Research Article

Evidence for Excess Energy in Fleischmann–Pons-Type Electrochemical Experiments

D.D. Dominguez,* D.A. Kidwell, K.S. Grabowski and D.L. Knies

Chemistry and Materials Science Divisions, Naval Research Laboratory, Washington, DC 20375-5320, USA

A.E. Moser and J.H. He

Nova Research Inc., Alexandria, VA 22308, USA

Abstract

The production of excess energy in palladium cathodes electrochemically loaded with deuterium (the Fleischmann–Pons Experiment) has been debated in the literature since its first publication in 1989. In a subset of 61 trials, we electrochemically loaded palladium–rhodium foil cathodes with deuterium from alkaline solutions of heavy water in specially designed closed calorimeter cells. We observed excess energy bursts in the range 2.4–44.3 kJ in 6% of these experiments. Additionally, a conservative estimate of the total integrated output energy is greater than the total integrated input energy in these experiments. This paper documents the steps taken to examine these results thoroughly for calibration/measurement errors and instrumental artifacts. A 2.4 kJ energy burst is at least four times greater than the energy released by oxidizing deuterium in the cell headspace. The data and subsequent elimination of alternative explanations for excess energy production lead us to conclude that the excess energy is real and of yet unknown origin.

Keywords: Calorimetry, Deuterium , Excess energy, Palladium

1. Introduction

The most significant claim in the early publications by Fleischmann and Pons was of excess energy production in palladium cathodes electrochemically loaded with deuterium [1–5]. Experiments were described in which "bursts" of excess energy were generated in palladium rod electrodes after several weeks or months of electrolysis. Excess energy produced at high current densities (500–1000 mA cm^{-2}) was tens of watts over many days and reached a cumulative total of MJ cm^{-3} of palladium and often caused the electrolyte temperature to reach the boiling point. These extraordinary results were attributed to unknown nuclear processes since any other cause such as chemistry or non-nuclear physical energy was implausible [1–5]. The neutron and tritium generation rates were orders of magnitude

---

*E-mail: dawn.dominguez@.nrl.navy.mil. Fax: 011-202-767-0594; Tel: 011-202-767-2998

lower than produced by D–D fusion reactions at high temperatures for the given amounts of excess energy measured. Thus, the excess energy claim seemed to defy conventional understanding of chemistry or nuclear physics and to require new science to explain its origin.

Since the early publications by Fleischmann and Pons, numerous accounts of excess energy production in palladium cathodes electrochemically loaded with deuterium have been reported [6–13]. However, in spite of mounting evidence, criticism has been that the excess energy observed is either due to overlooked chemistry, measurement errors (such as calibration issues), or instrumental artifacts [14,15]. Due to the significant potential scientific and practical payoffs should this evidence be correct, further research has been conducted.

Excess energy in the early Fleischmann and Pons work can be classified as two types: (1) Type A was a relatively constant gain in the power out vs. the power in (Fig. 1a) that starts fairly quickly and is not dependent on the current density. We have seen Type A behavior occasionally in our systems but these offsets ($<10\%$ in our cases) could be dismissed as due to calorimeter calibration shifts or attributed to unknown chemistry. (2) Type B behavior is a large energy burst (Fig. 1b) that happens after considerable electrolysis and was observed in one of the early Fleischmann and Pons experiments [2,3]. These bursts are rarer than Type A behavior but are almost impossible to dismiss as calibration errors or stored energy. For our work, we adopted the sandwich electrode configuration attributed to Vittorio Violanti (ENEA) [13]. Experiments at Energetics Technologies (ET-Omer, Israel), SRI Int. (Menlo Park, CA), and ENEA (Frascati, Italy) have also reported excess energy with varying levels of reproducibility with this electrode configuration. Energetics Technologies found Type B excess energy in eight of approximately 800 experiments ($\sim1\%$). In six of their experiments, the excess energy measured was 1–3 MJ [16]. In 23 attempts at replicating the Energetics Technologies results, eleven SRI experiments (48%) generated 100–500 kJ excess energy [17,18]. Selecting only those results where the percentage of excess power is at least 50% greater than the input power at any given time, SRI found 4 of 23 (17%) experiments produced an excess but none of these were clearly Type B behavior. Similarly, 4 of 10 (40%) experiments at ENEA produced at least 50% excess power with one of Type B behavior [18,19]. The choice of at least a 50% excess power is arbitrary, but is large enough to exclude measurement artifacts. Other excess energy-producing experiments carried out at ET, SRI and ENEA exhibited smaller power bursts (mW) often seen superimposed on low levels of excess power (mW) lasting for many days (up to 40 days). Although using a different electrochemical cell design, Storms reported that 3 of 80 (4%) Fleischmann–Pons-type experiments showed excess energy [20].

Two types of excess energy are shown in Fig. 1. Figure 1a shows a slow rise in excess energy vs. time. Figure 1b shows a large energy burst that resembles those bursts that are the subject of this paper. The constant rise in excess energy vs. time is seen and we termed this Type A heat. By integration over a long time, this small excess can be an appreciable amount of excess energy, claimed by some to be above that possible from chemical means or storage. On the other hand, the constant rise could be construed as a calibration error or a change in instrumental calibration.

This paper describes our observations of Type B behavior from a subset of 61 similar cathodes out of more than 300 separate experiments. This subset was chosen to focus on a palladium–rhodium cathode material prepared by the same process from the same source of palladium, alloyed in a similar manner, and electrolyzed in 1 M LiOD electrolyte with Pt anodes. High-quality commercial instrumentation custom designed for these electrochemical studies was used. The data presented do not include results from experiments on pure palladium cathodes, control samples, or cathode materials prepared under other conditions or run with anodes other than Pt.

