

Critique by Graham Hubler of report from DARPA project (2-21-2007)

**New Physical Effects in Metal Deuterides**

Authored by

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Submitted to Dr. Valerie Browning, DARPA DSO

Overall Comments

The purpose of this DARPA contract was to verify at an independent laboratory, the results of excess heat reported by Energetics, Inc. The experiments at SRI are reported here in sufficient detail to arrive at definite conclusions regarding the veracity of the Energetics method for producing heat from modified Fleischman-Pons electrolytic cells. While spectacular results of 2600% excess power (the best Energetics results to date but Energetics has ~12% success rate) were not obtained, the 70% success rate for cathodes that produced heat, and the several at 200% excess power is larger than is accustomed in this field and represent real progress in a US lab. The quality of the measurements of input power and output power, and the consistency checks and systematic checks on the apparatus are of high quality and leave no doubt that anomalous excess heat is produced in these experiments. My conclusion is that the contract goals have been fully met.

Specific comments follow in the order they appear in the report follow:

Table 2 – Pg. 21. The consistent loading of cathodes to high deuterium concentration is indeed remarkable and cannot be emphasized enough that this ability is the most important event in this area in 17 years. The ability to load has put a stamp of reproducibility on these experiments that was lacking and allows one to perform systematic investigations. This loading ability is also consistent with 5 cathodes supplied to NRL by Dr. Violante from ENEA where all 5 cathodes loaded to over 92% and as high as 98% in a Fleischman-Pons cell designed and furnished to NRL by Dr. Violante. Dr. Dawn Dominguez of NRL witnessed the first of these cathodes being loaded at NRL last year and when it reached 96% H/Pd in 12 hours she exclaimed “we spent 3 years in the 90’s trying to load H into Pd and never got above 85%”!

The SRI group measured excess heat in different cathodes with two completely independent, and completely different electronic measurement and data acquisition systems (using the same calorimeters). This is good experimental check.

SRI proposes an empirical equation to describe the excess power behavior;

$$P_{xs} \sim (i - i^0) (x - x^0)^2 |\Delta x / \Delta t|$$

where  $i$  is the electrochemical current or current density and  $i^0$  a critical current density threshold,  $x = D/Pd$  is the deuterium loading and  $x^0$  the threshold loading below which no effect is observed, typically  $x^0 \approx 0.88$ ,  $|\Delta x / \Delta t|$  is the rate of change of loading associated with the flux of D atoms through the interface, irrespective of sign. There is some utility in using this phenomenological equation to describe the excess heat behavior. It is not perfect but I consider it a starting point with which to unify the data, and it is a description under construction that may improve as more controlling features of the heat production become known. It somewhat described over 60 % of the results.

The data for ETH-035-9 (Figs. 15 and 16) is interesting as a null experiment and serves as a check on the calorimeter system. For long periods of time, the method used to measure and report the input power is very stable, the calorimetry used to measure the output heat production is very stable and the method used to compute the excess power from these two measurements is very stable and reports no excess heat. Similarly, Fig. 19 for cathode ETI 043-9 shows a dynamic range of 10 in input power with the system reporting null excess power over that range. This is another data set of many that gives confidence that the calorimetry is working as expected.

The experiment is generally run at 3C bath temperature. Several experiments were run where the temperature was varied during the experiment between 3C and 24C. One might expect the heat effect to diminish due to less solubility of H in Pd when the temperature was increased. In one cathode the loading did decrease but the heat increased. In another cathode, the loading increased with temperature. The temperature dependence of loading is interesting, and serves to show that there are multiple parameters governing the loading and heat production that are different for each cathode. One cannot use the solubility temperature dependence to predict loading. Temperature is a first order parameter in the behavior of solid-state systems. This preliminary data suggest that at least two competing parameters govern the heat generation as a function of temperature since there is no monotonic or simple relationship of heat to temperature. Developing this relationship of heat to temperature would provide clues as to the underlying process.

Pg 54. The analysis of the temperatures of the different temperature sensors is useful and convincing. This analysis, coupled with the one on the Pt cathode at the end of the report show that the heat is being generated inside the cell and that the likely place it is being produced is at the cathode.

This is very convincing evidence and should be expanded in future experiments with tighter control over the position of the sensors and the number of sensors.

Page 67. The replacement of the cathode with Pt conforms to expectations and is a very good check on the Pin/Pout measurement system. The thermal analysis of the temperature sensors is straightforward and convincing showing that the input power shows up at the cathode where it ought to be.

