

Research Article

# Long Term Anomalous Heat from 9 nm Pd Nanoparticles in an Electrochemical Cell

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## Abstract

We report 58 days of 120 milliwatts anomalous excess heat in a Fleischman-Pons type open electrochemical cell which integrates to 610,000 Joules of liberated energy, including 4 days of anomalous heat after electrolysis power was shut off. The Pd foil cathode was placed in tension and 9 nm Pd nanoparticles were deposited on the cathode in situ at the onset of the experimental run.

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*Keywords:* Fleischman-pons, anomalous heat, nano particles, Pd foil, heat after electrolysis

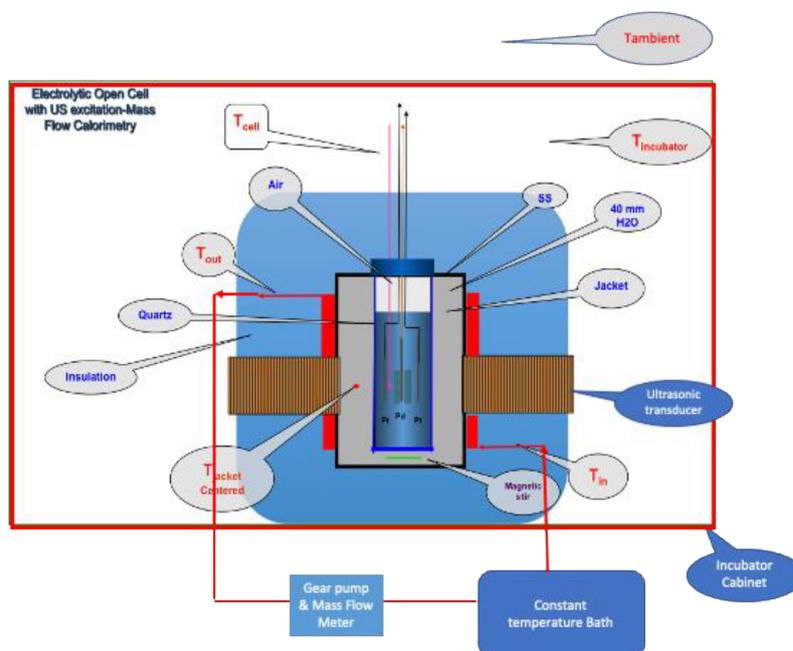
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## 1. Introduction

There have been numerous papers on the measurement of anomalous heat during the electrolysis with D<sub>2</sub>O on Pd cathodes since the first reports by Fleischman and Pons [1]. We describe this heat as the anomalous heat effect (AHE) rather than cold fusion (CF) or low energy nuclear reactions (LENR) since the underlying mechanism has not been discovered nor is there incontrovertible evidence that a nuclear process is involved. Since Arata first reported the AHE using gas loading methods on Pd nanoparticles at elevated temperature [2], many researchers shifted to performing variations of elevated temperature gas loading on Pd and Ni nanoparticle containing powders with considerable success [3]–[6]. Here we report for the first time the use of Pd nanoparticles in the electrolysis method of exploring the AHE that resulted in the appearance of the AHE with higher probability than for bulk Pd cathodes based upon SKINR data from over 1000 runs on Pd foils that seldom produced excess heat.

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**Figure 1.** Schematic representation of calorimeter system US4 at SKINR.

In this effort, 9 different calorimeters in the SKINR lab were employed including mass flow (1),  $^4\text{He}$  tight mass flow (1), Isoperibolic (6) and differential (1). The latter was constructed by SKINR and the mass flow and isoperibolic calorimeters were legacy calorimeters from Energetics, LTD. Definitive results were obtained with the open cell mass flow calorimeter and will be described in this report. Various less robust results were obtained in the other calorimeters and will be included later in the discussion.

