

NEDO FINAL REPORT

ELECTROCHEMICAL CALORIMETRIC STUDIES OF PALLADIUM AND PALLADIUM ALLOYS IN HEAVY WATER

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EXECUTIVE SUMMARY

The main feature of the Fleischmann–Pons effect is excess heat production. My experiments designed to measure excess heat focused on the use of two types of isoperibolic calorimeters. Cells A and B transfer heat mainly by conduction while the three Fleischmann–Pons type cells transfer heat mainly by radiation. The first set of experiments in cells A and B used palladium cathodes. Small levels of excess power were observed in Cell A but none in Cell B. This result is in agreement with previous experiments at China Lake, California using the same two palladium cathodes. There were also periods of unusual fluctuations in the temperature readings in Cell A for the thermistor closest to the cathode that persisted for several weeks. These sudden temperature increases occurred during the same time period as when the excess heat was observed. The switching of these experiments to pulse electrolysis also produced an excess heat effect in Cell A but not in Cell B.

The second set of experiments in cells A and B used small platinum particles in Cell A and palladium particles in Cell B as cathodes. These experiments were designed to give a fluidized bed effect, but the small particles were actually too heavy to be suspended in the solution. Nevertheless, the deuterium gas evolution during electrolysis caused the particles to jostle about and expose new surface areas to give dynamic conditions. Excess power was observed for the palladium particles in Cell B, but, as expected, the platinum particles in Cell A gave no measurable excess power. Each cell was later switched to pulse electrolysis, which caused the excess power to become larger for the palladium particles in Cell B while no excess power was measurable for the platinum particles in Cell A.

The first set of experiments using the Fleischmann–Pons type cells used a Pd–Ce–B alloy in Cell A-1 and a Pd-0.5 B (weight %) alloy in Cell A-2. Both of these alloys were obtained from the Naval Research Laboratory, Washington, D.C. USA. The third cell (A-3) used a Pd–Ce alloy obtained from Martin Fleischmann. Surprisingly large fluctuations in excess power measurements (± 20 mW) were observed for individual data points. This was traced to the effect of the experimental error in the measurement of temperature ($\pm 0.01^\circ\text{C}$) on the P_{calor} term and to fluctuations in the cell voltage. The large time constants for this cell design (90 minutes), however, show that averaging techniques are essential to obtain more accurate results. Furthermore, the cell constants show fluctuations that indicate daily calibrations are necessary to obtain the accuracy claimed by Fleischmann and Pons. No excess heat was detectable for the Pd–Ce–B alloy in Cell A-1. The ratio of power out/power in (X) for this experiment was 1.002 ± 0.008 . The Pd-0.5 B alloy showed two different episodes of excess power production that reached levels of 200 mW (0.6 W/cm^3). The Pd–Ce alloy began producing excess power after fifteen day of electrolysis and gave a fairly steady level of about 100 mW with a peak of about 200 mW (1.3 W/cm^3).

The second sets of experiments using the Fleischmann–Pons cells involved the deposition of palladium from solution onto a copper cathode (Szpak co-deposition method). Rather large excess power was observed in Cells A-2 and A-3 (approximately 400 mW) while a small excess power level (100 mW) was observed in Cell A-1. Since this method produced small palladium particles that broke loose and floated in the solution, recombination cannot be ruled out as a

possible source of the excess power. Nevertheless, the D₂O consumption during this study was consistent with Faraday's Law within experimental error for all three cells.

The third set of experiments in the Fleischmann–Pons type cells involved a thin palladium wire (50 μm diameter). Excess power averaging about 150 mW was observed using only electrolysis power in Cell A-2. The application of 0.4 amps through the palladium wire to give electromigration of D⁺ ions yielded no excess power effects in Cell A-1. However, these experiments came at the end of the NHE program and lasted only one week.

In summary, small levels of excess power were measured for a palladium cathode in Cell A and no excess power for a similar palladium electrode in Cell B. The second set of experiments gave no excess power for platinum particles in Cell A while excess power was measured for palladium particles in Cell B. The Fleischmann–Pons type cells gave excess power for Pd–0.5 B and Pd–Ce alloys, and no excess power for a Pd–Ce–B alloy. Electrodeposition experiments and electromigration experiments in the Fleischmann-Pons type cells also produced evidence for excess power production.

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INTRODUCTION

Fusion is the energy source of the universe and powers the sun and stars. In the coming century, petroleum reserves will dwindle and new energy sources must be found. Fusion – hot or cold – is a possible solution to this energy need. This is why the announcement of cold fusion by Fleischmann and Pons in 1989 created such a sensation. Although positive results for cold fusion effects have proved difficult to reproduce, they cannot be simply explained away as experimental errors. Whether or not cold fusion will prove to be a viable energy source remains an open question.

In view of the tremendous possible pay-off for cold fusion research, it is amazing that there are no government programs to fund this research in major countries such as the U.S., Great Britain, and Germany. This is due to the difficulty in reproducing cold fusion results as well as to the effective campaign waged around the world by prominent cold fusion critics. Japan is to be commended for its government program (NEDO, NHE) in this area despite the controversial nature of this research. My previous research on anomalous effects in deuterated materials (cold fusion) at China Lake, California and sponsored by the Office of Naval Research, produced excess power levels of 100–300 mW with a high of 520 mW. The excess power density was typically 1–5 W/cm³ of palladium. Only 28 out of 94 different experiments produced excess power (30% success), but the success ratio was high for Pd–B alloys (88%) and Johnson-Matthey palladium samples (61%) as shown in Table 10 of Ref. 1 (p. 42). The success ratio however, was very low for many other palladium materials.

My five month effort at the NHE Laboratory in Sapporo, Japan focused on excess heat measurements using both steady state and dynamic conditions. Two of the palladium materials tested had previously produced the excess heat effect at the NAWC laboratory in China Lake, California. Both of these samples showed similar excess power effects at the NHE laboratory. The excess power, however, was rather small but still detectable using accurate calorimetric methods. New methods tested at NHE laboratory include pulse electrolysis, fluidized bed experiments, and electromigration studies using thin palladium wires.

PALLADIUM CATHODES IN CELL A AND CELL B

A. INTRODUCTION

The calorimetric design used in Cells A and B has been described in a previous publication (Fig. 1 in Ref. 2). These cells transfer heat mainly by conduction. The small electrochemical cell consists of a long, narrow test tube (1.8 cm diameter and 15.0 cm length) that is filled with 18.0 cc of 0.1 M LiOD. The electrochemical cell is positioned in a calorimetric jacket within a secondary compartment that contains two thermistors positioned on opposite sides of the cell wall and at different heights from the bottom of the cell (1.9 cm and 4.5 cm). Two additional thermistors measured the bath temperature and the room temperature. In previous experiments, the secondary compartment was filled with distilled water. In order to increase the sensitivity and to shorten the time constant for these cells, the first experiments at NHE used aluminum foil wrapped around the outside of each cell including the two thermistors, in place of the distilled water. This reduced the cell constant by about a factor of three and produced rapid responses by the thermistors to any power changes within the cell. Although there was continuous recording of all six temperatures (four cell temperatures, bath temperature, room temperature) as well as both cell voltages, there was no data acquisition system connected to these two cells. Therefore, measurements were recorded by notebook during working hours at the NHE laboratory.

