Cryogenic Calorimetry of "Exploding" PdD_x Wires

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Abstract

Reports in the literature have shown that thin PdDx structures have yielded anomalous effects (heat and nuclear products) when stimulated by different forms of electro diffusion. We have designed, constructed, and operated a calorimeter operating at 77 K with a minimum detectability of less than 0.1 J and an accuracy of less than 0.06 J, which utilizes an "exploding wire" technique to examine the effect of a destructive electro-diffusion on a highly loaded PdD_x wire. We have shown, using a very thin Pd wire cathode and a thin Pt wire anode, that highly loaded PdD_x wires can be formed using high-voltage electrolysis of very high-purity D_2O. Highly loaded PdD_x wires can disintegrate ("explode") to form microscopic particles when subjected to high current density pulses at 77 K. Under certain conditions PdD_x wires can yield excess energy when subjected to high-current density pulses at 77 K. © 2012 ISCMNS. All rights reserved.

Keywords: Cyrogenic calorimetry, Deuterium loading, Electrochemical, Detectability, Exploding wires

1. Introduction

Several groups [1,2] have reported anomalous effects (heat and nuclear products) in thin PdD_x materials stimulated by different forms of electro diffusion. We have extrapolated this technology to the electrical heating of thin PdD_x wires, which resulted in destructive high-speed melting, i.e., "exploding wires." Nairne reported using exploding wire techniques over 225 years ago [3]. Over 150 years ago Faraday reported using exploding wire technology to produce fine metal particles [4]. Celani et al. [5,6] have reported the electrochemical loading of thin Pd wires to approximately 1:1 and the electrochemical sealing of their surface. Such sealed wires can be immersed in liquid nitrogen (LN) and analyzed for anomalous effects at those temperatures or soon after warming up, according to Tripodi [7]. Celani et al. [8] reported using pulsed microsecond electrolysis to induce excess power. We hypothesized that electrically exploding highly D-loaded Pd wires immersed in LN should release the deuterium and cause the evolution of gaseous N_2 equal to the electrical energy passed through the wire due to the enthalpy of vaporization of LN.

Since a correlation between the rates of excess heat and [3]He and [4]He production has been reported [9,10], we will analyze the off-gases for excess He and non-natural isotopic He ratios.

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2. Experimental

2.1. Electrochemical methods

We have adapted the original H_2O high-loading/sealed-cathode techniques of Celani and Tripodi to D_2O. This is not a trivial effort, since the loading process requires ultra-clean materials and ultra-pure reagents. Unfortunately, most available D_2O is chemically impure when compared to 18 MΩ-cm deionized H_2O. We have been using high-purity D_2O (Sigma–Aldrich #P192341), which also provides the high isotopic purity necessary to yield high D loading. To maintain this isotopic purity, all transfers are performed under dry N_2 or Ar.

To achieve high electrochemical loading of deuterium (D/Pd ratio $\gg$ 0.9), cleanliness of all materials is of the utmost importance. Figure 1 is a diagram of the electrochemical cell used for loading the Pd. The specifics of the electrochemical cell have been reported elsewhere [11]. In the present work, a 5–6 cm length of 99.9% Pd wire (Goodfellow, Oakdale, PA), 50 μm in diameter, is attached to four lengths of 0.25 mm Pt lead wires in the center of the cell. This allows for in situ accurate 4-wire resistance measurements of the Pd cathode. The anode is a 30-cm–long, 1-mm-diameter Pt wire, wound helically around the Pd wire, and fixed by a cage made of six quartz pillars forming a cylinder of $\sim$2 cm in diameter.

After the wire is spot welded, the whole cell and the quartz cylinder are immersed in ethyl alcohol held in an ultrasonic bath, followed by sonication in 18.3 MΩ.cm deionized water and oven drying. The Pd cathode is then annealed by applying a series of current steps that resistively heat the cathode until it ultimately is red-hot, then slowly cooled by reducing the current in steps. This procedure is repeated until the Pd resistance does not change upon annealing. This final resistance is considered R_0. Annealing can reduce the wire's internal stress and the number of grain boundaries. Grain boundaries are where H/D recombination can occur to yield H_2/D_2 gas and provide a conduit for the gas to diffuse out. After annealing, the cell is again cleaned and dried.