Our results demonstrate that the large excess energy observed in our experiments was a real phenomenon worthy of scientific inquiry and was NOT due to calibration/measurement errors. Although under different conditions than the sets discussed here, our remaining 240+ experiments showed no excess energy or Type A behavior and therefore will be discussed elsewhere.
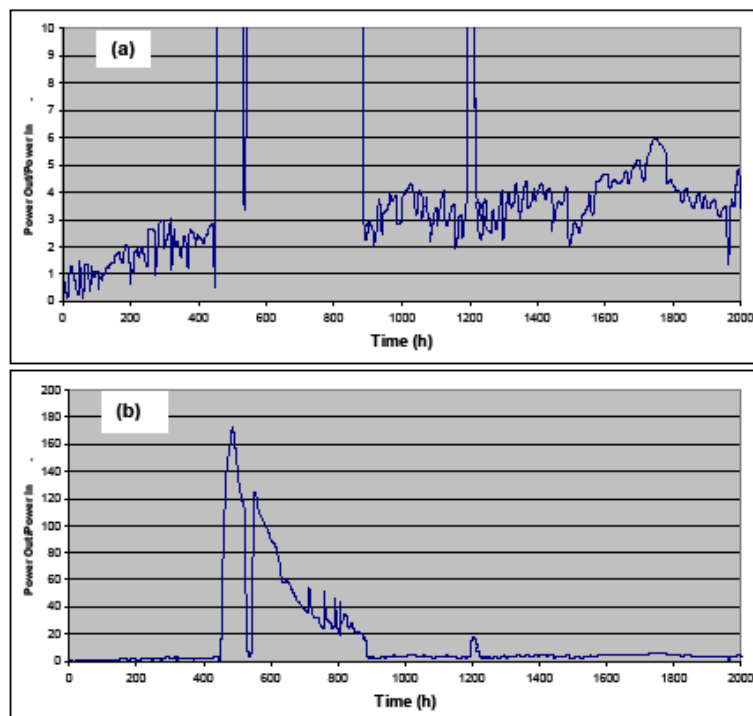
Figure 1. Examples of two types of excess energy taken from the literature. Figure 1a is an expansion of Fig. 1b. The data were acquired in an open cell configuration [2,3] and re-plotted from [2]. A ratio of 1 would indicate that the power out = power in, which would be expected from conventional chemistry.

2. Experimental

2.1. Materials

A 90 at.% palladium –10 at.% rhodium alloy (abbreviated as $Pd_{90}Rh_{10}$) was prepared using hydrogen-torch melting on an alumina plate. High-purity palladium (99.95%, Produits Artistiques Métaux Précieux (PAMP)) and rhodium were used. In the preparation, rhodium pieces were initially wrapped with palladium foil to reduce rhodium oxidation. The torch melting process lasted for a few minutes until a melt ball formed. After air cooling, the palladium–rhodium alloy was repeatedly cold-rolled and annealed at 850°C in a vacuum furnace (10^{-5} –10^{-6} Torr) to form 50 μm thick ribbons. The ribbons were then annealed at 450°C for 30 min and 850°C for 90 min in a vacuum furnace. Prior to each new electrochemical experiment, the 50 μm thick foil cathodes were chemically etched in 50% *aqua regia* for 2 min.

Heavy water electrolyte (1 M LiOD) was freshly prepared in a glove bag with an argon atmosphere prior to each new electrochemical experiment by dissolving lithium foil (99.9%, Johnson Matthey) in deuterium oxide (99.9 % isotopic purity, Cambridge Isotope Laboratory). High surface area catalysts, 0.5% palladium on alumina (Sud-Chemie) and Pt electrode on carbon fiber paper (Johnson Matthey), were used to recombine the evolved deuterium and oxygen gases. The recombination catalysts were contained in the perforated chamber above the electrodes near the cell top (Fig. 2).
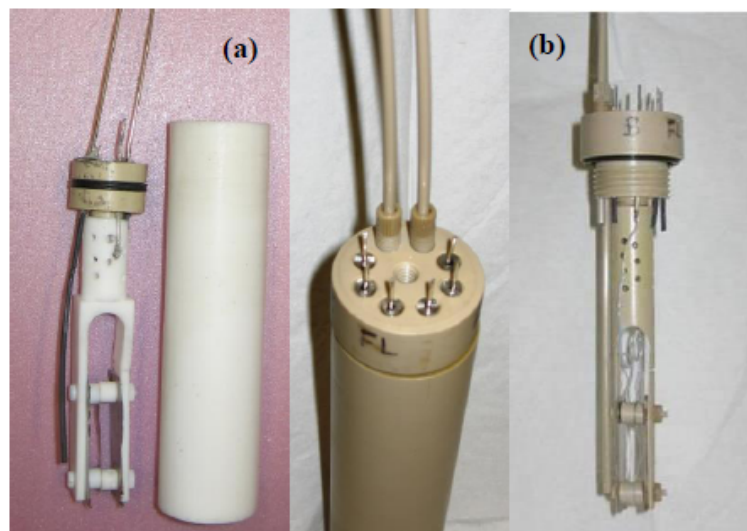
Figure 2. Photographs showing (a) the Teflon cell with PEEK cell top fitted with two syringe needles and black polypropylene tubing for chemical additions to the electrolyte and (b) PEEK cell with PEEK tubing replacing the syringe needles and polypropylene tubing inside the cell.

2.2. Electrolytic cells

Experiments were conducted in two different types of specially designed electrochemical cells. The initial excess energy observation occurred during an electrochemical experiment with a $Pd_{90}Rh_{10}$ cathode in an all-Teflon cell (25 mm internal diameter, 13.5 cm length) with a PEEK (PolyEther Ether Ketone) cell top (Fig. 2a). Two stainless steel syringe needles (18 gauge) penetrated through the PEEK top to the cell interior to allow chemical additions to the electrolyte with minimal disturbance. One needle was used as an air vent and the other as an addition port. Black polyethylene tubing was attached to the addition port needle so electrolyte could be drawn into a syringe from the cell bottom during chemical additions and electrolyte exposure to the stainless steel would be minimal (there is some splashing during the cell operation inside the cell). In later experiments, Teflon cells were replaced with identically-sized all-PEEK cells. In the redesigned cells, PEEK tubing (0.125 in, 3.2 mm diameter) replaced the syringe needles to eliminate the possibility of shorts and reduce contamination by metals, in particular, those that might leach from the nickel-plated brass Luer-lock tips. Photos of a PEEK cell and interior PEEK cell parts are presented in Fig. 2b.

Thermodynamically closed (no correction for evolved chemical enthalpy is needed) electrochemical cells were used with the ENEA/Violante "sandwich" electrode configuration. The electrode dimensions for the cells were: cathode (40 mm × 5 mm × 50 μm), Pt (99.9%) foil anodes (45 mm × 20 mm × 180 μm) and cathode–anode spacing of 5 mm. Teflon-coated 0.5 mm diameter Pt wires provided connections by spot-welding them to Pt disks and to 1 mm diameter Pt wires extending through the PEEK cell top. The Pt disks made contact with the electrodes through pressure applied by finger tightening screws threaded through the electrodes, Pt disks and PEEK spacers.