## 2. Experimental

Figure 1 is a schematic view of the open cell mass flow calorimeter designated US4 [7]. This calorimeter (built by Energetics, Inc., modified by SKINR to provide vertical tension on cathode) is designed to bathe the cathode in ultrasound stimulation using 4 ultrasound transducers placed equidistant around the cell centered on the cathode vertically. The ultrasound transducers were not used in this experiment. A unique feature of this calorimeter is a water jacket surrounding the cell containing the electrolyte. The water jacket served to transmit the ultrasound acoustic waves (when used) through the water jacket to the walls of the quartz cell, and then into the electrolyte and then to the cathode. Energetics obtained modest heat results using this method of stimulation [7] and this mass flow calorimeter proved to be a reliable and yield accurate heat data in our previous AHE studies. In the present experiment, the ultrasound transducers were not used as we were interested in just using the mass flow calorimeter to test the nanoparticle inspired cathodes. Also implemented in this cell was spring actuated constant vertical tension of  $4.8\text{E-}5$  Newtons/ $\text{m}^2$  ( $1/3$  the Pd yield strength of  $180\text{ N/m}^2$ ) on the  $8\text{cm} \times 0.8\text{cm} \times 100\mu\text{m}$ , 0.9995 purity Pd foil cathode. When a Pd foil cathode is loaded with H, the change in volume between the alpha and beta phases causes the cathode to expand and crinkle and become misshapen. The spring loaded tension was used to allow the cathode to expand and therefore minimize



**Figure 2.** Photos of US4 calorimeter; a) anode-cathode (non-tension version) assembly and electrochemical cell, b) SS chamber, c) assembled calorimeter in incubator cabinet.

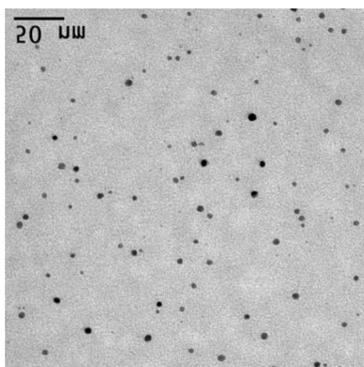
the deformation of the cathode. It was hoped that this feature would prevent detachment of Pd nanoparticles deposited on the foil surface.

Surrounding the water jacket were Cu coils that formed the mass flow portion of the calorimeter and the cell, water jacket and coils were placed inside a stainless-steel (SS) cylindrical chamber. The SS chamber was covered in insulation and placed inside an incubator shown in Fig. 2. Outside of the incubator was a constant temperature bath that fed water to the inlet of the mass flow coil and the heated water returned through a gear pump and mass flow sensor to the constant temperature bath.

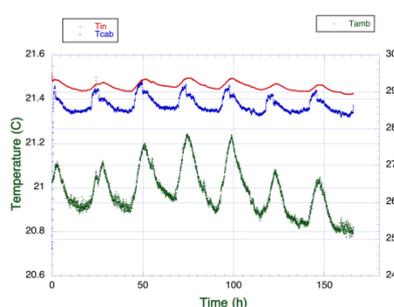
There were six PT100 thermal sensors in the system shown in Fig. 1: water input temperature to the mass flow coil ( $T_{in}$ ), water outlet temperature from the mass flow coil ( $T_{out}$ ), temperature in the water jacket centered on the cathode ( $T_{jack}$ ), cell electrolyte temperature centered on the cathode ( $T_{cell}$ ), temperature in the incubator cabinet ( $T_{cab}$ ) and the ambient temperature outside of the cabinet ( $T_{amb}$ ). The thermal power measured by the mass flow system was  $Power = Mass\ Flow \times (T_{out} - T_{in})$  where the product is read directly as Watts. The anodes were 4 Pt wires wound around Teflon supports as shown in Fig. 2. Several electrolytes were used, depending on the test being conducted; 0.1M LiOD in  $H_2O$ , 0.1M LiOD in  $D_2O$ , 0.1M LiOH in  $D_2O$ . For the long term run that is the primary focus of this report, the electrolyte was 0.1M LiOD in  $H_2O$ .

The 4 point-probe technique was used to measure the cathode resistance in situ. The electrolysis current and voltage were measured at the sampling rate of 50,000 Hz, averaged, and reported at 1 Hz. The 6 temperature sensors, cathode resistance and mass flow sensor were all reported at 1 Hz. Also shown in Fig. 1 is a magnetic stir in the bottom of the water jacket. This was implemented by Energetics as necessary to obtain robust mass flow calorimetry operation. The stir inserts energy into the calorimeter that must be accounted for. Energetics found that the stir caused a 0.786 C positive offset in  $T_{out}$ ,  $T_{jack}$ ,  $T_{cell}$  and that this offset was stable over a period of years.  $T_{in}$  is not influenced by the magnetic stir. Therefore, to obtain accurate heat output from the calorimeter, 0.786 C was subtracted in the software from  $T_{out}$  ( $T_{cell}$ ,  $T_{jack}$  were not corrected) in order to make  $T_{in} - T_{out}$  a precise measure of heat output.