In my last cold fusion experiments conducted at China Lake, California in 1995, a Johnson-Matthey palladium cathodes (1 mm x 2.0 cm) produced approximately 200 mW of excess power in one cell, but no excess power effects in a second cell (Fig. 31 and 32 of Ref. 1). These same two palladium cathodes were used in cells A and B in my first experiments at the NHE laboratory.

B. CALORIMETRIC EQUATIONS

The calorimetric equations that describe the heat conduction type Cells A and B are:

$$[E(t)-\gamma E_H]I+P_x = a+K\Delta T+P_{\text{gas}}+P_{\text{calor}} \quad (1)$$

where

$$P_{\text{gas}} = (\gamma I/F) \{ [0.5 C_{P,D_2} + 0.25 C_{P,O_2} + 0.75 (P / (P^* - P)) C_{P,D_2O(v)}] \Delta T + 0.75 (P / (P^* - P)) L \} \quad (2)$$

$$P_{\text{calor}} = C_{P,D_2O(l)} [M^\circ - (1+\beta) (\gamma I t / 2F)] (d\Delta T / dt) - (1+\beta) (\gamma I / 2F) C_{P,D_2O(l)} \Delta T \quad (3)$$

In these equations, P_x is the excess power (if any), P_{gas} is the power carried away from the cell by the D_2 , O_2 , and D_2O vapors that exit the cell while $[E(t)-\gamma E_H]I$ represents the electrochemical input power to the cell (Ref. 3). Furthermore, $E(t)$ is the cell voltage, γ is the faradaic efficiency, E_H is the thermoneutral potential of D_2O , ΔT is the difference between the cell temperature and the bath temperature, C_p is the heat capacity at constant pressure, P is the vapor pressure of the D_2O -LiOD electrolyte, P^* is the atmospheric pressure, L is the heat of evaporation of D_2O , M° is

the moles of D₂O initially added to the cell, and β represents the loss of D₂O by evaporation (see Ref. 1 and Ref. 3 for details). These cells were typically run under steady state conditions where $(P_{\text{gas}}+P_{\text{calor}}) \ll K \cdot \Delta T$ and where the power loss out of the top of the cell (term a) is insignificant, therefore, our calorimetric equation becomes simply:

$$[E(t)-\gamma E_H]I+P_x = K \cdot \Delta T \quad (4)$$

These approximations are valid within the accuracy of this cell (± 20 mW) for the condition of nearly steady cell temperatures that are in the range of 40 – 60°C. Under these conditions when there is no excess power (P_x), the cell constant is given simply by $K=P_{EL}/\Delta T$ where P_{EL} is the electrochemical power added to the cell. If there is excess power present in the cell, the true cell constant could be expressed theoretically as $K=(P_{EL}+P_x)/(\Delta T_{EL}+\Delta T_x)$. However, it is not possible experimentally to distinguish the temperature increase due to the excess power (ΔT_x) from that due to the electrochemical power (ΔT_{EL}). If it is assumed that there is no excess power in the cell ($P_x=0$), then the apparent cell constant is $K'=P_{EL}/(\Delta T_{EL}+\Delta T_x)$. Therefore, $K' \leq K$ and K' will decrease as P_x increases. This is often an excellent indicator of excess power developing in cells of the type A and B.

C. EXPERIMENTAL RESULTS

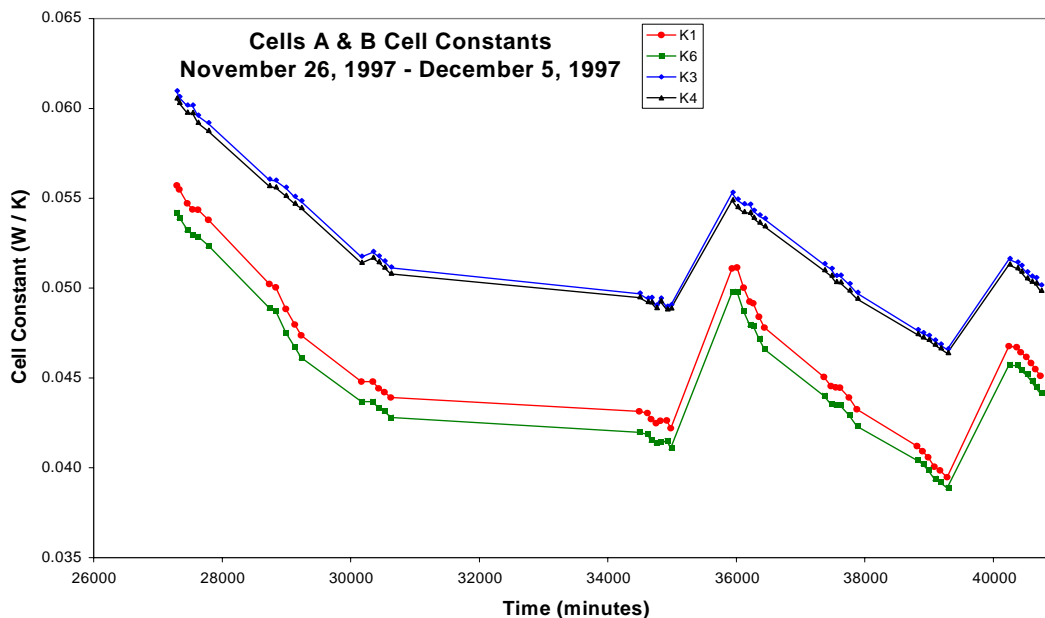


Figure 1. The change of the apparent cell constants with time for Cell A (K_1 , K_6) and Cell B (K_3 , K_4).

Figure 1 shows the apparent cell constants for each thermistor in Cells A and B. Thermistors 1 (lower position) and 6 are located in Cell A, and thermistors 3 (lower position) and 4 are located

in Cell B. There is an unusual decrease in K_1 and K_6 (Cell A) on November 27, 1997 and again on December 2, 1997.

On these same two days the cell temperature for Cell A showed an unusual increase although the electrochemical power applied to the cell was decreasing. This effect is shown in Figure 2. The cell currents were maintained at 300 mA except for November 29 - December 1 (200 mA) and December 5 (350 mA). The cells were run in series, hence the same current passed through both cells.