The electrolyte solution used in the experiments (0.5×10^{-4} M $SrSO_4$) is prepared from D_2O (inside a glove bag filled with N_2 or Ar and sealed) or H_2O and stirred overnight. The starting electrolytic current is 2–3 mA, equivalent to 200–300 mA/cm^2, low enough to minimize crack formation. To determine the stoichiometric ratio of H/D atoms dissolved into the Pd cathode during the electrochemical loading process, in situ four-probe resistance measurements of the Pd cathode are performed using a Hewlett Packard 4338A milliohmeter. The relative ratio of the resistance of the loaded Pd wire to the initial Pd wire is known to be a function of the average stoichiometric ratio of H/D to Pd, as has been shown in previous publications [12]. After a stable resistance value is obtained at this low current, the current is increased to 5.0 mA.

After achieving the maximum possible loading, Hg in the form of a 2.5×10^{-4} M Hg_2SO_4 solution is added to the electrolyte. Hg is reduced cathodically on the Pd surface and forms a nearly homogeneous amalgam bond. The presence of Hg atoms at the surface poisons the recombination of D atoms, thus reducing the formation of D_2 gas and in turn inhibiting de-loading of the Pd wire. Hg_2SO_4 solution is added, 1 ml at a time, until the resistance stops decreasing. As the Hg is added, the current is reduced in an attempt to maintain the loading at reduced current. After the loading is stabilized even at a minimal current (such as 1 mA), the electrolysis is stopped, and the wire is immediately transferred to the cryogenic calorimeter filled with LN.

2.2. Cyrogenic calorimetry

Figure 2 shows a schematic layout of the cryogenic calorimeter designed at SRI, which comprises a stainless steel (SS) dewar, a silicone rubber gasket, a Delrin^{TM} adapter and thick Delrin^{TM} cap for good insulation, a $^1/_4''$ opening for boiling off N_2 gas, and two copper current rods and blocks to fix the loaded Pd wire for the excess heat measurement. The gas outlet is sent to an Aalborg GFM-17 0–5 l/min calibrated mass flow-meter with a 0–5 V analog output. The Dewar flask is filled with a certain amount of LN. The copper rods and gas outlet are exposed to the environment to be
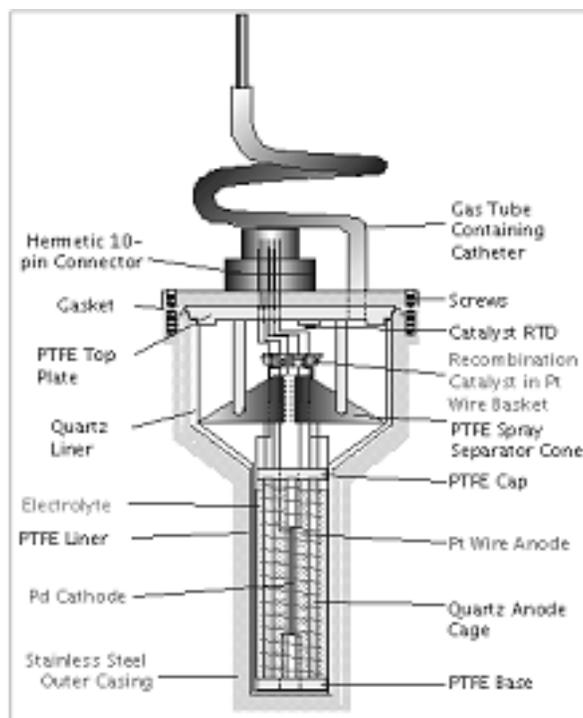
Figure 1. Degree of loading cell used to load and seal thin wires.

connected to the electrical cables and gas mass flow meter. The parts exposed to the room temperature environment can transfer heat to the LN, especially through the copper rods (which is a good current conductor and also a good heat conductor), so that the LN boils off at a certain rate. An integration of the mass flow rate gives the total amount of N_2 gas evolved. The whole system is placed inside a cylindrical acrylic shield to minimize the ambient environmental fluctuation.