Pd nanoparticles (NP) were synthesized in the U. Missouri Medical School following protocols described in the U.S. patent 20170009366 entitled, “EGCG Stabilized Pd nanoparticles, method for making and electrochemical cell” [8]. Initially, 9 nm diameter NP were emphasized and during the experimental program sizes down to 5 nm diameter were studied. The size distribution at any size was  $\sim \pm 1.7$  nm. A mass of 379 mg of Pd nanoparticles were added to electrolyte consisting of 150 ml of 0.1M LiOD in  $H_2O$  just prior to starting the experiments, turning the clear electrolyte to a black color. The electrolyte became transparent within 2 days from time electrolysis began as Pd nanoparticles plated out on cathode (as determined by supporting experiments outside of a calorimeter where the electrolyte could be observed). Figure 3 is a TEM image of a typical 9 nm batch of Pd NP.



**Figure 3.** Transmission electron micrograph (TEM) image of nominal 9 nm Pd nanoparticles. Scale marker is 20 nm.

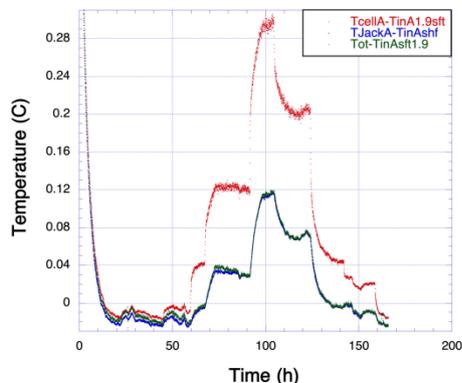


**Figure 4.**  $T_{in}$ ,  $T_{cab}$ ,  $T_{amb}$  versus time showing effects of daily room temperature variation.

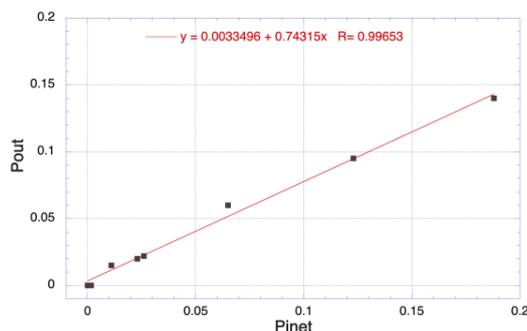
### 3. Initial Test Data

Figure 4 displays  $T_{in}$ ,  $T_{cab}$  and  $T_{amb}$  for 166 hours. There is very poor summertime temperature control in the room as  $T_{amb}$  shows swings of 2.7 C. The incubator cabinet reduces the swing to less than 0.2 C. Note that the cabinet and constant temperature bath were regulated to about 21.4 C which is  $\sim 5$ C less than ambient temperature so that the cabinet and constant temperature bath only use cooling cycles. Temperature variations in  $T_{in}$  are further reduced by the constant temperature bath to 0.07 C. All three sensors are highly correlated in time.

Figure 5 displays 166 hours of test data for a Pt cathode, showing the variation of temperatures with input electrical power. During the test, the electrical power was applied for open-cell electrolysis in a constant current mode and the input power was computed using densely sampled electrical currents and voltages during the electrolysis of 0.1M LiOD in  $H_2O$  with a thermal neutral potential correction of 1.482 V. With a mixed electrolyte, the precise value to assign for the thermoneutral potential is unknown so the value for  $H_2O$  was used as a lower limit to the correct value. Plotted are  $T_{cell}-T_{in}$ ,  $T_{jack}-T_{in}$  and  $T_{out}-T_{in}$ , where  $T_{in}$  is delay shifted by 1.9 hours optimized by least squares fitting. This is due to the fact that the constant temperature bath is correlated with  $T_{amb}$  while  $T_{cell}$ ,  $T_{jack}$ , and  $T_{out}$  are correlated with  $T_{cab}$ , and it takes 1.9 hours for  $T_{in}$  to respond to  $T_{cab}$ . A benefit of mass flow calorimetry is that the heat signal is a differential of  $T_{in}$  and  $T_{out}$  so that the daily temperature variations are largely removed when  $T_{in}$  is subtracted from  $T_{out}$  as can be seen in Fig. 5. The sensors for  $T_{cell}$ ,  $T_{jack}$  and  $T_{out}$  are highly correlated in time and  $T_{out}$  and  $T_{jack}$  are so highly correlated that  $T_{jack}$  could serve as a secondary  $T_{out}$  for measurement of heat output. Note that  $T_{cell}$  is larger than  $T_{jack}$  as it should be since the heat is generated at the cathode.  $T_{jack}$  lags  $T_{cell}$  in time by 6 minutes



**Figure 5.** Tcell-Tin, Tjack-Tin and Tout-Tin for different input powers versus time where Tin is time delayed by 1.9 hours.



