

Calorimetry Of Pulse Electro-Melting of PdD_x Wires

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Abstract. Several groups have reported anomalous effects (heat and nuclear products) in thin PdD_x materials stimulated by different forms of electro-diffusion. We have designed and tested a calorimeter utilizes an “exploding wire” technique to examine the effect of a destructive electro-diffusion on a highly loaded PdD_x wire. We have shown that highly loaded PdD_x wires can be formed using high voltage electrolysis of very high purity D₂O with a very thin Pd wire cathode and a thin Pt wire anode. The addition a partial monolayer of a recombination poison yields a highly loaded PdD_x cathode. Following that step with the addition of a larger amount of that same poison seals the loaded wire and allows transfer to a cryogenic calorimeter. Our liquid nitrogen boil-off cryogenic calorimeter has been shown to have an accuracy of less than 0.4J.

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. The ultimate extrapolation of this technology is the electrical heating of thin PdD_x 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]. Celani *et al*[4-5] 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 N₂ equal to the electrical energy passed through the wire due to the heat capacity and enthalpy of vaporization of LN.

Since considerable attention has been directed toward demonstrating a correlation between the rates of excess heat and ³He and ⁴He production [7, 8], we will analyze the off gases for excess He and non-natural isotopic He ratios.

2. Experimental

Although some experiments have been performed, the primary effort during this year has been to design, build, and test the equipment necessary to load deuterium into palladium, seal the deuterium inside, measure the energy released during electrical stimulations, and measure He-4 products produced both in the electrolytic cell and during the stimulated energy release.

We have adapted the original H₂O high loading/sealed cathode technique to D₂O. This is not a trivial effort since the loading process requires ultra-clean materials and ultra-pure reagents. Unfortunately, most available D₂O is chemically impure when compared to 18 MΩ-cm de-ionized H₂O. We have been using high-purity D₂O (Sigma-Aldrich #P192341), which also provides the high isotopic purity necessary to yield high D loading. In order to maintain this isotopic purity all transfers are performed under dry N₂ or Ar.

5 x 10⁻⁵ M SrSO₄ in D₂O is prepared under dry conditions. Approximately 5 ml of Hg₂SO₄ saturated D₂O is similarly prepared and stirred overnight. After cleaning all components are rinsed with deionized H₂O, followed by pure ethanol before drying. ~ 5 cm length of 0.050 mm diameter Pd wire (Alfa # 40730) is

attached to 4 lengths of 0.25 mm Pt wire and attached to the cell shown diagrammatically in Fig. 1. This allows for *in situ* accurate 4-wire resistance measurements of the Pd cathode. This cell is closed with its silica quartz vessel and the Pd resistance measured.

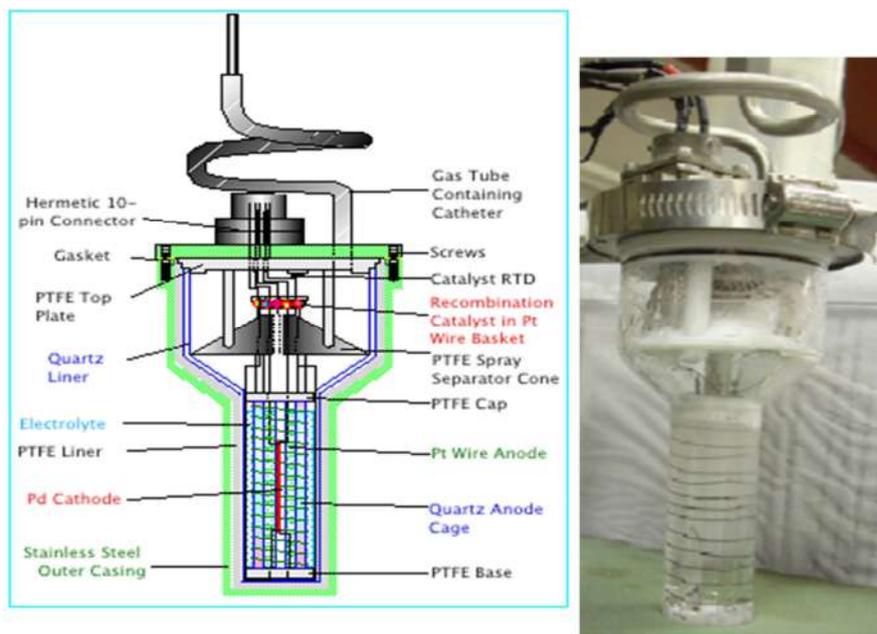


Fig. 1 - Degree of loading cell used to load and seal thin wires.

A current is passed along the length of the Pd to resistively heat the wire and anneal it in place. The current is raised slowly to $\sim 0.75\text{A}$ where the wire glows a bright orange color. Experience has shown this to be adequate to properly anneal the wire. The current is then lowered slowly to 0A at room temperature where the resistance is again measured. This procedure is repeated until the Pd resistance does not change upon annealing. This final resistance is considered R_0 .