Since the LN inside the Dewar flask is continuously boiling off without further replenish, an absolute steady state base flow rate cannot be reached. Instead, the flow rate decreases very slowly (the decay rate is less than 2 ml/min or 0.03 ml/s when the base flow rate is below 1.8 l/min). However, within a short time, a quasi-steady state is reached. Theoretical base and details will be published elsewhere. When a high-voltage pulse of less than 0.1 s is provided, the system responds to the input heat by the boiling off of excess N_2 gas, which can be seen as a sharp pulse in the flow rate of less than 1.5 s duration. An integration of this pulse after baseline subtraction gives the total excess gas volume evolved by the pulse. The input energy is provided by a 50 V, 8 A, four-quadrant power supply (Kepco BOP 50-8, Flushing, New York). The power supply is triggered using software developed using the Labview® (National Instruments, TX) development system, which also is used to collect the current, power, and flow rate data.

National Instruments PCI-6173 and PCI-6143 cards are used to both initiate the output pulse and collect data. The current, voltage, and flow rate, which are measured at a sampling rate of 10,000 s^{-1}, are used to calculate both the energy input to the calorimeter and the volume of N_2 evolved by the pulse. From the heat of vaporization of LN at 77 K, 5.56 kJ/mol, equivalent to 4.32 mL/J at room temperature, the evolved excess N_2 gas after the pulse could be compared with the theoretical value calculated from the input energy. We calibrated the volume of N_2 evolved at different input
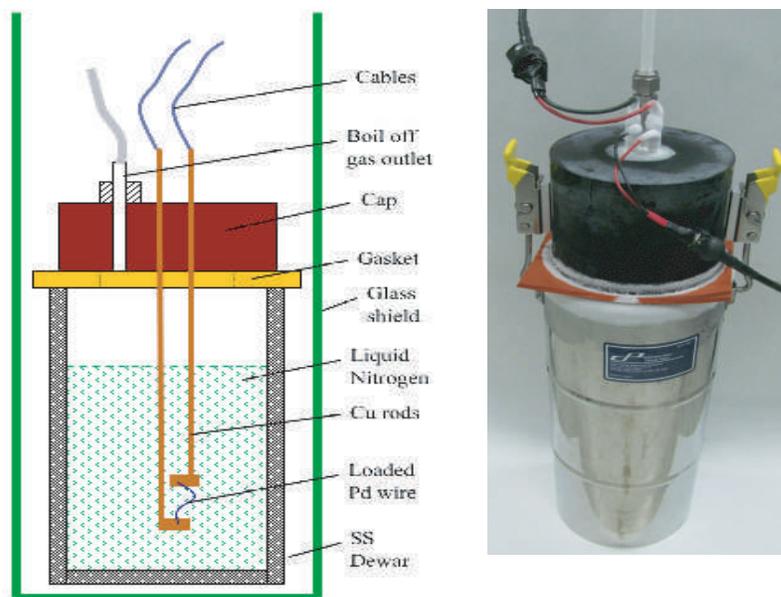
Figure 2.   Schematic diagram and photograph of the cryogenic calorimeter.

energies by using different length pulses and current levels into a current shunt immersed in the LN calorimeter, in that way, the input energy could be controlled. We also calibrated the system by stimualting at least nine blank Pd wires, and calculating the output energy from the increased volume of N_2 gas evolved.

3. Results and Discussion

3.1. Calorimeter calibration

Figure 3 shows five typical behaviors for the base flow rates of boiled-off nitrogen gas from the LN in the Dewar flask. The data are collected every 5 ms until 50 s and after 52 s, and at every 0.1 ms in the interval from 50 to 52 s, during which the pulse is applied and excess gas volume is measured. The flow rate usually fluctuates around an average rate with a standard deviation of about 0.013–0.014 l/min, except for baseline 3, which has a standard deviation of 0.02 l/min. Note that the high-frequency fluctuation comes from electronic noise. The stability of the system is very important, and shielding from the environmental perturbation is also recommended.