**Figure 6.** Mass flow calorimeter efficiency measured to be 74.3%.

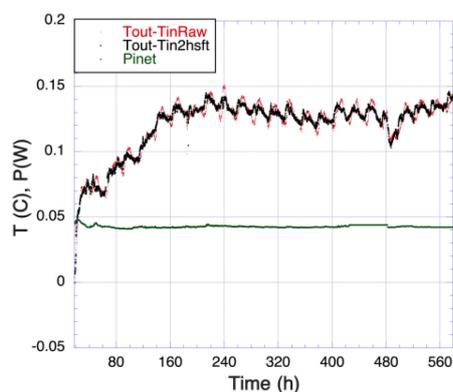
and Tout lags Tcell in time by 7.2 minutes after a step change in input power. The calorimeter time constant is 4 hours so the several minutes time lags do not need to be included in a time correction. Figure 6 displays the measure of the efficiency of the calorimeter of 74%.

#### 4. Excess Heat Detection

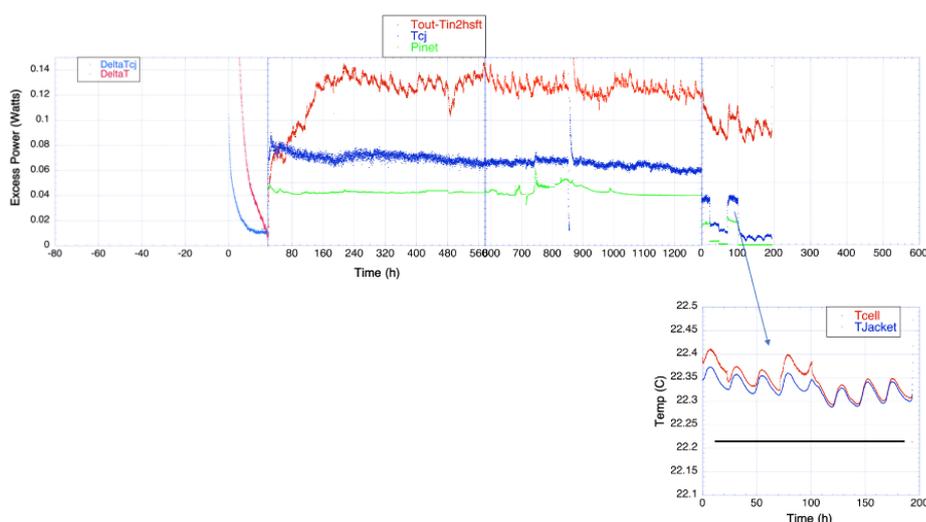
Figure 7 displays the first 560 hours of electrolysis for Tout-Tin (raw data) and Tout-Tin (Tin shifted by 1.9 hours) and the input power, Pinet, where the thermoneutral potential correction to the input power was employed. Notice shifting Tin 1.9 hours produces less temperature variation ( $\pm 0.02$  Raw data vs  $\pm 0.01$  shifted Tin) and the daily temperature swings are much reduced.

Several observations require comment. First, the excess power appears early at 4 hours after electrolysis is turned on and plateaus at 20 mW excess up to hour 65. During the first 48 hours, the nanoparticles were being slowly deposited and being slowly reacted with H and D. At 65 hours, excess power increases again to new level of 90 mW excess at  $\sim 160$  hours and remains at this level up to hour 560. Daily variations of Tout - Tin are not completely removed due to influence of Tamb on Tin.