2.3. Calorimeter and calibration

The four-position calorimeter, custom made for this application by Hart R&D Inc., Mapleton, UT, was a Peltier-type system with a linear response from 0 to 10 W and $\pm$1 mW sensitivity. The Hart calorimeter is described in more detail
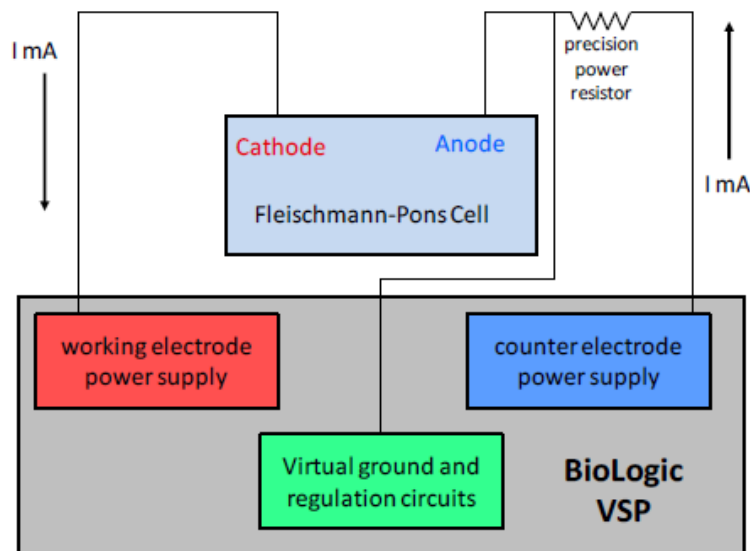
Figure 3. Schematic drawing showing basic experimental design with the Fleischmann–Pons cell, BioLogic VSP power supply, and a precision power resistor.

elsewhere [21,22] and was typically maintained at 25.00, 40.00, or 60.00°C in a water bath with a thermal stability of $\pm$ 0.002°C. The calorimeter was initially and intermittently calibrated using a 2.7 ohm stainless steel-coated Inconel resistor immersed in water inside non-operating cells and with external 100 Ω resistors (calibration heaters) provided for each calorimeter position. Calibration experiments were also run periodically using Pt or Ni foil cathodes in 1 M LiOD, and using Pd foil cathodes in 1 M LiOH with electrolysis occurring. Additionally, each experiment was calibrated during the initial application of power into the cell with the assumption that lower power operation would show no excess energy.

2.4. Experimental procedures and data collection

Calorimetric measurements were carried out isothermally under constant current or constant power conditions. A schematic drawing showing the basic experimental design is shown in Fig. 3. In a given experiment, two or three cells were placed in the calorimeter and run concurrently under identical conditions. Power was supplied to the cells using three of five channels from a computer-controlled power supply (BioLogic VSP Modular Potentiostat/Galvanostat/electrochemical impedance spectroscopy). The input power to an electrochemical cell was determined as the product of the current supplied by the VSP and the cell voltage. Current input to the cell was confirmed by measuring the voltage drop across a wire wound precision power resistor (0.5–5 Ω, 1%, 10 W). Electrolytic loading of a cathode was started at a low current (50 mA) or low power (50 mW) input to the cell. During a typical experiment, the current/power was gradually increased to a maximum of 2 A or 9 W in 8–10 steps of 4–6 h duration each.

Chemical compounds (Raney nickel, cobalt sulfate and nickel sulfate) known to produce oxide or magnetic interfaces on the surface of the cathodes were occasionally added to the electrolyte in attempts to initiate excess energy production. The chemicals (reagent grade) were added to the electrolyte (24 mL) in the cells in 10–50 mg quantities

during cell operation by: (1) placing the additive in a 2 mL all-glass syringe, (2) venting the cell by removing the vent port seal, (3) removing the addition port seal and attaching the syringe to the addition port, (4) pumping electrolyte into and out of the syringe a few times, (5) removing the syringe and resealing the cell. Additions were usually made sequentially in the order listed above once the input power stabilized at its maximum programmed value. Most additions did not produce excess energy. Raney nickel (Raney nickel is a 1:1 alloy by weight of aluminum and nickel and the aluminum undergoes oxidation) reacting with hydroxide is exothermic and 50 mg should produce 488 J from standard heats of formation. Raney nickel reaction with hydroxide is rapid but the heat evolution was often obscured by the endothermic spike due to the addition. In any case, if chemistry were causing the heat bursts, it should occur after every addition.

Four point resistance measurements were made in initial experiments. However, to reduce the measurement complexity and make the system more robust and reliable, these measurements were discontinued in later experiments. It was also our opinion that the information gained from resistance measurements was not worth the risk of a possible extra energy source due to a possible intermittent instrument failure. Limited tritium measurements were made on electrolyte solutions from heat producing and non-heat producing cells before and after electrolysis using the liquid scintillation method on a Beckman LS-6500 Multi-purpose Scintillation Counter. No evidence of tritium production was observed. The cathodes were not checked for tritium.

Electrochemical and calorimetric data were collected at 1 s intervals using EC-Lab software provided by BioLogic. Experiments were carried out in a limited-access building located in a controlled-access laboratory. The building was vibration-isolated and RF-shielded and the laboratory space within was temperature controlled to $20.0 \pm 0.1°$C. Examination of ingress logs showed that no unauthorized individuals entered around the times of the events.

3. Results and Discussion

During the course of this work, it was determined that many sources of palladium used historically in successful Fleischmann–Pons experiments actually came from one producer (Engelhard). ICP-MS analysis for trace impurities on older cathodes indicated a change likely was made in the palladium processing by the supplier [23]. Older cathodes had Al, Rh, and Pt present whereas newer cathodes had Zr, Hf, and Y, but little Rh or Pt. A change in processing using zirconia crucibles likely occurred to account for the new presence of Zr and Y. The levels of these impurities were in the ppm range so the palladium met the supplier stated purity. However, newer lots did not always etch the same and some were mechanically harder than older lots. The $Pd_{90}Rh_{10}$ alloy was developed as it was thought the hypothesized processing changes might have been responsible for newer palladium cathodes showing no excess energy (about 100 attempts for us) whereas the success rate claimed for older palladium materials was much higher for other investigators.