After a stable resistance is obtained, the cell assembly is again rinsed with DI water and ethanol and dried. Then $\sim 20\text{ ml}$ of $5 \times 10^{-4}\text{ M SrSO}_4/\text{D}_2\text{O}$ is added to the cell. After measuring a stable resistance with electrolyte present, $\sim 2.5\text{ mA}$ is applied across the cell. After a stable resistance value is obtained, the current is doubled to 5.0 mA . After the resistance has stopped coming down on the right side of the maximum (see the R/R_0 versus $H(D)$ loading curve in Fig.4), $\sim 1\text{ ml}$ of $\sim 5 \times 10^{-5}\text{ M Hg}_2\text{SO}_4$ is added to the cell. R/R_0 is often reduced at this point possibly due to the partial recombination poisoning of the Pd surface. Hg_2SO_4 solution is added, one ml at a time, until the resistance stops coming down. The electrolytic current is then reduced in steps to see if the resistance stabilizes at a value below $R/R_0=1.6$. If not, more Hg_2SO_4 is added. When R/R_0 is unchanged and below 1.6, the electrolysis is stopped, the Pd cathode removed and moved to the calorimeter.

The wires are then immersed in liquid nitrogen in a cryogenic nitrogen boil-off calorimeter, shown in Fig. 2. 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 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 and any excess energy produced from the extremely fast electro-migration inside the PdD_x will boil off a known given volume of nitrogen. Fig. 2 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. All of the vaporized gas is measured using an electronic mass flowmeter. The calorimeter is calibrated using a 50 watt 1 ohm resistor. The voltage, current, and time are 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.

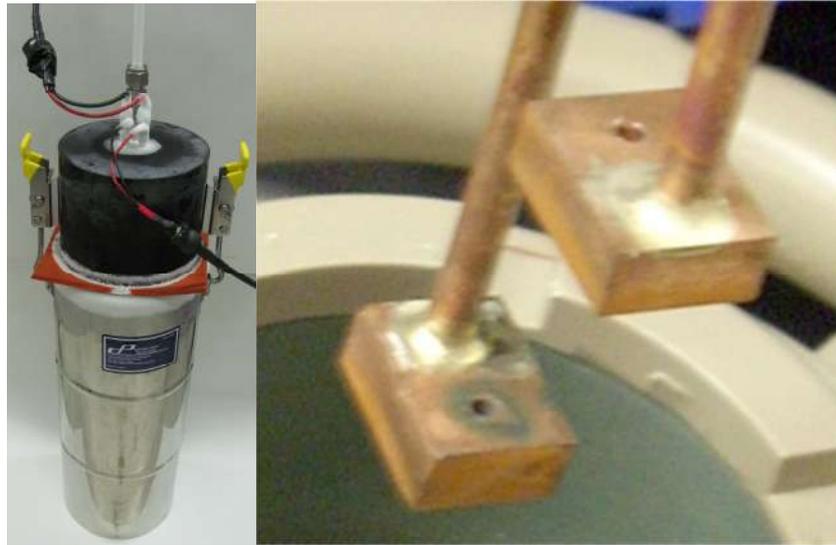


Fig. 2 - Photographs of the cryogenic calorimeter and its cathode connection blocks.

3. Results

The data collected and a photograph of the Pd wire during this annealing process are shown in Fig. 3. The blue line shows the voltage, the blue the current steps and the green line shows the R/R_0 measured

Low while the current is off. molarity Pd/SrO₄/D₂O electrolysis experiments have been performed using 50 μ m wires. These wires were then sealed electrolytically using Hg₂SO₄. A typical cell response to current steps and Hg₂SO₄ additions is shown in Fig. 4. R/R_0 goes through a maximum very quickly as you would expect for such a thin wire. Then small amounts of Hg₂SO₄ are added to enhance the loading and seal the wire. Finally the current is reduced in step with little or no loss of loading. These wires have been successfully transferred to a liquid nitrogen (LN) vessel without loss of loading. Calibration of the cryogenic calorimeter is shown in Fig. 5 as joules electrical input versus N₂ volume evolved. The red dot at ~ 0.4 J represents exploding wire results from a 50 μ m diameter pure Pd wire.