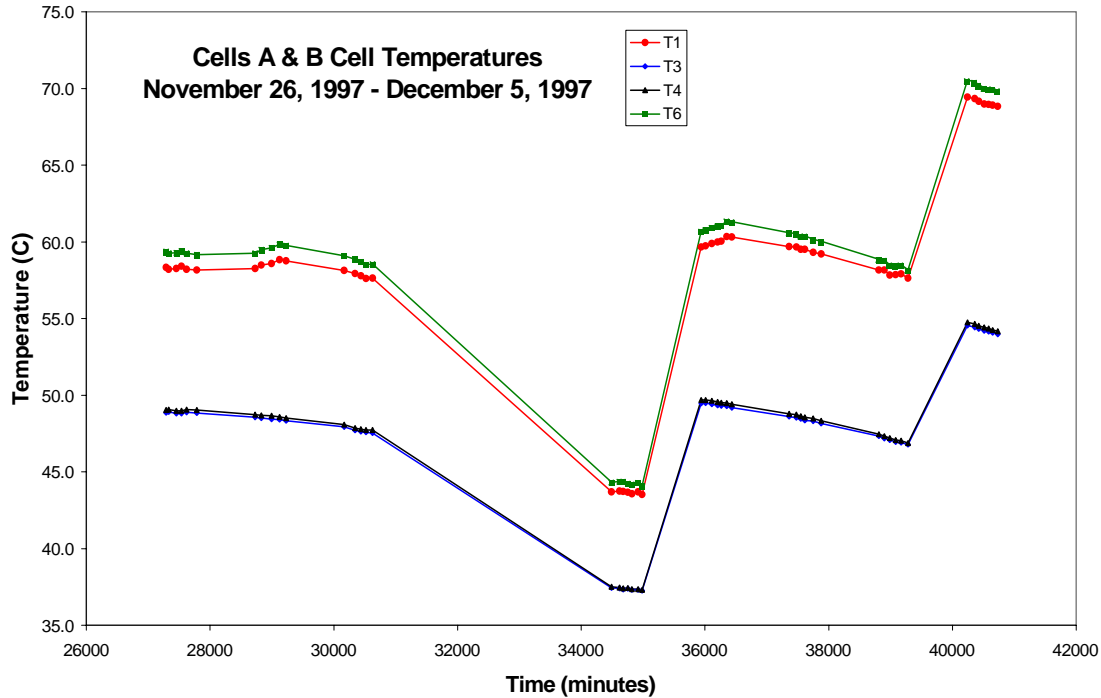


Figure 2. Cell temperatures verses time for Cell A (T1, T6) and Cell B (T3, T4).

During the same time period, strange fluctuations were often observed for the temperature readings for Cell A. Stray dots could be seen on the chart recording for thermistor 1, while thermistor 6 showed normal readings. An example of these random jumps in temperature is shown in Figure 3. These strange temperature excursions for thermistor T_1 were first observed on November 22, 1997 and continued until December 15, 1997. The thermistor connections were checked and tightened on December 10, 1997, but these thermistors fluctuations continued. This effect was never observed in any following experiment. These thermistors were all identical and consisted of manganese, cobalt, and nickel sintered oxides that were glass coated and covered with a thin Teflon sleeve.

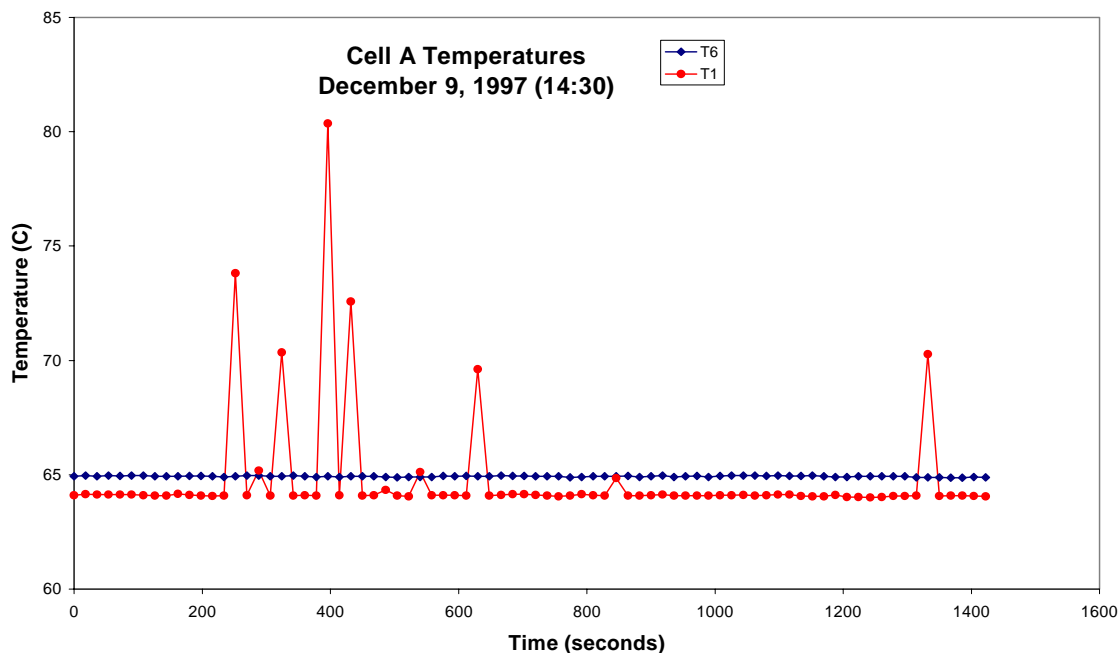


Figure 3. Thermistor readings versus time for Cell A (T_1 , T_6).

These temperature excursions quickly returned to normal within the time period of the separate measurements (18 seconds). This suggests that the sudden rise and decline in the temperature readings for thermistor T_1 is due to electromagnetic radiation from the palladium cathode rather than actual increases in the temperature. Thermistor T_1 was located directly in line with the palladium cathode while thermistor T_6 was positioned higher on the outside cell surface. A schematic of the cell and thermistor positions is shown in Figure 4.