However, deviations from the quasi-steady state are also seen as thermal fluctuations and slight baseline drifts. The thermal fluctuation usually starts and ends in about 20–30 s, which is seen as a rise/drop in flow rate and then a return to the average. From the base flow rate collected before and after the application of the pulse, we are able to locate the position of the excess flow peak, whether it is collected when the system is steady, on a rising/decreasing wave, or drifting to another baseline. The nearest few seconds should be used as the baseline for the later cases, and the error will still be minimal, since the response to the pulse only lasts for 1.1–1.2 s. In extreme cases, where sharp rises/drops (∼1 s) are concurrent with a thermal fluctuation wave, the error could be as high as ± 0.25 ml (which was obtained by picking a high peak, calculating the difference with the nearest low average, then integrating for 1.2 s). Otherwise, the difference is usually between 0.1 and 0.2 ml if fluctuation occurs. The error percentage is obviously less at higher input energies. Therefore, upper and lower bounds of 0.25 ml from the theoretical value are considered the absolute limits of
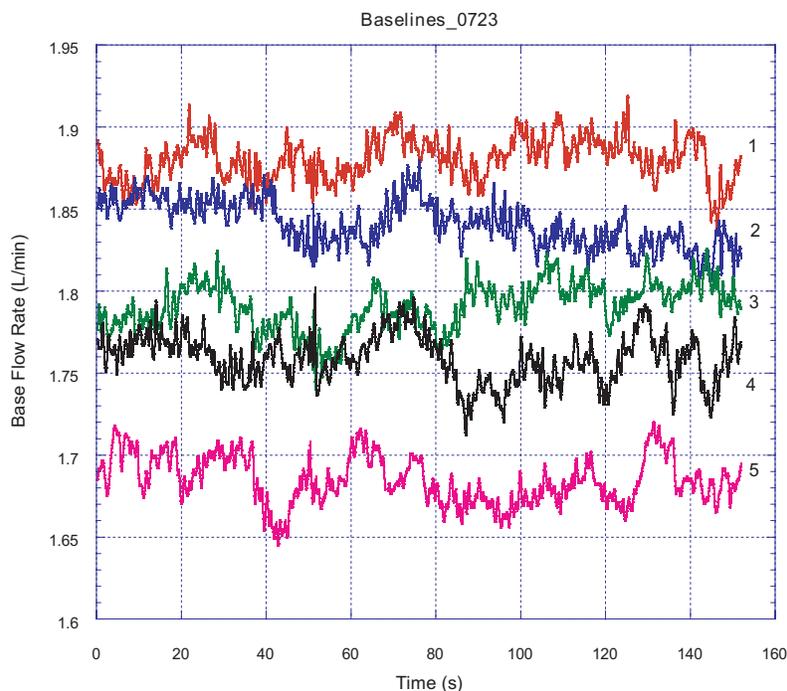
Figure 3. Typical base flow rate variation with time measured by the cryogenic calorimeter.

error. If the measured (and calculated) excess gas volume is obviously much more than 0.25 ml, it is clear that excess heat has been generated. If the excess gas volume is approximately 0.25 ml or less, excess energy is difficult to prove.