The Pd-rich Pd–Rh alloys are an exception to the general rule that Pd alloying results in decreased absorbed hydrogen [24,25]. Desorption via non-electrochemical recombination reactions (Tafel reactions) is less efficient when using Pd–Rh alloy than when using pure Pd [26] potentially allowing more efficient loading. We decided to incorporate Rh at levels near its miscibility point with Pd rather than at trace levels as in the older material. The Pd–Rh alloys are significantly more resistant to chemical etching. This was thought to be important, as the etching step is one of the least controlled steps in the cathode preparation. It was expected the enhanced chemical resistance would allow for more reproducible surface features. It is known that mechanical properties of elemental metals can be improved by even small alloy additions. Also, alloy addition has a pronounced effect on grain size distribution and indentation hardness. Following our standard rolling and annealing procedures, typical grains were 20–60 μm in size. After the *aqua regia* etch, the foils typically exhibited rough grains with steep sides and deep grain boundaries.

Historically, many electrochemical experiments were run for months before excess power was observed. Long run times were hypothesized to concentrate impurities on the cathode surface [7]. Initially, our experiments were carried

out in closed Teflon cells with no capability for chemical additions, and no excess power was produced. To mimic the concentration process and improve the prospects for observing excess power, cells were modified to allow chemical additions. However, prior to the change in cathode material from pure palladium to the $Pd_{90}Rh_{10}$ alloy, cells run with chemical additions still showed little or no excess power.

The first calorimetric experiment with a $Pd_{90}Rh_{10}$ foil cathode (cathode #1) and chemical additions showed excess energy. The experiment was carried out in constant current mode at 25°C in a Teflon cell (Fig. 2a) and the data obtained are displayed in Fig. 4. The figure shows plots of electrochemical input and output powers to/from the cell, current,
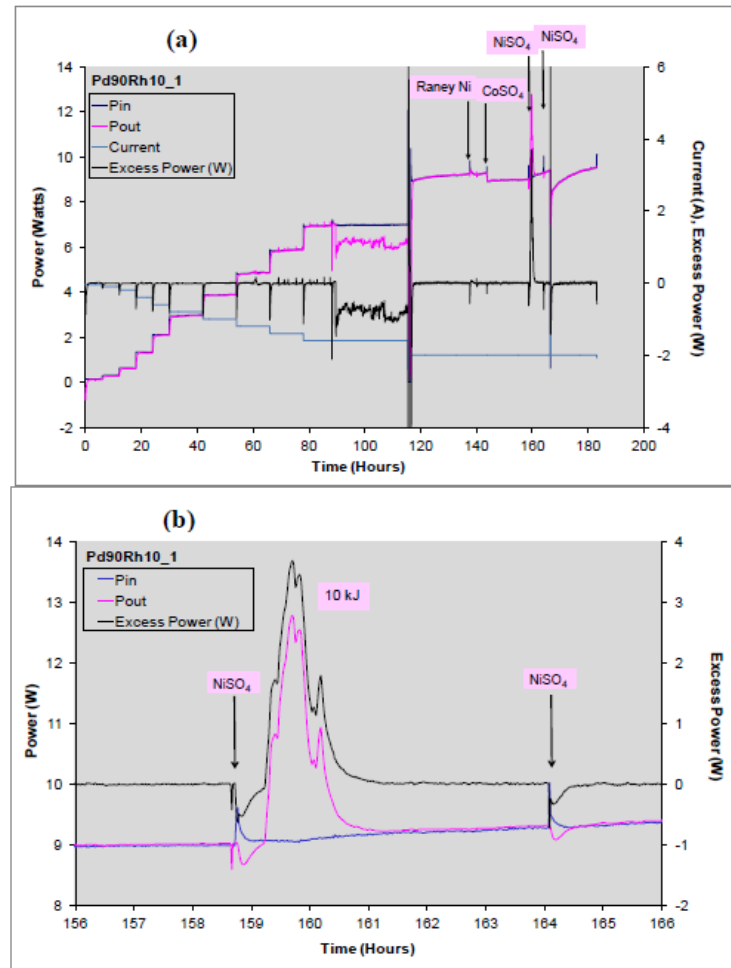
Figure 4. (a) Plots of input power (P_{in}), output power (P_{out}) on left vertical axis, and current, excess power on right vertical axis as a function of time for $Pd_{90}Rh_{10}$ cathode #1 run at 25°C in a Teflon cell with chemical additions to the 1 M LiOD electrolyte as indicated. Cumulative excess energy is not plotted because of a data gap (due to a loose connection) from 89 to 116 h. (b) An enlargement of the power plots shown in (a) from 156 to 166 h.

and excess power ($P_{out} - P_{in}$) vs. time. Input and output powers were calculated continuously. The steady state data during the initial eight step increase in current were fit to provide an in situ calibration, assuming no excess energy was produced during that time. The variation in fitting coefficients between runs was less than 1% over two years, which confirmed the stable performance of the Hart calorimeter. Additional calibrations performed using resistors placed inside the cells agreed with those obtained from the power steps. In other experiments, using pressure vessels and H_2 combustion, the energy produced was within 1% of that calculated from literature value.

After loading the palladium-rhodium cathode (cathode #1), an instability in the P_{out} measurement occurred at about 89 h due to a loose connection on the Hart calorimeter that persisted until the system was temporarily stopped, repaired, and restarted at about 116 h with a constant current of 2 A (Fig. 4). Once the system regained stability, chemical additions (Raney nickel, cobalt sulfate and nickel sulfate) were made to the cell. As shown in Fig. 4, an endothermic transient is observed as the consequence of introducing cooler material into the cell during each addition. About 36 min following the third chemical addition, evidence of excess power appeared in the data. Excess power peaked at a maximum of almost 4 W with 9 W input (42% excess) and persisted for over 90 min (Fig. 4b). A fourth chemical addition (nickel sulfate) was added to the electrolyte solution following appearance of the spike and recovery of the baseline. The fourth addition produced no additional excess energy.