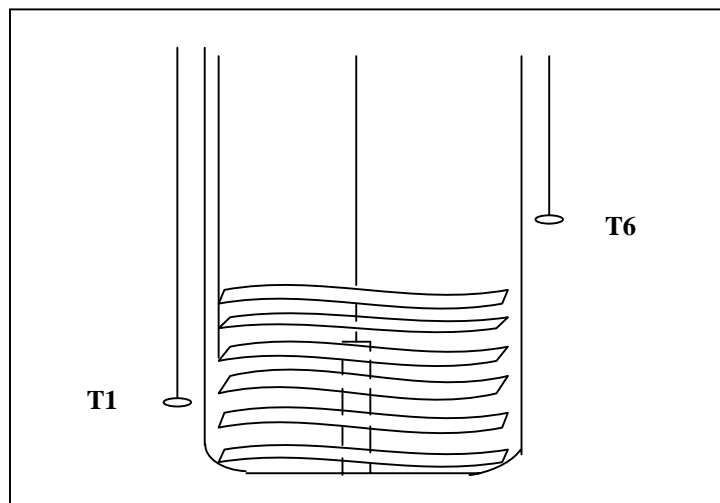


Figure 4. Schematic of positioning of thermistor T_1 and T_6 relative to the palladium cathode rod and platinum anode coil.

It is readily seen that any electromagnetic radiation from the cathode could pass directly between the platinum coils to reach thermistor T_1 , while thermistor T_6 is completely screened from the cathode by the platinum anode coils. Furthermore, the intensity of such radiation would be much less for thermistor T_6 since its distance from the cathode (R) is approximately four times that of thermistor T_2 ; 4 cm vs. 1 cm (Intensity $\propto 1/R^2$).

Cells A & B were designed mainly for sensitivity to any power changes within the cell. Their small size (18.0 cc electrolyte) also gave a fast response to any power changes. The time constant for these cells was measured to be approximately 15 minutes. Figure 5 shows the response in Cell A to an increase in power of 20 mW produced by increasing the cell current from 64.09 mA to 69.20 mA at 10329 minutes and then setting it back to 64.11 mA at 10424 minutes. The temperature response by thermistors T_1 and T_6 show that this increase in power is readily detectable. Other studies showed that power changes as small as 5 mW could be detected by the change in the cell temperature.

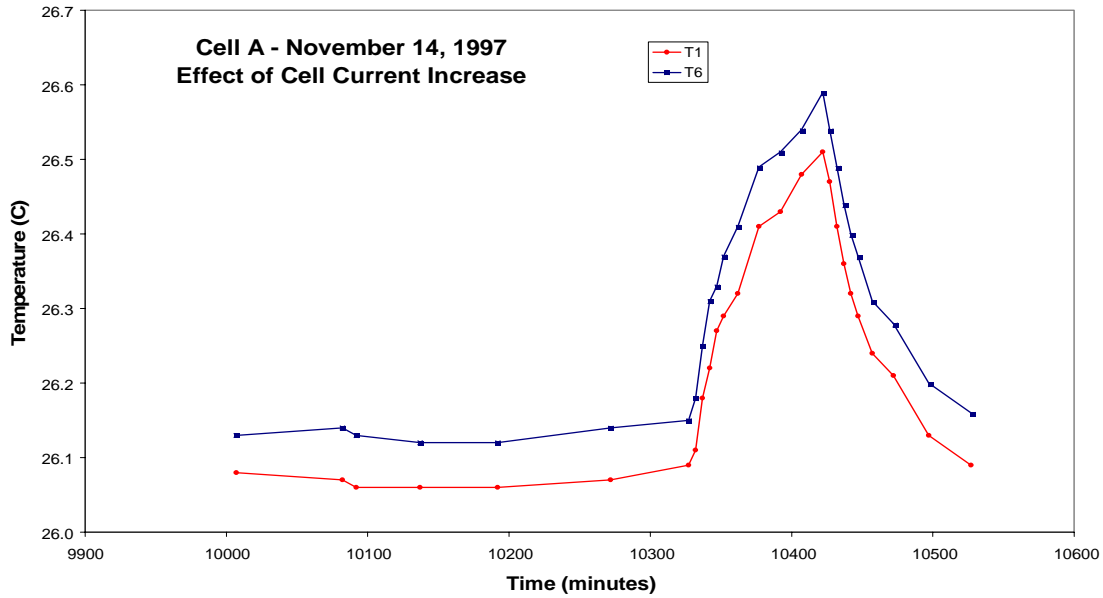


Figure 5. Response of thermistors T₁ and T₆ in Cell A to the increase in current from 64.09 mA to 69.20 mA (20 mW increase in power).

Despite this sensitivity to any power changes in the cell, no unusual increases in temperature were ever observed for Cell B. There were several increases in temperature measured in Cell A; for example, November 27, 1997 and December 2, 1997, as shown in Figure 2. There were no large bursts of excess power in Cell A although such effects would have been readily detected.

D. EXCESS POWER ANALYSIS

Measurements of excess power are more complicated than the detection of power changes since the small size of cells A and B along with the use of aluminum foil in the secondary compartment makes their cell constants sensitive to the cell electrolyte volume. The relationship of the cell constant to the cell volume was determined experimentally and is expressed by the following equations:

$$K_1 = 0.00195V_A + 0.01722 \quad (5)$$

$$K_6 = 0.00189V_A + 0.01686 \quad (6)$$

$$K_3 = 0.00172V_B + 0.02685 \quad (7)$$

$$K_4 = 0.00170V_B + 0.02699 \quad (8)$$

where V_A and V_B represent the volume of electrolyte (cc) in each cell at any given time. For a cell volume of 18.0 cc, these equations yield cell constants of $K_1 = 0.05232$ W/K, $K_6 = 0.05088$

W/K, $K_3 = 0.05781$ W/K, and $K_4 = 0.05759$ W/K. During these calibrations it was assumed that there was no excess power present in the cells ($P_x = 0$). If any excess power were actually present, this will simply minimize our determination of excess power since our cell constants will then be too small. The major error in these calculations is the measurement of the electrolyte volume in cells A and B. This was done by a volumetric syringe during each D_2O addition as well as by calculations based on the cell current. Nevertheless, the cell volume at each D_2O addition could not be determined more accurately than 18.0 ± 0.5 cc. This introduces an error of $\pm 1.9\%$ in the calculation of the cell constants. This will produce an uncertainty in the excess power of ± 28 mW for a cell operating at $50.00^\circ C$ ($\Delta T = 28.48^\circ C$). These cells are much more sensitive in detecting changes in the cell power than in accurately determining the exact amount of excess power.

An accurate record was kept of all D_2O additions to Cell A and B. From the beginning of the experiments on November 7, 1997 through December 29, 1997, there was 100.5 cc of D_2O added to Cell A and 103.5 cc added to Cell B. This rate of D_2O consumption is equivalent to 2.42 cc per day at 300 mA in Cell A and 2.49 cc per day in Cell B. Theoretical calculations based on 300 mA yield 2.43 cc of D_2O consumption per day. Therefore, there is no significant recombination of the D_2 and O_2 gases in either cell ($\gamma = 1.0$ in Equation 1). The small differences in the D_2O consumption in Cells A and B can be attributed to experimental error in the volume measurements of the D_2O additions.

