sub>x</sub>	33	0.32 ± 0.01	0.81 ± 0.06	0.49 ± 0.07	153 ± 22
61	Ni/NiD <sub>x</sub>	29	1.59 ± 0.01	2.45 ± 0.06	0.86 ± 0.07	54 ± 4

shown in Table 8. All the experiments were performed using 50 μm Ni wires. Again the H(D) loading at the surface is expected to be higher than the bulk loading reported in this table, such that many of these wires can have surface loadings of at least 0.7.

#### 4. Conclusions and Future Work

We have shown that we can load and seal 50 μm diameter PdH<sub>x</sub> and PdD<sub>x</sub> wires electrolytically and transfer those wires to a cryogenic calorimeter without loss of loading. Our cryogenic calorimeter can resolve as little as 0.4 J of input energy with a reproducibility of ~0.06 J.

As reported earlier, we performed our cryogenic stimulation on seven deuterided Pd wires and five hydrided (natural) Pd wires. Excess energy had been measured from five of the seven PdD<sub>x</sub> wires and from three of the five PdH<sub>x</sub> wires. Generally, the amount of excess energy was greater for the deuterided system than for those electrolyzed in natural H<sub>2</sub>O.

In this paper, we extended this technology to hydrides and deuterides co-deposited on highly loaded wires of similar composition. The relevant hypothesis here is that vacancies can be produced in abundance if (Pd or Ni) co-deposition occurs near 300 K at above a high threshold surface loading (0.95 or 0.70), and that at high loading sigma-bonded D<sub>2</sub> or HD can form at an octahedral site near the vacancy (as long as the other octahedral sites are occupied). This hypothesis also claims that these diatoms are important to the excess energy production process.

As can be seen in Table 6, all 12 of the co-deposited PdD<sub>x</sub> on PdD<sub>x</sub> wires showed excess energy. The largest amount of excess (3.9 J) occurred when the greatest input energy (5.08 J) was required due to the thickness (250 μm) of the wire. This showed that both the reproducibility and the absolute energy produced was greater with the co-deposited PdD<sub>x</sub> than with the bulk PdD<sub>x</sub> wire. In addition the one PdH<sub>x</sub> on PdH<sub>x</sub> wire also showed excess energy. However, due to the poor statistics we cannot draw any important conclusions from this latter result.

To test the importance of the substrate wire acting as a reservoir for the H(D) to maintain the high loading of the co-deposited PdH(D)<sub>x</sub>, we co-deposited the palladium hydride on to pure Ag wire. Since Ag does not form a hydride or allow for H diffusion, this permitted comparison of a substrate that can act as a hydrogen reservoir to one that cannot, and therefore cannot sustain a de-loading flux from the bulk metal. As can be seen from Table 7, the co-deposited material on Ag showed less absolute and percentage excess energy (and on one occasion none at all) than did the material co-deposited on PdD<sub>x</sub>. This suggests that a well-loaded H(D) reservoir helps achieve high surface loading. Hence, we feel that at least in this system, the presence of H<sub>2</sub> or D<sub>2</sub> in an octahedral site around a vacancy in the Pd lattice and a substrate that acts as an H or D reservoir acts to enhance the amount of excess energy yielded during stimulation.

Because of recently publicized reports of excess energy in the Ni/hydrogen system we re-examined the nickel/natural water system. Because of the apparent success of producing excess heat with our co-deposition experimental protocol,

we adopted this protocol for Ni system, instead of electrolyzing in aqueous carbonate or sulfate as have been reported elsewhere [11]. We performed four electrolysis experiments using natural H<sub>2</sub>O and three using D<sub>2</sub>O. As seen in Table 8, the results suggest that the nickel/natural hydrogen system can be a viable system to produce excess energy. Wire No.61 (Ni/NiD<sub>x</sub>) showed the largest excess energy density since it was performed using the thinnest co-deposition layer. This suggested that the nickel/deuteride or mixed nickel deuteride/hydride system may be an appropriate material to produce excess energy without using the expensive precious metals.

These results distinctly demonstrate the importance of this co-deposited layer, and that the reservoir of D/H could enhance the generation of excess heat, which substantiates our hypothesis. Also, The destructive stimulation method leads to excess energy in most of the systems studied and never when applied to pure Pd wires.

We intend to perform gas phase measurement of He isotopes from the headspace of future stimulated calorimeter experiments and on some of the electrolysis cells' headspace gas. We also anticipate using our metal vaporization inlet to the He isotope mass spectrometer to analyze any Pd fragments for anomalous He isotopic ratio.

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