Calculated energy generated during the 90-minute interval was about 10 kJ. Chemical energy produced by metal salt additions cannot account for the excess energy observed. In fact, the most energetic chemical reaction conceivable in the cell would be the combustion of deuterium. That reaction could produce approximately 600 J (see below). The 10 kJ observed in the experiment is at least 15 times greater than the energy released by oxidizing deuterium. It is not known whether chemical impurities were fully or even partially responsible for triggering the energy burst observed. Moreover, since this was the first large excess energy burst seen in our laboratory and metal syringe needles were used, it was hypothesized that a short of the needle to ground could have caused the burst.

Although, calculations could show that a short through the electrolyte would be insufficient to cause the apparent energy, this prospect was thoroughly examined. While there was no evidence that a short had occurred during the excess energy-producing experiment with cathode #1, the cells were redesigned to eliminate the possibility of a short in future experiments. The redesigned cells were all plastic (PEEK) except for the Pt wire feed through penetrating the PEEK cell tops, which were protected with a tight-fitting plug (not shown). Notably, PEEK tubing replaced the metal syringe needles and the polyethylene tubing in the new cells as shown in Fig. 2b.

$Pd_{90}Rh_{10}$ cathode #27 was run in an all-PEEK cell without chemical additions. Excess energy was observed with this cathode where an electrical short was thought to be physically impossible. However, a special condition on the external wiring MAY have permitted a short to form intermittently.[a] Figure 5 shows the time evolution of the calculated excess power and cumulative excess energy possibly obtained on $Pd_{90}Rh_{10}$ cathode #27. At the start of the experiment, the electrochemical cell was operated with a constant current of 20 mA. The current was stepped up to 50 mA at 8 h while maintaining a power balance. But, at 9.6 h the cell began to produce a large amount of excess power and it continued to do so for the next 5 h. During this time, while the input power fluctuated, the power output approached a maximum of ∼10 W. No chemical additions were intentionally made during this experiment as the step increase in input power was not completed. However, the cell may have been contaminated with chemical impurities that were carried over from additions made in previous experiments as the input tubes were not acid cleaned to avoid degradation

---

[a]Briefly, the VSP can supply the required amount of power without generating an error if there is a direct short of the anode to earth ground, the VSP power supply is in constant power mode, and the electrolyte is 1M. If the VSP were in constant current mode, an error message would be reported during such a short. Errors were not reported during constant current mode operation of cathodes 1 and 60, but were intermittently seen for cathode 27. Regardless of the mode of operation, the resistance of the short to earth ground must be less than 2-3 ohms for the VSP to supply sufficient power to account for the observed heat. We have no evidence that shorts occurred during the observed excess energy events and during the many hours of null results, no errors were ever reported.), then the VSP could not supply sufficient power to account for the observed heat. We have no evidence that shorts occurred during the observed excess energy events and in the many hours of null results, no errors were ever reported.
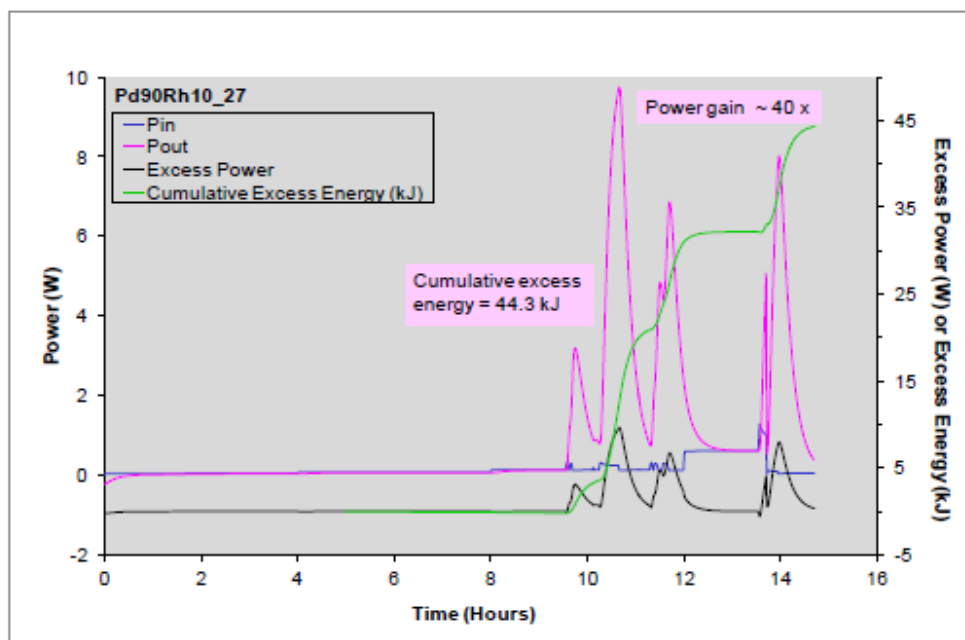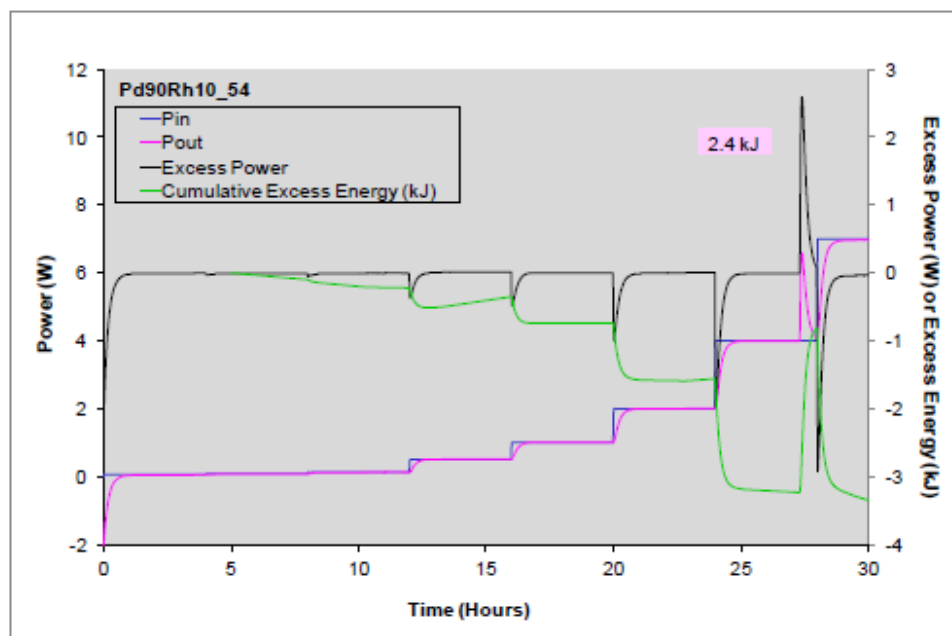
Figure 5. Variation of input power (P_{in}), output power (P_{out}) on left vertical axis and excess power, excess energy on right vertical axis with time for $Pd_{90}Rh_{10}$ cathode #27 in 1 M LiOD run at 25°C in an all-PEEK cell. The total electrical input energy from 0 to 14.7 h was 8.3 kJ. The cumulative excess energy exceeded the total input energy by 45 kJ.

of the PEEK. The cumulative excess energy generated from the series of bursts was 44 kJ, assuming a short did not occur. This represents a maximum power gain of almost 40 times and an energy gain over 6.