The change of cell constants with time at 300 mA can be expressed by the equation:

$$\Delta K/\Delta t = (\Delta K/\Delta V) \cdot (\Delta V/\Delta t) \quad (9)$$

where $\Delta V/\Delta t$ equals -0.001677 cc/min. for Cell A and -0.001729 cc/min for Cell B based on their measured rates of D_2O consumption. Using the values in Equations 5 – 8 above for $\Delta K/\Delta V$ yields

$$\Delta K_1/\Delta t = (0.00195 \text{ W/K}\cdot\text{cc}) (-0.001677 \text{ cc/min}) = -3.27 \times 10^{-6} \text{ W/K}\cdot\text{min} \quad (10)$$

$$\Delta K_6/\Delta t = (0.00189 \text{ W/K}\cdot\text{cc}) (-0.001677 \text{ cc/min}) = -3.17 \times 10^{-6} \text{ W/K}\cdot\text{min} \quad (11)$$

$$\Delta K_3/\Delta t = (0.00172 \text{ W/K}\cdot\text{cc}) (-0.001729 \text{ cc/min}) = -2.97 \times 10^{-6} \text{ W/K}\cdot\text{min} \quad (12)$$

$$\Delta K_4/\Delta t = (0.00170 \text{ W/K}\cdot\text{cc}) (-0.001729 \text{ cc/min}) = -2.94 \times 10^{-6} \text{ W/K}\cdot\text{min} \quad (13)$$

Actual experimental measurements for $I = 0.300$ A during periods of no excess power yield very similar changes in the cell constants with time, i.e. $\Delta K_1 / \Delta t = \Delta K_6 / \Delta t = -3.3 \times 10^{-6}$ W/K·min for Cell A and $\Delta K_3 / \Delta t = \Delta K_4 / \Delta t = -2.7 \times 10^{-6}$ W/K·min for Cell B. These experimental decreases in the cell constants with time can also be seen in Figure 1. This effect is due to the decreasing volume of liquid during electrolysis and its replacement by gases which are better insulators (Ref. 3). The slightly larger changes in the cell constants with time for Cell A versus Cell B could be due to the inclusion of time periods where excess power was present. The time dependent equation for any of the cell constants at any given cell current (I) can be expressed by the equation:

$$K(t) = K_0 - (I/0.300) (3.09 \times 10^{-6}) (t - t_0) \quad (14)$$

where K_0 is the cell constant at time $t = t_0$. The value 3.09×10^{-6} is the mean value for the change of the cell constant with time at $I = 0.300$ A as expressed in the Equations 10 – 13. The values for K_0 are calculated from Equations 5–8 based on measurements of the cell volume at the time of D_2O additions (t_0). The output power of the cell is then given by $P_{out} = K(t) (T_{cell} - T_{bath})$ or $K \cdot \Delta T$ in Equation 4. The amount of excess power (P_x) can then be calculated from Equation 4. Figure 6 shows excess power results for Cells A and B during the time period November 26 – December 5, 1997.

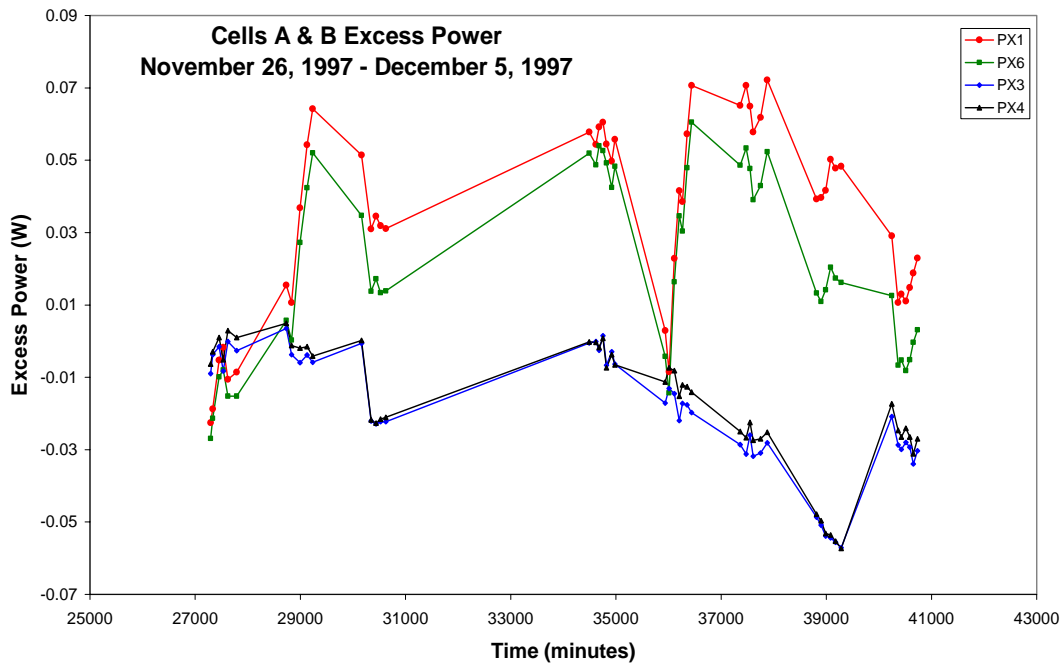


Figure 6. Excess power measurements for Cell A and Cell B during the time period of November 27 – December 5, 1997.

There are excess power increases in Cell A on November 27 and then again on December 2. The levels of excess power exceeded 60 mW several times based on our data analysis. Cell B, in contrast, shows zero or negative excess power effects. The negative values for excess power

should not be attributed solely to experimental error, but rather to our minimizing excess power by assuming it to be zero during calibrations and by neglecting any power carried away by the gas stream (P_{gas}). The general decrease in cell constants even after re-filling the cells with D_2O (Figure 1) suggests that excess power was present in both cells during the calibration period. At any rate, the unusual increase in cell temperature on November 27 and December 2, 1997 lends support to the existence of an excess power effect in Cell A.