Figure 8 displays the raw data for the entire 1500 hour run, uncorrected for the calorimeter efficiency. The system equilibrates for the first 18 hours prior to turning on the electrolysis at 25 mA under current control. After  $\sim 160$  hours,

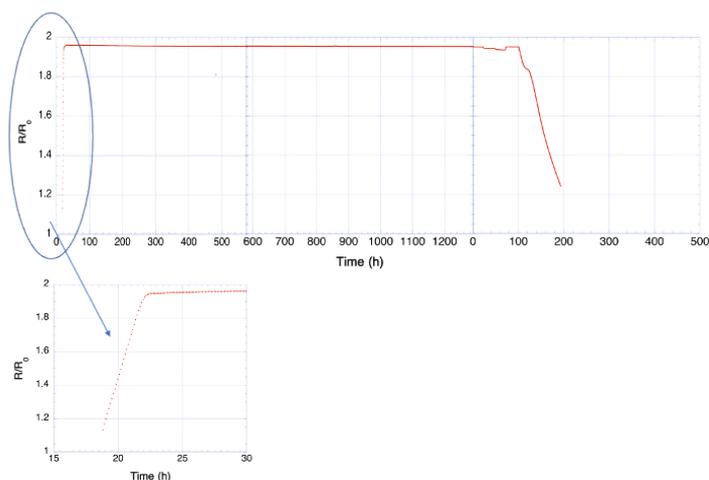


**Figure 7.** Tout-Tin (raw data, red) and Tout-Tin (Tin shifted by 1.9 hours, black) and input power, Pinet (green), for first 560 hours of electrolysis. The plotted values of delta T are proportional to the amount of power being produced. For a mass flow calorimeter, the deltaT is directly measured as power in Watts, uncorrected for the calorimeter efficiency.



**Figure 8.** Raw temperature and power data, uncorrected for the calorimeter efficiency, for entire 1500 hour run. First 18 hours - Tout (red), Tin (blue). 18-1500 hours, power out as Tout-Tin (red), Tcell-Tjack (blue), power in (green). Arrow points to raw data for Tcell and Tjack for last 200 hours. Black horizontal line is T of Tcell and Tjack before electrolysis and after cathode removed from cell.

the excess remains (red line) at  $\sim 90$  mW until the power is reduced at 1300 hours. The total energy released from this raw data was  $0.09 \times 1400 \times 3600 = 453,000$  Joules over 58 days. The blue line is Tcell – Tjack and the green line is the input power. Note that the daily variations are completely removed from the Tcell-Tjack data. This is due to the fact that Tcell and Tjack are both influenced by Tcab and there is no influence from Tamb. A plot of Tcell-Tout (not shown) produces an identical curve since Tjack, and Tout are highly correlated as we have already established.



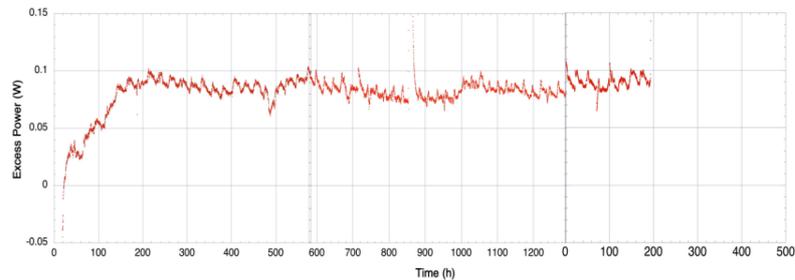
**Figure 9.** The resistance ratio  $R/R_0$  versus time. Scale change after 1300 hours.

There is a temperature excursion at 860 hours caused by loss of power to the constant temperature bath as confirmed by the timing of the temperature excursions reported by the sensors that showed  $T_{in}$  leading the excursions in time.