The total decoupling of excess heat and the input power conditions seen in several cathodes is remarkable, unexplained, and more than any experiment reported indicates a source of energy in this system (Figs. 26, 27, 30, 33, 34, Modes B and C according to SRI's nomenclature). This behavior has been reported before in Fleischman-Pons cells and in gas systems. The consistency of calorimeter performance in running these cathodes, and the failure of extensive systematic checks by the authors to uncover possible malfunction of the calorimeter are convincing to me that the effect is real. Furthermore, the excess power was controllable in the sense that it disappeared when the cathode was stripped, (see Fig. 27) taking away the deuterium in the cathode. This helps answer a question about recombination of O and D as the cause of the excess heat. When the cathode is stripped, there is a burst of deuterium injected into the system. If recombination of D and O were producing the heat, the heat would increase due to more D in the system or stay the same if the amount of O were the rate-limiting step. The fact that the heat abruptly shuts off indicates the recombination is not a viable explanation. These are strong, if not definitive indications that the calorimeter is working properly.

In some instances, the cathode loaded under very small currents, and the excess power was sustained under very low or no currents as in the case of the CNT covered cathode. These results suggest that under the right conditions, significant excess power might be realized. The CNT cathode also points to the fact that increased surface area seems to produce more heat. This suggestion has been in the field supported by not very much evidence. This experiment is significant since it is a data point in that direction that needs to be confirmed by repeated experiments. If this effect is a surface effect, then it stands a much better chance of being scaled up to greater power production than it would if it were a bulk effect.

Every time that cathodes are run, something new is learned. One example of this is the running of the last 3 cathodes where the electrolyte was unchanged. These cathodes loaded unusually rapidly and produced heat and additional behaviors that provided new information. If this practice is repeatable, then it may be one more way to increase repeatability. One speculation is that an impurity that poisons either the H-charging process or poisons the mechanism of heat production is "gettered" by the previous cathode and removed from the system so that subsequent cathodes are not poisoned. This result also indicates that this heat producing effect is at the surface, since these cathodes produced heat in a relatively short period of time. Such new, empirical information is vital to getting this system to the point of repeatability. Another example of this occurred in NRL's experiment at NSLS, Brookhaven. The last cathode we ran was inadvertently crumpled up and thrown into the trash in cleaning up after preparation. Upon this discovery, the foil was straightened out by rolling it with a beaker and inserted into the cell. This cathode loaded in 1 hour up to H/Pd 0.95 – faster than Dr. Violante had ever seen. We speculate that introduction of cold work just prior to electrolysis may be a new method to increase reproducibility.

These examples point to the difficulties that were experienced in this field in the process of getting to where it is today. The process has been very slow since there is no

understanding of the underlying physics to guide the experimental parameters and new information has been accrued very slowly. However, there is reason for optimism due to the cathode preparation of ENEA, Dr. Violante, the superwave loading, and the ~70% reproducibility of heat production. New features of this phenomenon will be found much quicker than in the past. With a reproducible system, more in situ measurements can be made that I believe are the key to determining the cause(s) of this heat effect.

The measurements of Tritium were not in the proposal and are an added feature of the work. The results of increased T content do not correlate well with heat and are difficult to interpret other than to note as interesting. The checks and rechecks evident in the power production experiments are not evident in this work. I consider the T measurement interesting but incidental to the task at hand for this project.

The material measurements made by NRL are preliminary. The SEM and ICP-MS did not turn up any conclusions that were definitive. The total amount of energy produced by any of these cathodes was not enough to produce isotope shifts large enough to measure. X-ray diffraction indicated the residual H in the cathodes, and neutron profiling of Li indicated up to tens of ppm alloyed into the surface of the Pd. This is good preliminary work that looked into what measurements are most useful to monitor the condition of the cathodes. This data is still being assessed.

#### Conclusions and Recommendations.

A number of aspects to the SRI experimental set up was explained and critiqued in my report of a year ago. Many of the questions I had at the time have been answered in this report. I find little to quarrel with regarding experimental design, equipment, and measurement methods. The quality of the data presented here is excellent, voluminous, and convincing regarding the question of whether or not anomalous heat is produced. It unquestionably is produced. The success of this project hinged on reproducing the Energetics, Inc. results using their apparatus. In my opinion this task has been accomplished. Over 70% of the cathodes produced heat, and the level of heat production was very much higher than the baseline noise and errors in the measurement of power in and power out. Moreover, the system was well behaved over many days of running – a fact that experimentalists appreciate as it is much more satisfying to believe data from well-behaved systems than to agonize over data from systems that produce unknown and unexpected glitches.