E. DISCUSSION

The change of the cell temperature with time can be theoretically calculated from $\Delta T = P / K$ where $\Delta T = T_{\text{cell}} - T_{\text{bath}}$, thus $d\Delta T/dt = dT_{\text{cell}}/dt$. Therefore,

$$d\Delta T/dt = dT_{\text{cell}}/dt = K^{-1} dP/dt - PK^{-2} dK/dt \quad (15)$$

Since dP/dt is generally negative during electrolysis and dK/dt is always negative (see Equation 14), the first term in Equation 15 is negative while the second term is positive. Thus, theoretically the change in cell temperature with time can be either negative, zero, or positive. For our experiments, dT_{cell}/dt is usually negative except when excess power is present (see Figure 2). For example, Cell A on December 2, 1997 yields $dT_{\text{cell}}/dt = -0.00147$ K/min from Equation 15 while the experimental value is $dT_{\text{cell}}/dt = +0.00129$ K/min due to the presence of excess power. In contrast, Cell B yields $dT_{\text{cell}}/dt = -0.00051$ K/min from Equation 15 for this same day, and the experimental value is quite similar (-0.00056 K/min). For excess power, the above equation should become

$$\Delta T = \Delta T_{\text{EL}} + \Delta T_x = (P_{\text{EL}} + P_x) / K \quad (16)$$

Therefore, there is an additional term in the derivative given by

$$d\Delta T_x/dt = K^{-1} dP_x/dt - P_x K^{-2} dK/dt \quad (17)$$

Both terms in Equation 17 are positive when excess power is increasing in a cell, hence this can account for the increase in cell temperature with time on November 27, 1997 and December 2, 1997 as shown in Figure 2. The only other possible explanation would be some artifact in the cell. The increase in the cell temperature occurred several times at approximately the same electrolyte level. However, it is difficult to understand how the electrolyte level could affect both thermistors equally when they are located at different positions in the cell. Furthermore, they were many days when no unusual temperature increases occurred at this electrolyte level.

F. ADDITIONAL STUDIES

No other significant excess power effects were observed, and these experiments in Cells A and B were turned off on December 30, 1997. These experiments were turned on once again on January 5, 1998 for additional calibrations with the cathodes now in a de-loaded condition. These measurements showed only zero or slightly negative excess power for both Cell A and Cell B. On January 22, 1998 Cell A was switched to a pulse input power and on January 30, 1998 pulse power was applied to Cell B. Under pulse power conditions, Cell A showed the production of excess power while the excess power in Cell B was zero or negative. These pulse power experiments were done jointly with Dr. Tripodi of Italy and will be discussed separately in an Appendix to this report.

PALLADIUM ALLOY CATHODES IN FLEISCHMANN - PONS TYPE CELLS

A. INTRODUCTION / EXPERIMENTAL

The palladium cathodes selected for calorimetric studies were Pd-Ce-B, Pd-0.5B (0.5 weight % boron), and Pd-Ce. The first two samples were prepared at the Naval Research Laboratory in Washington, D.C. for cold fusion studies, and the third sample (Pd-Ce) was obtained from Martin Fleischmann. In order to test possible effects of the polishing procedures, the Pd-Ce-B sample was polished only by myself using silicon-carbide paper. The Pd-0.5B sample was polished solely by Mari Hosoda using normal NHE procedures involving diamond paste. The third sample, Pd-Ce, gave excess heat in a previous study at China Lake, but now contained a deep, long crack that was difficult to remove. This sample was also polished by Mari Hosoda to remove the crack while the final polish was done by myself using silicon-carbide paper. The final dimensions of these rods were 4.40 x 20.05 mm for the Pd-Ce-B sample ($V=0.305 \text{ cm}^3$, $A=2.92 \text{ cm}^2$), 4.71 x 20.1 mm for the Pd-0.5B ($V=0.350 \text{ cm}^3$, $A=3.15 \text{ cm}^2$), and 3.16 x 19.54 mm for the Pd-Ce cathode ($V=0.153 \text{ cm}^3$, $A=2.02 \text{ cm}^2$). These cathode rods were each spot welded to platinum lead wires that were sealed in thin glass rods. The spot weld areas for each cathode were covered with Epoxy for protection and strength. These electrodes along with the normal platinum anode cage structures were assembled in the Fleischmann – Pons cells. The platinum spiral anode is supported by a thin Kel-F disk containing glass rods at the base of the cell. The Pd-Ce-B was in Cell A-1, the Pd-0.5B was in Cell A-2, and the Pd-Ce was in Cell A-3. The cell tops were sealed with silicon rubber and 90 cc of 0.1 M LiOD was added to each cell. These cells were assembled in the water bath and connected to the Icarus 2.00 data acquisition system. This experiment was turned on at 10:00 a.m. on December 5, 1997.

B. CALORIMETRIC EQUATIONS FOR FLEISCHMANN – PONS CELLS

The Dewar-type electrochemical cells are silvered in their top portions so that heat transfer is confined almost exclusively to radiation across the lower, un-silvered part. The calorimetric equations, therefore, are given by

$$P_{\text{calor}} = P_{\text{EL}} + P_x + P_H - P_{\text{out}} - P_{\text{gas}} \quad (18)$$

where

$$P_{\text{EL}} = [E(t) - \gamma E_H] I \quad (19)$$

$$P_{\text{out}} = K (T_{\text{cell}}^4 - T_{\text{bath}}^4) \quad (20)$$

$$P_{\text{gas}} = (\gamma I / F) \{ [0.5 C_{p, D_2} + 0.25 C_{p, O_2} + 0.75 (P / (P^* - P))] C_{p, D_2O(v)} \Delta T + 0.75 (P / (P^* - P)) L \} \quad (21)$$

$$P_{\text{calor}} = C_{P, \text{D}_2\text{O} (l)} [M^\circ - (1+\beta) (\gamma I t / 2F)] (d\Delta T / dt) - (1+\beta) (\gamma I / 2F) C_{P, \text{D}_2\text{O} (l)} \Delta T \quad (22)$$

and P_H is the power added to the cell during the heater calibration cycle each day at midnight. Each heat capacity value along with the heat of evaporation of D_2O (L) and the vapor pressure of D_2O (P) were always calculated based on the measured cell temperature. The equations for these temperature-dependent calorimetric parameters are given in Appendix A.

C. EXPERIMENTAL RESULTS

The excess power for the Fleischmann – Pons cells can be calculated from Equation 18 above using a cell constant calculated from the first heating pulse. However, these results gave surprising large fluctuations in the excess power measurements that were ± 20 mW or larger. Fleischmann and Pons, however, report an accuracy of ± 1 mW or less for these Dewar cells. It was realized that this difference stems from the use of individual temperature and voltage measurements in the cell rather than using averaged values. Due to the rather long time constants of these cells (90 minutes), the actual temperature of the cells represents a large averaging effect of any variations in the power added to the cell. Therefore, the data analysis for these cells must involve extensive averaging over rather long time periods to accurately determine any excess power. For example, an experimental variation of only $\pm 0.01^\circ\text{C}$ in a single measurement of either the cell temperature or the bath temperature produces a variation in P_{calor} (Equation 22) of ± 16 mW. This is due to the large value of $C_{P, \text{D}_2\text{O} (l)} M^\circ$ (water equivalent of the cell) that is 496.0 J/K. When this is multiplied by ± 0.01 K / 300 seconds ($d\Delta T / dt$), the above error range is obtained. This error was obvious when the P_{calor} term was displayed versus time for each cell. The 300 seconds is the time period between data sampling by the Icarus data acquisition system. Another error results from experimental fluctuations in the cell voltage due to gas bubbles. For example, a variation of ± 0.02 V in the measurement of $E(t)$ (Equation 19) at a cell current of 0.5 A will give an experimental error of ± 10 mW for the electrochemical power added to the cell. These errors in the cell temperature, bath temperature, and cell voltage measurements can give compound errors of ± 42 mW in any measurement of excess power based on a single point. Data averaging of all these measurements is an absolute necessity to minimize errors in the Fleischmann–Pons calorimetry. This calorimetric system, in principle, continually averages any change in power within the cell over a rather long time period (90 minutes).