Excess power and cumulative excess energy produced with $Pd_{90}Rh_{10}$ cathode #54 run in an all-PEEK cell, in constant power mode without chemical additions are shown in Fig. 6. In this instance, the excess power burst occurred with an input power of 4 W and excess power production reached a 2.5 W maximum, or approximately 63% of the input power. The integrated value of excess energy generated from the burst was about 2.4 kJ. The cell returned to power balance after a step increase in power to 7 W. Again, no chemical addition was intentionally made to the electrolyte since the step increase in power was incomplete.

$Pd_{90}Rh_{10}$ cathode #60 was run in an all-PEEK cell with chemical additions. Excess power and cumulative excess energy obtained in the mostly constant power experiment with cathode #60 are presented in Fig. 7. The figure shows the cell in power balance with $P_{out} = P_{in}$ and excess power equal to near zero at the start of the experiment. The cell remained in power balance during step increases in power to 9 W in constant power mode and for another 2 h near 9 W while in constant current mode. Then, the cell voltage suddenly increased, raising the input power to a preset limit of 12 W, and a large excess power burst was observed, followed by a second similar burst approximately 10 h later. Excess power from these bursts reached ~83% of the input power, or about 10 W maximum. Integrated values of excess energy produced in the two bursts were 18.2 and 14.7 kJ, respectively, which was 6–8 times greater than in cathode #54. The trigger for these excess energy bursts is unknown. The first burst occurred before any chemical addition was intentionally made to the electrolyte. A Raney nickel addition was made prior to the second excess energy burst. However, it is not known whether the addition was in any way responsible for initiating the burst.

Figure 6. Plots of input power (P_{in}), output power (P_{out}) on left vertical axis and excess power, excess energy on right vertical axis as a function of time for a $Pd_{90}Rh_{10}$ cathode #54 run at $60°C$ in an all-PEEK cell with 1 M LiOD.

For a closed electrochemical cell, power output should equal power input. Thus, the expected excess power ($P_{out} - P_{in}$) should equal zero. Deviations from this expectation may be attributed either to simple chemistry or, if shown not to be a measurement artifact, to new science. Energy can be stored in two forms during electrolysis. In the first, energy is used to heat the cell contents. The negative spikes observed in the excess power plot during the power steps are due to the instantaneous change in the electrochemical input power whereas the Hart calorimeter response is limited by its time constant ($\sim$15 min) needed to heat the components. From several non-energy-producing cells, it takes approximately 8 kJ (7.8 ± 0.6 kJ, $n = 7$) to heat a cell to its steady-state operating temperature with a power input of 9W (see Fig. 7a). This heat can be recovered when power is removed and the cell cools down. The second form is stored chemical energy. The most energetic chemical reaction conceivable in the cell would be combustion of deuterium by oxygen. If only oxygen filled the headspace ($\sim$25 mL, 1 atm pressure) above the electrolyte (to produce maximum oxidizing energy) and deuterium was somehow sequestered in the palladium cathode and suddenly released to react with the oxygen, approximately 600 J could be produced. This is four times less than the 2.4 kJ observed on the low end of the energy bursts (cathode #54). Furthermore, stored chemistry (the production of H_2 and O_2 is accounted for in our energy balance) is not evident because such stored chemical energy must come from somewhere in addition to the energy used to heat the cell. If there were appreciable stored energy, the cumulative excess energy would be more negative than 8 kJ by that amount of stored chemical energy. This has not been observed in our experiments. The heat pulses cannot arise from the heat content of the cell as there is no known mechanism in an isothermal system by which this heat can be converted to a heat pulse and thereby concentrate the heat. This would violate the first law of thermodynamics. To reiterate, the observed energy bursts must come from some other source

than cumulative stored energy. Although we believe it to be unrealistic, and if one assumed that all the excess input energy went into stored chemical energy powering some unknown chemical reaction (which in itself would be very energy dense) instead of heat, one still could not account for the two cells with $Pd_{90}Rh_{10}$ cathode #27 (Fig. 5) and cathode #60 (Fig. 7), where the cumulative energy output ($\sim$25 kJ) greatly exceeds the energy input even considering the 8 kJ necessary to heat the cells.

Following each of these excess energy-producing experiments, an extensive investigation was undertaken to examine the possible cause of these events. These efforts focused on electrical shorting as the only instrumental artifact that could conceivably explain the data. In these investigations, the requirements and consequences of electrical shorts deliberately produced in the power supply, inside the cell or external to the cell and calorimeter were exhaustively explored. Some of the excess power data could be reproduced by shorting the power supply in a certain manner as explained in footnote a. However, the likelihood that a short ($\sim$1 Ω) could form and then disappear and reform in the manner necessary to mimic the data (cathode #60) was extremely remote, given the care taken to prevent such an occurrence. Detailed results of our investigations on the effect of electrical shorts in the experiments described will be published separately.