Several of Energetics Inc. runs produced very large power gains (9X, 15X and 26X). However, in private conversations, their success rate for getting any excess power, as of less than a year ago, was less than 15%. In my view, this SRI/Energetics/ENEA effort has been more successful due to the 70% success rate for obtaining excess power. This reproducibility is more important at this time than the large power gains since experiments to obtain more empirical data on the parameters that produce power excess are vastly more efficient at producing results.

At the moment, the Energetics results aside, the amount of power produced is not over 2 watts and for only hours at a time. This is not very much power and is not in a usable form at this point. But if 2 watts were available in usable form, for days and weeks at a time, then there are many DoD applications of such power levels. It may take as little as a factor of 10 increase in the power level observed here, and of course, continuous running, to achieve a 1 Watt power source. So it is not unreasonable from a DoD point of view to continue with development of this technology, regardless of the mechanism(s) responsible for it that will eventually be uncovered. I believe that enough is now known that much more rapid progress will be possible in bringing an operational understanding to anomalous heat production in these cells.

Specific comments and questions that will be asked of SRI at a future meeting.

In Fig. 1, where are the T1, T2 and T3 sensors placed?

From our visit last year, I remember a jar placed on a scale that housed the recombinator that was connected to the cell with a plastic tube. Figure 1 does not conform to this memory. Why?

Page 8 The thermal conductivity at 25C of D2O is 2.5% smaller than H2O.

The viscosity at 25C of D2O is 22.9% greater than H2O

The density at 25C of D2O is 10.7% greater than H2O

The specific heat at 25C of D2O is 12.5% greater than H2O

If all calibrations were performed using H2O then there will be a systematic error in the calibration caused by these differences in properties between H2O and D2O. As explained on page 11, this is folded into the calibration constants. It seems that to be rigorous, the calibration should be done in D2O with a Pt cathode (this was done as the last cathode in the experiments). However, these differences must be below the calibration error of 5%, since D2O cells show null power for long periods of time when they are not producing heat.

Page 9, Fig. 2. It is to be explained why ostensibly identical calorimeters can differ in their calibration constants by 20%.

Page 12. The thermal time constants are ~5 minutes for the cell to equilibrate and ~53 minutes for the calorimeter to equilibrate after an abrupt change in input conditions. Is there any superwave pattern seen in the temperature of the liquid? The time constant is such that it may be seen.

Please clarify Table 2 since it contains samples a, b, c and the text only has numbers.

Page 14. The 50 K/s measurement rate on the input power wave form should satisfy Al Ehrlich as to whether or not there is a phase lag in the I-V response and therefore and error in input power measurement.

Perhaps it is later in the report, but how is the error in the calorimeter determined, and the noise in the calorimeter?

Page 16. What causes the output power to be so large for the first~4 hours in Fig. 7? Similarly for Fig. 8? What does it mean on page 17 line 3 to say “when sensible calorimetry was first achieved?”

Page 19. Item 3). It is remarkable that the voltage should change so abruptly. The authors speculate that there was a change in the surface of the cathode. In future experiments, it is recommended here that the cathode be continuously monitored by a TV camera to see if there is a correlation with the data and a noticeable change in the cathode position or appearance, or a change in the color of the electrolyte.

SRI Data Acquisition.

Pg. 20. Again, how is the 3-sigma error of 5% of  $P_{in}$  obtained? The noise in the data often look very small so that it is easy to believe that the 5% is a conservative number – but how is it obtained?

Page 22. first paragraph – are the samples labeled wrong? does not agree with table.

\*\*General comment. – use of independent data acquisition system is good experimental check.

Page 23.

How do you measure the calibration of a temperature sensor during the experiment?

5<sup>th</sup> paragraph insert the words “to measure” in front of the Pd resistance.

Page 30 Paragraph beginning with “Fig. 13”. Figure D is Figure 14.

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Page 33, Figure 14 in 4<sup>th</sup> paragraph is Fig. 15.

Page 39 – last paragraph – Figure Hb is Fig. 20.

Pg. 42. If the bath temperature is 3C and the melting temperature of D2O is over 4 C, does the LiOH prevent it from freezing?

Bottom of 4<sup>th</sup> paragraph – insert “producing” between of and excess.

Pg 54. The analysis of the temperatures of the different temperature sensors is useful and convincing once the position of the sensor is known. A diagram of where the sensors were placed for of this experiment would help clarify this explanation.