Calibration of the cryogenic calorimeter was carried out using both a 10 Ω resistor and blank (as received) Pd wires. We applied a series of current pulses of 0.3–2A for durations of 100–500 ms to the 10 Ω resistor and measured the evolved gas volume. Each experiment was operated three times to determine the statistical error. This calibration method provides a wide range of input energy, and the results are presented in Fig. 4. The measured gas volume at each input energy level lies very close to the theoretical line and well within the limits of error. The response time of the calorimeter is ∼3 s after the input stimulation pulse, which is found to be significantly different from that of the calorimeter using thin wires (1.1–1.2 s). A high current pulse is applied and the power generated is usually over several hundred watts, which can momentarily heat up the wire causing the thin wires to break in a few milliseconds. Therefore, we performed calibrations with thin pure Pd wires. Figure 5 shows the measured gas volume for each of the 9 blank wires tested, and its corresponding theoretical gas volume. It is seen that the measured/calculated gas volumes are very close to the theoretical values (within ±0.25 ml). These data confirm that no excess heat was generated with blank Pd wires, and that the calorimeter yields repeatable results. With this calibration method, the maximum input energy is limited by the energy needed to break or melt the thin wire. Using heat capacity data from HSC® software by Outokumpo, we calculated that only 0.75 J is required to melt a 5 cm long Pd wire of 50 μm diameter in LN, if heat conduction is neglected. For a 6 cm long wire, the energy needed is 0.9 J. In many cases, the wire breaks at a weak point, so the input heat is far less than the energy needed to melt the whole wire.
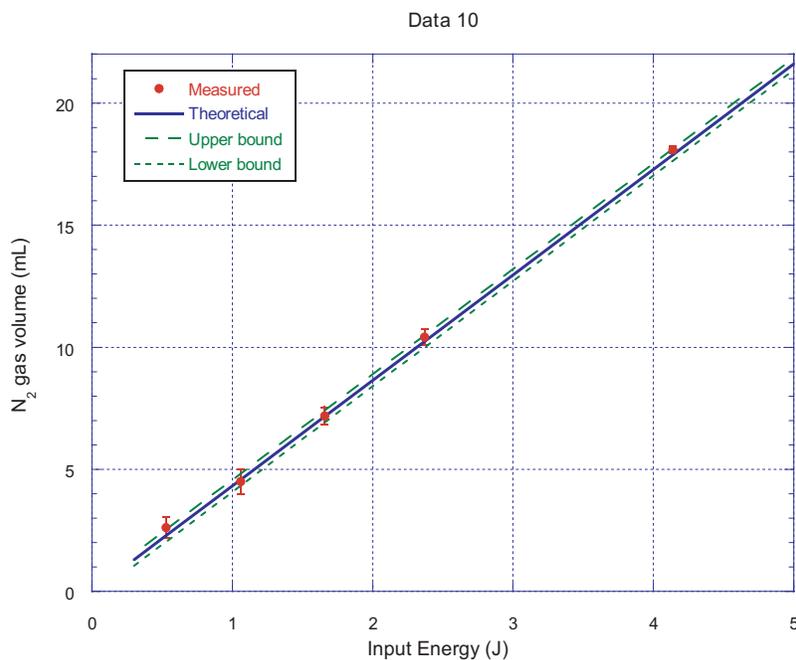
Figure 4. Calibration of the calorimeter using a series of electrical pulse across a 10 Ω resistor.

3.2. Electrochemical results

Figure 6 shows a typical annealing curve and a photograph of the Pd wire during this annealing process.

Low-molarity $Pd/SrO_4/D_2O$ electrolysis experiments were performed using 50 μm wires. These wires were then sealed electrolytically using Hg_2SO_4. A typical cell response to current steps and Hg_2SO_4 additions is shown in Fig. 7. R/R_0 (the ratio of the instantaneous Pd resistance to its starting resistance) went through a maximum very quickly, as was expected for such a thin wire. Then, small amounts of Hg_2SO_4 were added to enhance the loading and seal the wire. Finally, the current was reduced in steps with minimal loss of loading. These wires were then successfully transferred to a cryogenic calorimeter without loss of loading.

In addition to the input pulse, the gas volume measured may be affected by the enthalpy of melting/volatilizing the wire as well as the gas evolution from the desorption of any hydrogen/deuterium. For these reasons, the results from PdD_x wires will be compared with the energy released from pure Pd or Pt wires as well as the results from PdH_x.

3.3. Calorimetry results

Figure 8 shows typical calorimetric responses to current pulses being sent through a PdD_x wire and a 10 Ω resistor.

The average response time for blank Pd wires is 1.22 s, with a standard deviation of 0.035 s. Therefore, response time of 1.2 s is used for the calculation of PdD_x wires for ease of calculation and also to minimize the error. For the 10 Ω resistors, the response time is around 2.9 s. There are always two major peaks seen in the flow rate of the evolved gas after the pulse (in some cases, the second peak is finely divided into two peaks) with pure Pd wires, PdD_x wires, and calibration resistors.