Results of the four excess energy-producing experiments presented have some similarities and differences worth noting. Experiments were all carried out on $Pd_{90}Rh_{10}$ foil cathodes in 1 M LiOD electrolyte and all displayed large magnitude ($\geq$2.4 kJ) excess energy bursts that could not be accounted for by chemistry. Since the cathode volumes were about 0.01 cm^{-3}, the excess energy generated was approximately 1 MJ cm^{-3} which is similar to that observed by Fleischmann and Pons [1–3]. Two of the four cathodes were run in experiments with constant current while the other two cathodes were run with constant power. The four experiments were run isothermally at three different temperatures, 25, 40, and 60°C, and excess energy bursts were obtained in three different Hart calorimeter positions and run using three different VSP channels. During each excess energy-producing experiment, one or two additional cells, run concurrently under identical conditions in the calorimeter, did not produce excess energy. These disparate results indicate a power supply or calorimeter malfunction is an unlikely source of experimental error. Moreover, there doesn't seem to be any individual temperature, cell, calorimeter position or VSP channel that is particularly favorable for producing the excess energy results observed. In addition, null results acquired on more than 100 other $Pd_{90}Rh_{10}$ cathodes and on a large set of palladium cathodes run before and after the excess energy results serve as control experiments and provide sufficient evidence that the instruments were performing correctly throughout and measurement or calibration errors were non-existent.

We observed large amounts (tens of kJs) of excess energy in four out of 61 similar experiments ($\sim$6%). These bursts are much greater than chemical energy and are similar to those observed in other laboratories. We cannot rule out an instrumental artifact for one cathode. However, the other three cathodes have signatures that differ from a short in substantial ways. For example, cathode #60 requires more power than a short could provide and has none of the disturbances in other channels that would indicate a short. The result from cathode #27 *could* be due to an instrumental artifact caused by a short under very selective conditions as it had disturbances in the other channels and a lower power output which could be provided by the power supply. As such, the demonstration of cathode #27 as an unconventional energy source should be discounted at this time. This particular kind of instrumental artifact will be discussed in detail in a subsequent paper, but an instrumental artifact is not consistent with the results from the other three positive cathodes. Although the number of events is small, these results taken in combination with others acquired under varied conditions reduces the chance of an unrealized systematic error. Thus, we propose that this data set showing large events whose energy production is above chemistry in a thoroughly vetted system demonstrates new science that should be explored.
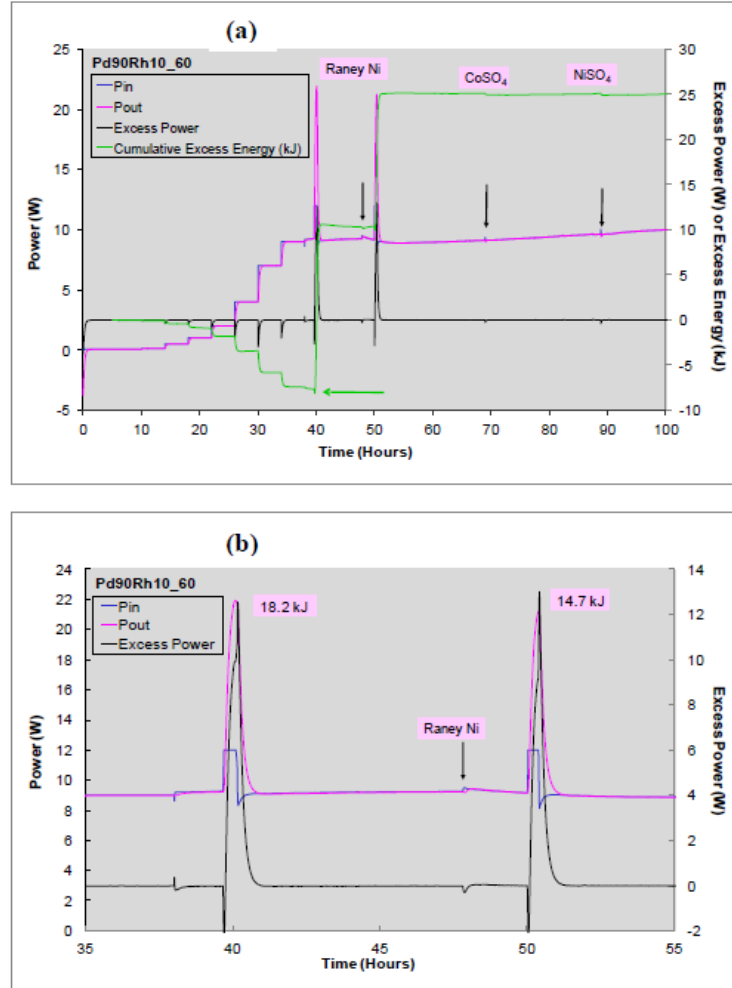
Figure 7. (a) Plots of input power (P_{in}), output power (P_{out}) on left vertical axis and excess power, excess energy on right vertical axis as a function of time for $Pd_{90}Rh_{10}$ cathode #60 run at $40°C$ in an all-PEEK cell with chemical additions to the 1 M LiOD electrolyte as indicated. (b) An enlargement of the power plots presented in (a) from 35 to 55 h showing the two large excess power bursts.

4. Conclusions

From over 300 Fleischmann–Pons-type calorimetric experiments, a subset of 61 experiments on a palladium–rhodium alloy cathode material, $Pd_{90}Rh_{10}$, electrochemically loaded with deuterium in 1 M LiOD electrolyte solution are presented. Three to four of these experiments produced Type B excess energy bursts too large ($\geq$2.4 kJ) to be of chemical origin. The large collection of null results confirmed that the instruments were performing correctly and measurement errors were non-existent. We achieved some success initiating a few excess energy events with incubation times of days (vs. weeks or months) using cathodes made with the palladium–rhodium alloy and with chemicals

deliberately added to the cells. Shorter incubation periods can minimize drifts that might occur over long experiment times and, thus, simplify the data analysis and interpretation. The levels of excess energy produced and reproducibility achieved in our experiments is comparable to what has been reported in some of the literature. Attempts to improve the reproducibility and understand the initiation and source of these energy bursts are continuing in our laboratory.

Acknowledgements

References

[1]   M. Fleischmann, S. Pons and M. Hawkins, Electrochemically-induced nuclear fusion of deuterium, *J. Electroanal. Chem.* **261** (1989) 301–308.

[2]   S. Pons, Calorimetry of the palladium–deuterium system, *Proc. of the First Annual Conference on Cold Fusion* (Salt Lake City, UT, 1990), pp. 1–19.

[3]   M. Fleischmann, S. Pons, M.W. Anderson, L.J. Li and M. Hawkins, Calorimetry of the palladium–deuterium–heavy water system, *J. Electroanal. Chem.* **287** (1990) 293–348.