My report on the Fleischmann–Pons calorimetry is based on my own recording of the cell temperature, voltages and currents taken during the workday at the NHE laboratory. This data was further selected to give nearly steady state conditions where the P_{calor} term is small. Averaged values of $d\Delta T / dt$ were used in all calculations. The cell constants were then calculated from Equation 18 under the assumption of no excess power. The cell constants for Cell A-1 are shown in Figure 7.

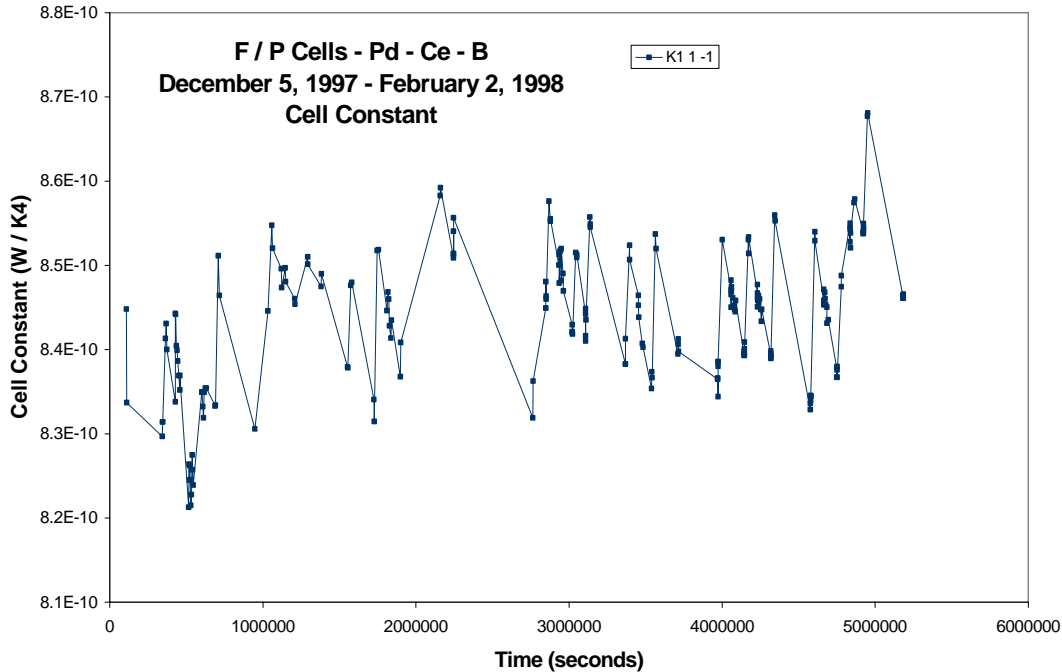


Figure 7. Experimental cell constants versus time for Cell A-1 (Pd-Ce-B).

If there were any excess power produced in the cell, it would cause the cell constant to decrease. The mean cell constant for this entire data set is $8.5118 \pm 0.0790 \times 10^{-10} \text{ W/K}^4$, thus the average experimental error is only $\pm 0.93\%$. This suggests that excess power, if any, for Cell A-1 is quite small. Using the time period between 1033800 – 2159400 seconds (December 16 – December 29, 1997) yields a cell constant of $8.4632 \pm 0.0642 \times 10^{-10} \text{ W/K}^4$ for Cell A-1. This time period covers typical operating conditions for this cell (0.3 – 0.6 A). This cell constant was used in Equation 18 to calculate the excess power in Cell A-1. The results are shown in Figure 8 below. The excess power is near zero from December 6 through February 2, 1998 (107100 – 5183400 seconds). At this time the current to the cell became unstable, and it was difficult to obtain any further useful steady state data. The ratio of the power out ($P_{\text{out}} + P_x$) to the power in (P_{EL}) from December 6, 1997 through February 2, 1998 is $X = 1.002 \pm 0.008$, thus there is no excess power within an error range of $\pm 0.8\%$. Improvements in this data analysis would require further averaging of the cell voltages, the cell and bath temperatures, as well as daily determinations of the cell constant from the heater pulse.

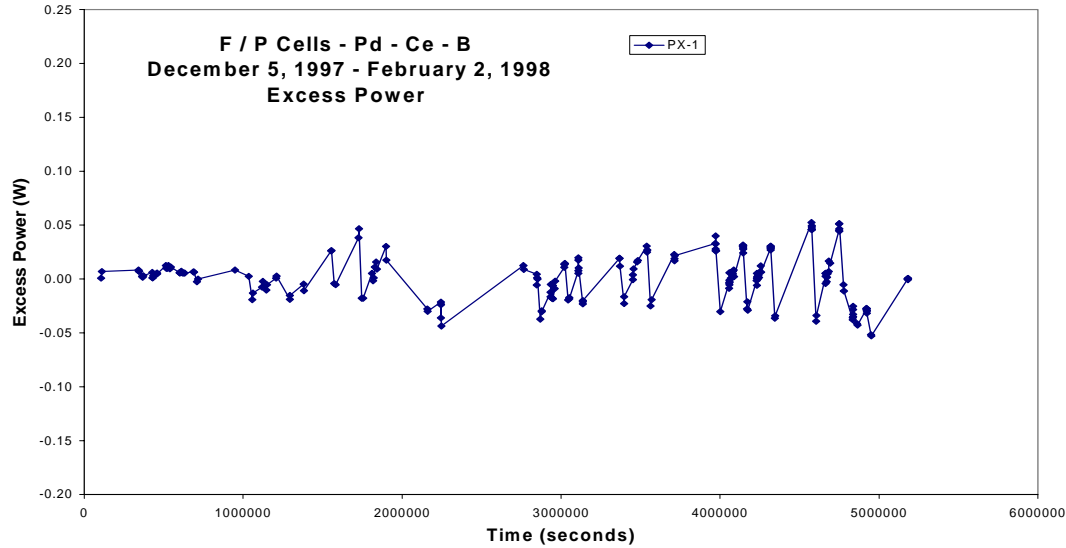


Figure 8. Excess power measurements for the Pd-Ce-B cathode in Cell A-1 (Pd-Ce-B).