For the resistors, the first rise is possibly related to the copper rods, which are very good heat conductors that almost
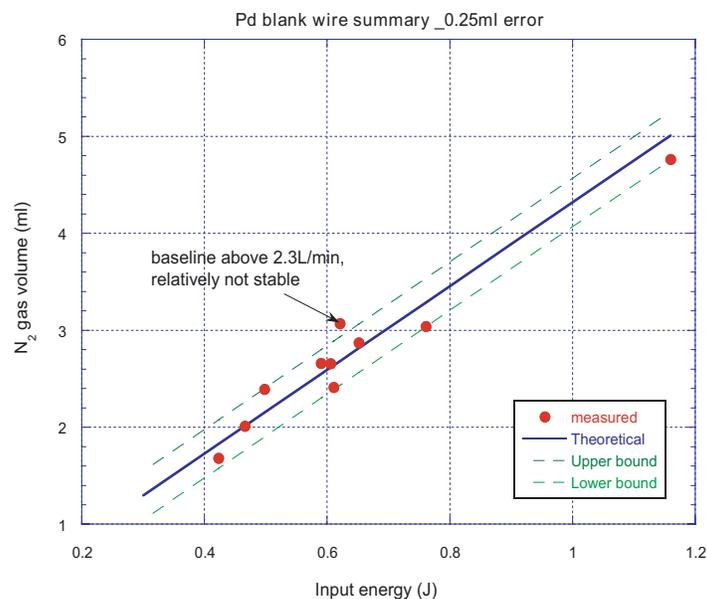
Figure 5.   Calibration of the cryogenic calorimeter using blank Pd wires.

immediately transfer the heat to the liquid nitrogen. The second rise is then related to the heat conducted from the heated resistor to the liquid nitrogen. For the wires, the faster response is probably due to direct heating of the liquid nitrogen after the wire disintegrates, together with the heating of the copper rods. The second peak is probably the heat released from the wire itself. Since the wire has faster heat conductance than the resistor, the temporal separation between the two peaks is less. Also, because the current is applied for 100 ms for the 10 Ω resistors, while it only lasts about 3–5 ms for the thin wires, the half-height-widths of the peaks are larger for the resistor calibration pulses.

Table 1 summarizes the calorimetric results for PdH_x and PdD_x wires for which the calorimeter showed a stable baseline. It is interesting to point out that after a large amount of testing with thin Pd wires, it seems that whether the wire would completely disintegrate into fine powders or simply break is determined by the nature 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 would 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 impairing the crystallographic structure or the intrinsic defects within the wire is unknown. It only happened in this one occasion.

None of the blank wires showed any excess heat. Among the three wires loaded with H, two didn't show any excess heat significantly greater than the input energy. One showed relatively high excess heat, but with an unstable baseline. Therefore, with limited data points in the present work, it is difficult to conclude whether PdH_x wires generate significant amount of excess heat. Whereas among the seven wires loaded with deuterium, five showed the generation of excess energy significantly higher than the error range. The amount of excess energy varies from $18.4 \pm 8\%$ to $51.9 \pm 7\%$ (excluding wire #8, which has an excess percent of $499.5 \pm 100\%$ due to the low energy input, but the baseline is over 2 l/min). Figure 9 clearly illustrates which wires generated excess energy. Three wires are within the error range, but
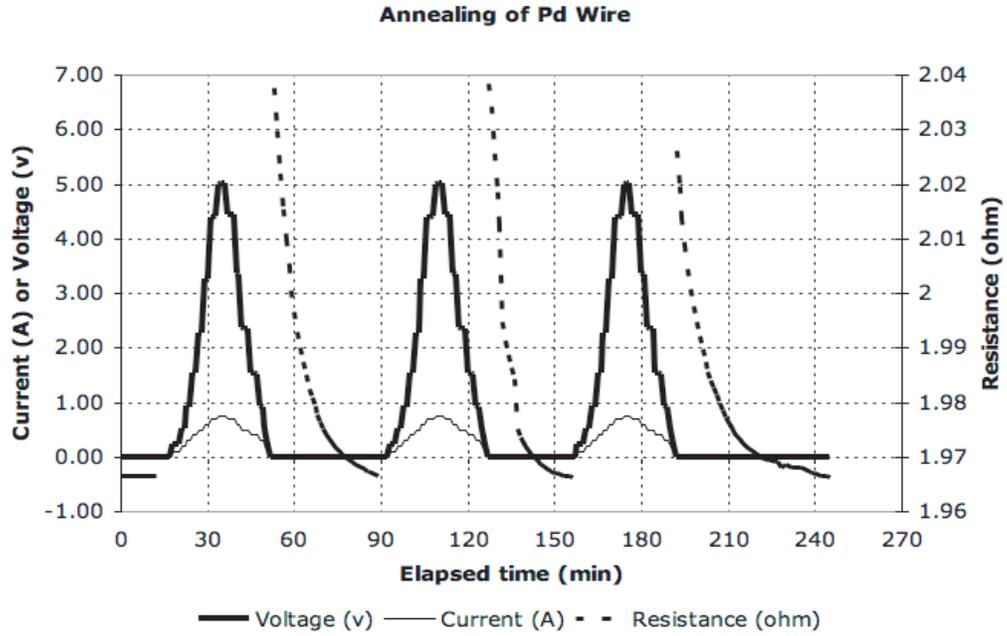
Annealing of Pd Wire