[4]   S. Pons and M. Fleischmann, The calorimetry of electrode reactions and measurements of excess enthalpy generation in the electrolysis of D_2O using Pd-based Cathodes, in: T. Bressani, E. Del Giudice, G. Preparata (Eds.), *The Science of Cold Fusion*, Conference Proc. , Vol. 33 (Italian Physical Society, Bologna, Italy, 1991), pp. 349–362.

[5]   M. Fleischmann and S. Pons, Calorimetry of the Pd–D_2O system: from simplicity via complications to simplicity, *Phys. Lett. A* **176** (1993) 118–129.

[6]   M.C.H. McKubre, R. Rocha-Filho, S.I. Smedley, F.L. Tanzella, S. Crouch-Baker, T.O. Passell and J. Santucci, Isothermal flow calorimetric investigations of the D/Pd system, in: T. Bressani, E. Del Giudice, G. Preparata (Eds.), *The Science of Cold Fusion*, Conf. Proc. , Vol. 33 (Italian Physical Society, Bologna, Italy, 1991), pp. 419–443.

[7]   M.C.H. McKubre, S. Crouch-Baker, A.M. Riley, S.I. Smedley and F.L. Tanzella, Excess power observations in electrochemical studies of the D/Pd system; the influence of loading, in: *Proc. of the Third Int. Conf. Cold Fusion, "Frontiers of Cold Fusion"* (Universal Academy Press, Tokyo, Japan 1992), pp. 139–150.

[8]   M.C.H. McKubre, S. Crouch-Baker, R.C. Rocha-Filho, S.I. Smedley, F.L. Tanzella, T.O. Passell and J. Santucci, Isothermal flow calorimetric investigations of the D/Pd and H/Pd systems, *J. Electroanal. Chem.* **368** (1994) 55–66.

[9]   M.H. Miles, R.A. Hollins, B.F. Bush, J.J. Lagowski and R.E. Miles, Correlation of excess power and helium production during D_2O and H_2O electrolysis using palladium cathodes, *J. Electroanal. Chem.* **346** (1993) 99–114.

[10] E. Storms, Measurements of excess heat from a Pons–Fleischmann-Type electrolytic cell using palladium sheet, *Fusion Technol.* **23** (1993) 230–256.

[11] I. Dardik, T. Zilov, H. Branover, A. El-Boher, E. Greenspan, B. Khachatorov, V. Krakov, S. Lesin and M. Tsirlin, Excess heat in electrolysis experiments at Energetics Technologies, Presented at the *11th Int. Conf. Condensed Matter Nuclear Science,* Marseilles, France, November 1–6, 2004.

[12] I. Dardik, T. Zilov, H. Branover, A. El-Boher, E. Greenspan, B. Khachatorov, V. Krakov, S. Lesin and M. Tsirlin, Progress in electrolysis experiments at Energetics Technologies, Presented at the *12th Int. Conf. Condensed Matter Nuclear Science*, Yokohama, Japan, November 27–December 2, 2005.

[13] V. Violante, F. Sarto, E. Castagna, M. McKubre, F. Tanzella, G. Hubler, D. Knies, K. Grabowski, T. Zilov, I. Dardik and C. Sibilia, Joint scientific advances in condensed matter nuclear science, in: 8th *Int. Workshop on Anomalies in Hydrogen /Deuterium Loaded Metals*, Sicily (2007) 1–9.

[14] DoE Review Panel, Report of the Review of Low Energy Nuclear Reactions (2004).

[15] K.L. Shanahan, Comments on "A new look at low-energy nuclear reaction research", *J. Environ. Monit.* **12** (2010) 1756–1764.

[16] I. Dardik, T. Zilov, H. Branover, A. El-Boher, E. Greenspan, B. Khachatorov, V. Krakov, S. Lesin, A. Shapiro and M. Tsirlin, Ultrasonically-excited electrolysis experiments at Energetics Technologies, in: *ICCF-14 Int. Conf. Condensed Matter Nuclear Science*, Washington, DC, USA (2008), pp. 106–122.

[17] M.C.H. McKubre, The importance of replication, in: *ICCF-14 Int. Conf. Condensed Matter Nuclear Science*, Washington, DC, USA (2008), pp. 673–688.

[18] M.C.H. McKubre, F.L. Tanzella, I. Dardik, A. El-Boher, T. Zilov, E. Greenspan, C. Sibilia, V. Violante, Replication of Condensed Matter Heat Production, in: *Low-Energy Nuclear Reactions Sourcebook,* J. Marwan (Ed.), ACS Symposium Series 998, Oxford University Press (2008), 219.

[19] V. Violante, F. Sarto, E. Castagna, M. Sansovini, S. Lecci, D.L. Knies, K.S. Grabowski and G.K. Hubler, Material Science on Pd–D System to Study the Occurrence of Excess Power, in: *ICCF-14 Int. Conf. Condensed Matter Nuclear Science*, Washington, DC, USA (2008), pp. 429–436.

[20] E. Storms, A study of those properties of palladium that influence excess energy production by the "Pons–Fleischmann" effect, *Infinite Energy* **2** (1996) 50–75.

[21] S.C. Barrowes and H.E. Bergeson, Linear, high precision, redundant calorimeter, *Fusion Technol.* **26** (1994) 365–368.

[22] D.D. Dominguez, D.A. Kidwell, D.L. Knies, J.H. He, K.S. Grabowski, G.K. Hubler and V. Violante, Are oxide interfaces necessary in Fleischmann–Pons-Type experiments? *J. Condensed Matter Nucl. Sci.* **8** (2012) 219–230.

[23] D.A. Kidwell, Considerations for ultra-trace analysis of metals in a palladium matrix, in: *ICCF-14 Int. Conf. Condensed Matter Nuclear Science*, Washington, DC, USA (2008), pp. 180–194.

[24] A. Zurowski, M. Lukaszewski and A. Czerwinski, Electrosorption of hydrogen into palladium–rhodium alloys, *Electochim. Acta* **51** (2006) 3112–3117.

[25] A.K.M. Fazel Kibria, Deuterium solubility and electrical resistance of palladium–rhodium alloys, *Int. J. Hydrogen Energy* **25** (2000) 997–1003.

[26]] A. Zurowski, M. Lukaszewski, A. Czerwinski, Electrosorption of hydrogen into palladium–rhodium alloys, *Electochim. Acta* **53** (2008) 7812–7816.