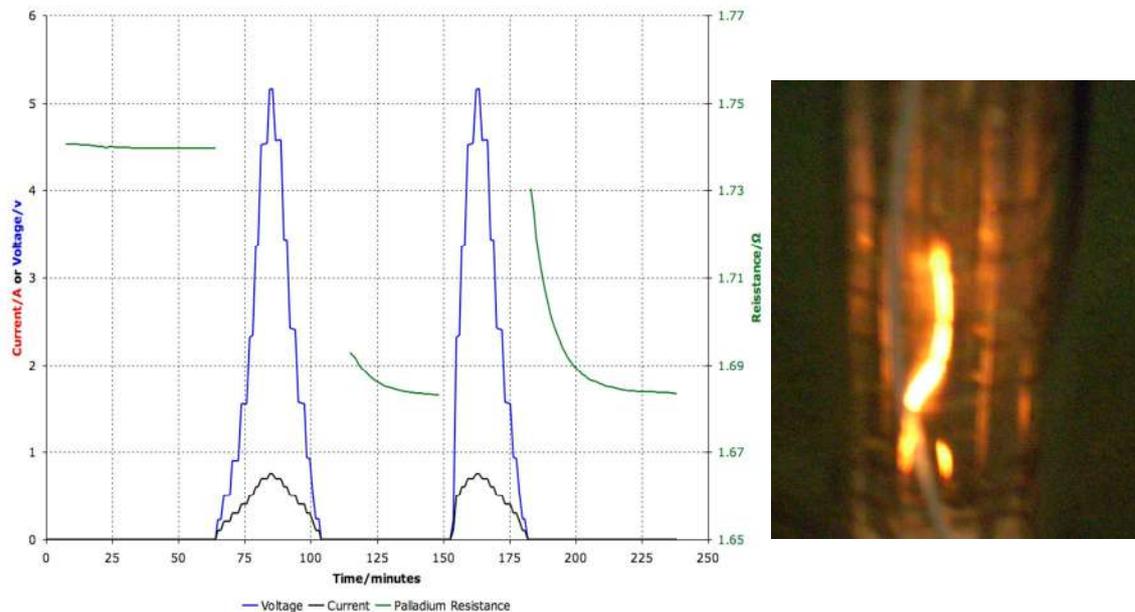


Fig. 3 - Plot of R/R_0 , current and voltage and photograph during Pd wire annealing.

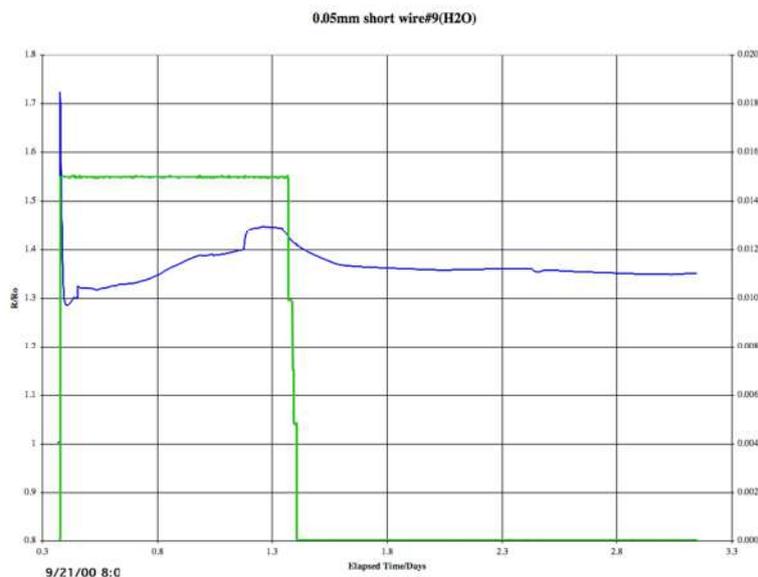


Fig. 4 - Plot of R/R_0 (blue) and Current (green) for H loading of Pd wire.

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 the energy released from pure Pd or Pt wires as well as the results from PdH_x .

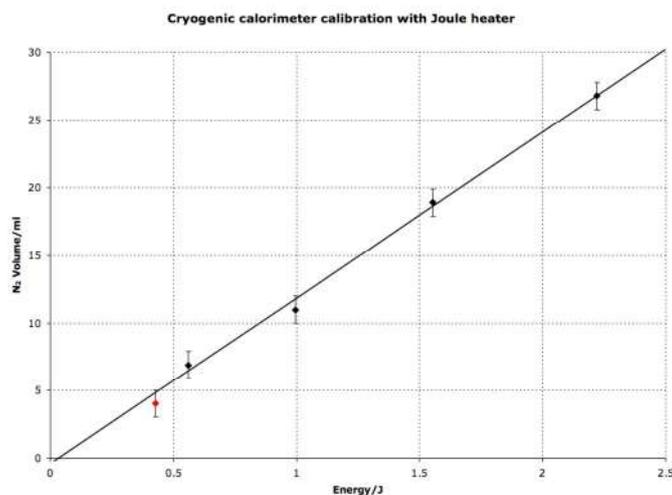


Fig. 5 - Calibration of cryogenic calorimeter and exploding pure Pd wire result (red dot)

4. Conclusions and Future Work

We have shown that we can load and seal 50 μm diameter PdH_x and PdD_x wires electrolytically. We have shown that we can transfer those wires to a cryogenic calorimeter without loss of loading. We have shown that we can measure as little as 400 mJ of input energy in the cryogenic calorimeter.

We have performed gas phase measurement of He isotopes from the headspace of various cells and are planning to perform this on most electrolysis cells' headspace gas and low-temperature stimulated wire effluent. We will also use a metal vaporization inlet to the He isotope mass spectrometer to analyze any Pd fragments for anomalous He isotopic ratio.

He insertion will be done by heating the Pd (or other wire) resistively in a tube to appropriate temperatures using sealed feed-throughs and selected pressures of He for a selected time. He insertion will be used to form defects in the Pd cathodes, which may facilitate anomalous effects.

Acknowledgements

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5. References

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