Figure 6. Plot of R/R_0, current, and voltage during Pd wire annealing.

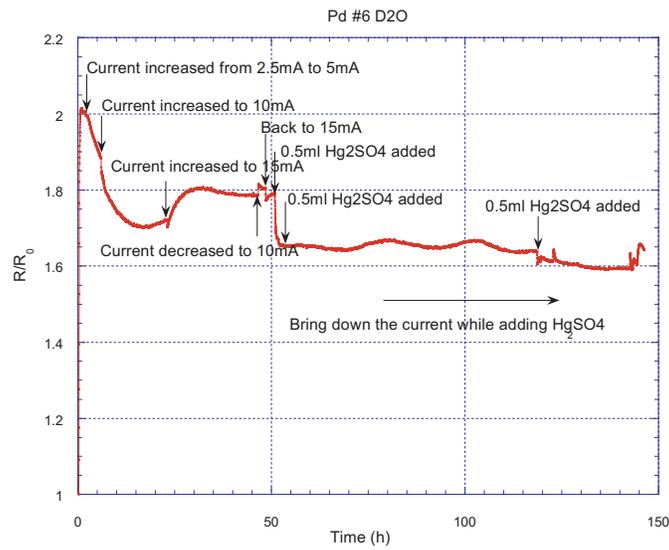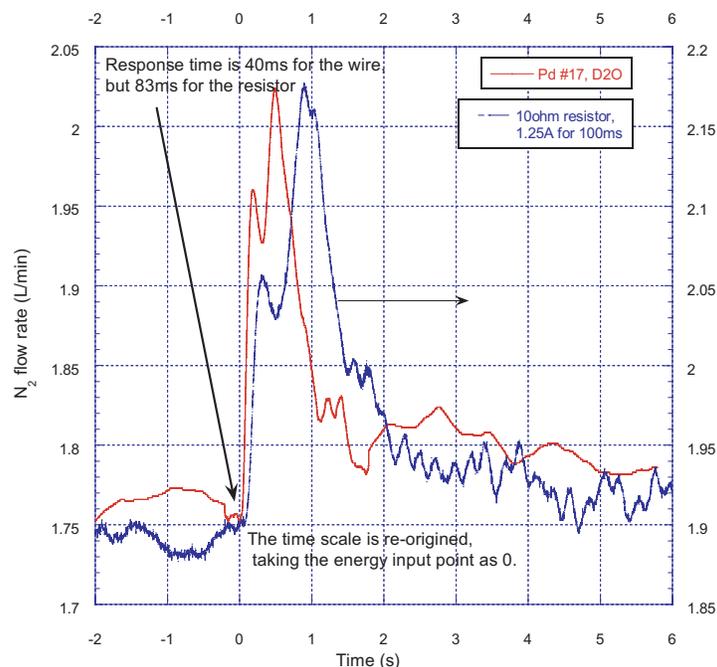**Figure 7.** Plot of R/R_0 for D loading of Pd wire.

Figure 8. Typical calorimetric response to a current pulse through a PdD$_x$ wire and a 10 Ω resistor.

Table 1. Cryogenic calorimeter results summary.