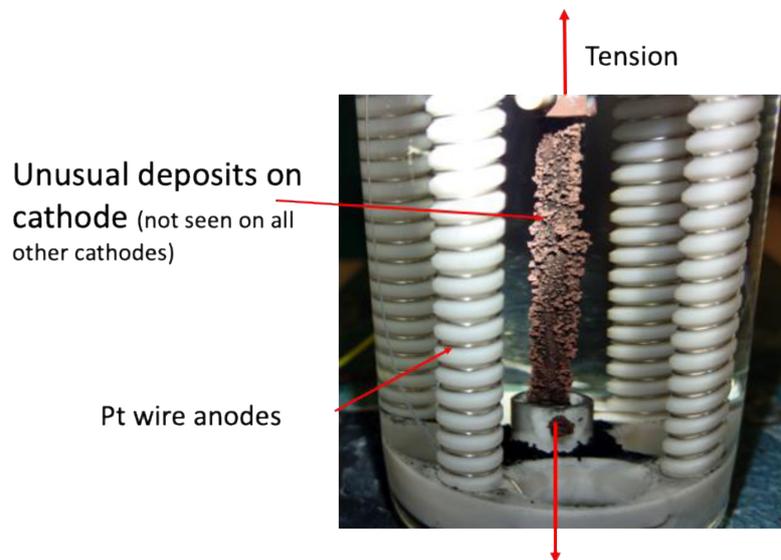
The last 200 hours of the run is especially interesting. During the last 200 hours the input power was manipulated where it was reduced in steps, increased and then set to 0 as shown in Fig. 8. The  $T_{cell}$ - $T_{jack}$  (blue curve) faithfully reports the power changes (green curve) since the power is sensed directly by  $T_{cell}$  and there are no daily temperature excursions to mask the changes. On the other hand,  $T_{out}$ - $T_{in}$  shows the general features of the power changes but does not drop to zero and keeps reporting the  $\sim 90$  mW excess power. The arrow points to the raw data for  $T_{cell}$ - $T_{jack}$  where the daily variations are clearly visible but note that both remain elevated and do not drop to 0 after power is removed. Therefore,  $T_{cell}$ ,  $T_{jack}$  and  $T_{out}$  all report elevated temperature for the last 100 hours when the input power was 0. The horizontal black line is the temperature of  $T_{cell}$  and  $T_{jack}$  before electrolysis. Both sensors returned to this value after the cathode was removed and the cell was reassembled. The 90 mW of excess heat for 1400 hours and 100 hours of heat after death were reported by all T sensors.

Figure 9 shows the resistance ratio  $R/R_0$  for the entire 1500 hour run. With application of charging current the ratio rose to 1.95 in 4 hours and remained there until the current was manipulated during the last 200 hours. For H/Pd, the literature maximum value for the ratio is 1.8 and for D/Pd it is 2.0 [9]. Since the value of 1.95 is not possible for H insertion, one might surmise the Pd loaded with D even in the mixed electrolyte. The presence of the Pd NP on the surface complicates the interpretation of the resistance data. Consequently, the D/Pd ratio of the deposited Pd is unknown and the amount of D and H in the Pd cathodes is also uncertain. The ratio only slightly responds to halving the input power at 1300 hours, reloads when full power is reapplied, then slowly deloads over 25 hours when the power is shut off before more rapidly deloading for the next 75 hours. At the end of the run the ratio of 1.25 corresponds to  $D/Pd = 0.25$  remaining in the cathode. Ed Storms has for years stated that the AHE can appear in Pd cathodes for loading as low as 0.2 [10].

Finally, we show the raw 90 mW excess power data for the entire 1500 hour run in Fig. 10. As already stated, the excess appears within 4 hours of the beginning of electrolysis, reaches a plateau up to 60 hours, climbs to a new plateau after  $\sim 160$  hours and remains at  $\sim 90$  mW for the remainder of the run, including the last 100 hours with the



**Figure 10.** Excess power versus time. Scale change at 1300 hours,



**Figure 11.** Cathode/anode support structure with stretched cathode still immersed in the electrolyte after removal of cell from the calorimeter.

input power shut down. Correcting the raw total energy released energy of 450,000 J by the calorimeter efficiency yields 610,000 J, the average power becomes  $\sim 120$  mW and the average coefficient of performance (COP) was 2.6.

Figure 11 is a photograph of the cathode in its holder in the electrolyte just after removal of the cell from the calorimeter. The deposits on the cathode were unexpected and unusual, not normally seen after experimental runs.

## 5. Discussion

The excess heat detection is substantiated by evidence that calorimeter was working as expected:

- Tcell greatly exceeds Tjack, Tout, as it should for heat generated only at cathode
- Tjack, Tout lag Tcell in time by about 6 and 7 minutes, respectively, also very reasonable
- Tout, Tjack, track each other quite precisely
- Tout, Tcell, Tjack all consistently report excess heat

- Daily room temperature variations substantially accounted for by subtracting time adjusted  $T_{in}$
- $T_{cell}$ ,  $T_{jack}$ ,  $T_{out}$  settled down to pre-run values after cathode removed and cell reassembled
- Mass flow calorimeter provides method to accurately overcome daily temperature variability
- Noise floor  $\pm 10$  mW.