Exp.	Material	x	Energy input (J)	Energy output (J)	% Excess energy*	Comments
8	PdD$_x$	0.88	0.12	>=0.69	500 ± 100%	Unstable baseline
9	PdH$_x$	∼ 1.0	0.68	0.74 ± 0.12	8.2 ± 18	Unstable baseline
10	PdH$_x$	>1.0	0.64	0.96 ± 0.12	47 ± 19	Unstable baseline
11	PdH$_x$	>1.0	0.37	0.49 ± 0.06	32.5 ± 16	
e 12	PdD$_x$	0.98	0.71	0.84 ± 0.06	18.4 ± 8	
13	PdD$_x$	0.93	0.94	1.22 ± 0.06	29.7 ± 6	
14	PdD$_x$	0.95	0.63	0.70 ± 0.06	11.7 ± 10	
15	PdD$_x$	0.96	0.53	0.51 ± 0.06	−3.5 ± 11	
16	PdD$_x$	0.97			-	Too brittle to measure
17	PdD$_x$	0.97	0.50	0.70 ± 0.06	40 ± 12	Wire disintegrated
18	PdD$_x$	0.90	0.82	1.25 ± 0.06	51.9 ± 7	

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

the other seven wires show measured energy clearly greater than the error range. Although no obvious correlation can be made between excess energy production and loading level, the amount of excess energy generated by the stimulation of PdD$_x$ is generally much more than that generated by PdH$_x$ wires.
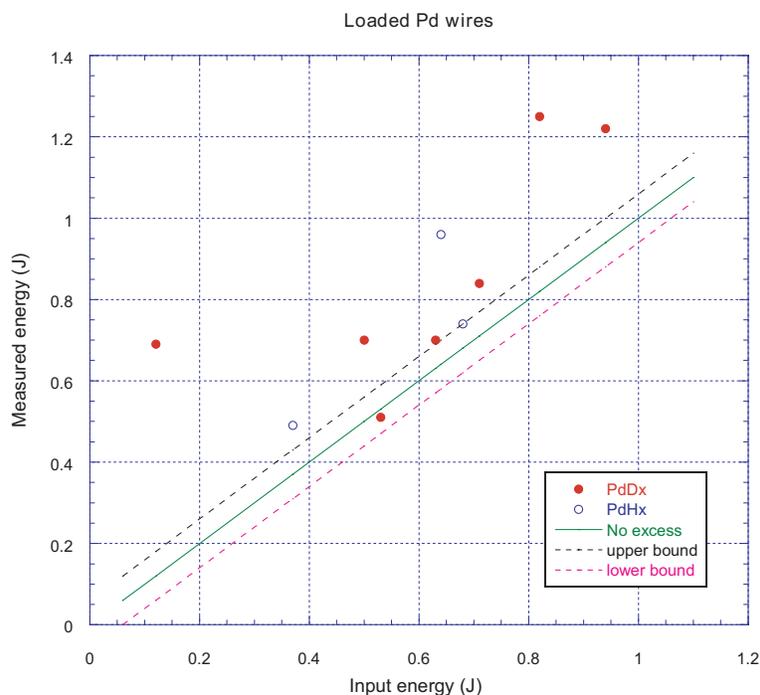
Figure 9.   Input energy and measured energy for all the Pd wires loaded with H or D.

4. Conclusions and Future Work

We have shown that the Tripodi technique for electrochemically forming highly loaded 50-μm-diameter PdH$_x$ wires can be extended to PdD$_x$ wires. We have designed, built, and operated a cryogenic calorimeter with a minimum detectability of less than 0.1 J and accuracy of less than 0.06 J. Under certain conditions when passing high current density pulses through highly loaded PdD$_x$ wires, output energies as high as 150% of input energies have been measured. We have shown that PdD$_x$ wires can disintegrate ("explode") when high current density pulses are passed through them at 77 K. In all cases seen so far, this disintegration leads to excess energy. No correlation can yet be made between the average deuterium loading level and excess energy.

We will collect gas from the calorimeter headspace during these "exploding wire" pulses and use mass spectroscopy to measure He isotope concentration in these gases. We will also use a metal vaporization inlet furnace to the He isotope mass spectrometer to analyze any Pd fragments for anomalous He isotopic ratios. We must measure more highly loaded PdH$_x$ wires using a stable calorimetric baseline in order to develop a statistically significant comparison.

Pd (and other metal and alloy) wires subjected to He insertion will be loaded and subjected to high current density pulses using the techniques described above in an attempt to maximize the excess energies. He insertion will be used to form defects in the Pd cathodes, which we feel should facilitate anomalous effects.

Acknowledgments

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