Somewhat unusual behavior of this cell in our experience of over 1000 electrochemical cell runs using Pd foils are:

- Clear 120 mW excess power for 1400 hours or 58 days (COP = 2.6)
- Total energy liberated is 610,000 Joules
- Heat after death for 100 hours until run deliberately stopped
- Unusual deposits on cathode post run are not usually seen
- Excess heat appears within hours of the onset of electrolysis.

Non-standard parameters used to run a Fleischmann-Pons type cell that may have contributed to the heat production are:

- Stretched cathode
- 9 nm nanoparticles in electrolyte
- 0.1M LiOD in  $H_2O$  electrolyte.

For the 58 days of heat reported in detail here, it could be the case that liberated H or D is recombined with O in the cell by an inadvertent or subtle recombination pathway and this caused the excess heat. As a check on this, 7 runs were conducted in thermoelectric and isoperibolic calorimeters, 3 with  $D_2O$  and 4 with  $H_2O$  electrolyte and 50 nm Pd NP. The cathode was Pd for 5 runs and Pt for 2 runs lasting from 6 to 14 days. The electrolyte volume was measured before and after each run. If there was no recombination, then a calculation of the electrolyte loss expected from Faradays law would predict the volume loss of electrolyte. The measured and calculated values for the electrolyte were equal within an average of 0.8%, thus proving that recombination in the cell was not the origin of the measured excess heat.

The run reported here was by far our best result. Many combinations of Pt or Pd cathodes, DD, HH, DH, HD (1<sup>st</sup> is 0.1 M LiOH or LiOD, 2<sup>nd</sup> is  $H_2O$  or  $D_2O$ ) electrolyte. Sub-9 nm nanoparticles were also run, but not with a stretched cathode. Some produced <60 mW heat from a few hours to several days with COP of  $\sim 0.2$  to 0.5, but about half produced no heat. Those that produced heat were shut down to try new material combinations since the effect was small. HH never produce heat. Heat was observed in mass flow, differential, and  $^4He$  tight mass flow calorimeters, in open cells with no recombiner catalyst or closed cells with recombiner catalysts. In one case, an HH cell produced no heat for 3 days, heat appeared after 4 hours when LiOD was added to the electrolyte. These runs were unremarkable due to the small amount of excess heat which was not far above the sensitivity of the calorimeters and would not have been published by themselves. They are included here to make it clear that one should not expect a COP of 2 in every run.

Prior to using 9 nm NP's, SKINR conducted many runs with 50 nm Pd NP. Some of these runs produced small amounts of excess heat but the defining characteristics were a general inconsistency where no 2 runs were alike and often the heat would appear for a few days and then drop to 0. Other material combinations that never produced heat were:

- 3 nm Au NP, magnetically polarized
- 50 nm Fe coated Pd NP
- 50 nm Ni coated Pd NP.

## 6. Conclusions

We report 58 days of 120 milliwatts anomalous excess heat in an electrochemical cell which integrates to 610,000 Joules of liberated energy for a COP of 2.6, including 4 days of anomalous heat after electrolysis power was shut off.

The Pd cathode was placed in tension and 9 nm Pd nanoparticles were deposited on the cathode in situ at the onset of the experimental run. The electrolyte was 0.1M LiOD in H<sub>2</sub>O, D/Pd ratio ~0.7 during run until last 200 hours, electrolysis current 25 mA for most of the run (Pinet = 0.048 W), and the Pd cathode loaded to R/R0 = 1.95 in 4 hours presumably with a mixture of H and D. Non-standard parameters used to run this Fleischmann-Pons type cell that may have contributed to the heat production are:

- Pd foil cathode placed in tension at 1/3 the yield strength
- 9 nm nanoparticles in electrolyte
- 0.1M LiOD in H<sub>2</sub>O electrolyte

Evidently NP size matters since over 100 runs with 50 nm Pd np never produced consistent heat but 9 nm NP did produce some heat in about 50% of runs. The mixed LiOD in H<sub>2</sub>O electrolyte coupled with the Pd NP on a Pd foil creates an unknown situation as to how H and D may be partitioned between the NP and the bulk Pd foil. Any attempt to assign the partition would be speculation so we offer no conclusion this detail. These new features are no guarantee that excess heat will be observed, but they may increase the probability of observation of small amounts of excess heat.

### Acknowledgement

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