The fact that there was no measurable excess power in Cell A-1 (Pd-Ce-B) provides an excellent opportunity for the analysis of factors that may affect the cell constant in the F/P type Dewar cells. These factors include the cell temperature, the cell voltage, the volume of electrolyte present in the cell, and the cell current. None of these factors showed a clear relationship with the cell constant. The highest correlation coefficient (R^2) was obtained for the relationship of the cell constant to the cell current. This is shown in Figure 9. It is readily seen that the cell currents were generally 0.400-0.600 A.

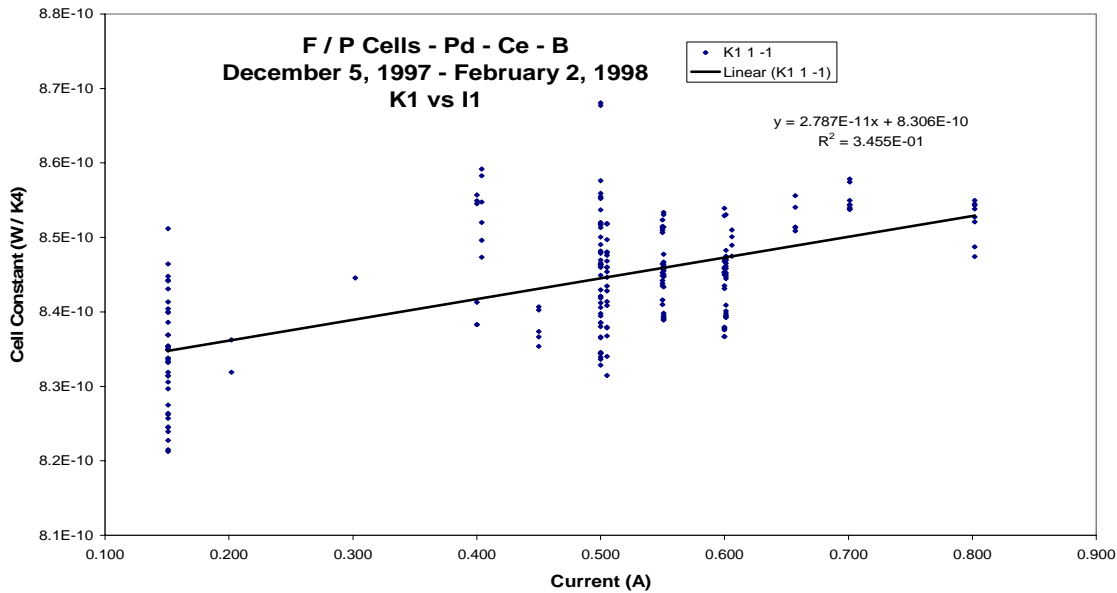


Figure 9. Experimental relationship of the cell constant to the cell current in Cell A-1 (Pd-Ce-B).

This cell was initially run for ten days at a current of 0.151 A. The cell constant varied apparently in a random manner from day to day during this time period. The large variations in the cell constant at this current illustrates the error in using a single heating pulse to determine the cell constant. Daily calibrations are necessary for high accuracy.

Similar averaging procedures were used to determine the cell constants for Cell A-2 (Pd-0.5B) and Cell A-3 (Pd-Ce). These cell constants are $8.1120 \pm 0.0976 \times 10^{-10} \text{ W/K}^4$ for Cell A-2 and $7.9999 \pm 0.0790 \times 10^{-10} \text{ W/K}^4$ for Cell A-3. Similar to the process used for Cell A-1, time periods were selected to minimize any contributions from excess power. These time periods were 2847900-3973800 seconds (January 6 – 19, 1998) for Cell A-2 and 1033800-1381800 seconds (December 16 – 20, 1997) for Cell A-3. The excess power that is calculated from Equation 18 using these cell constants is shown in Figures 10 and 11.

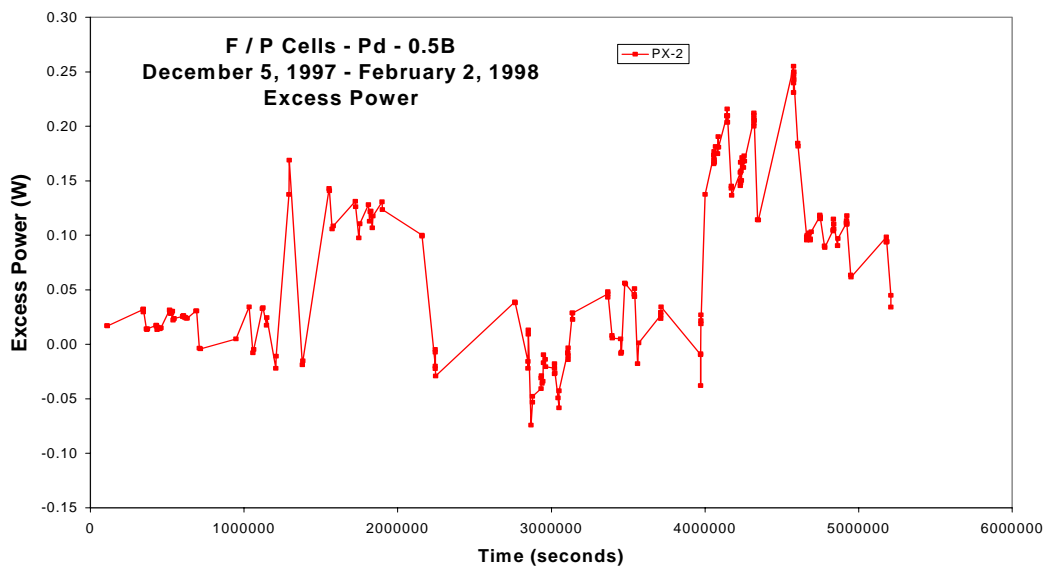


Figure 10. Excess power measurements for the Pd-0.5B cathode in Cell A-2.

Figure 10 shows two different episodes of excess heat production for the Pd-0.5B cathode in Cell A-2 that reach levels of 200 mW (0.6 W/cm^3). The Pd-Ce alloy (Figure 11) began producing excess power after fifteen days of electrolysis and gave a fairly steady level of about 100 mW with a peak of 200 mW (1.3 W/cm^3). Although these levels of excess power are not large, they are readily measurable when cell parameters are sufficiently averaged.

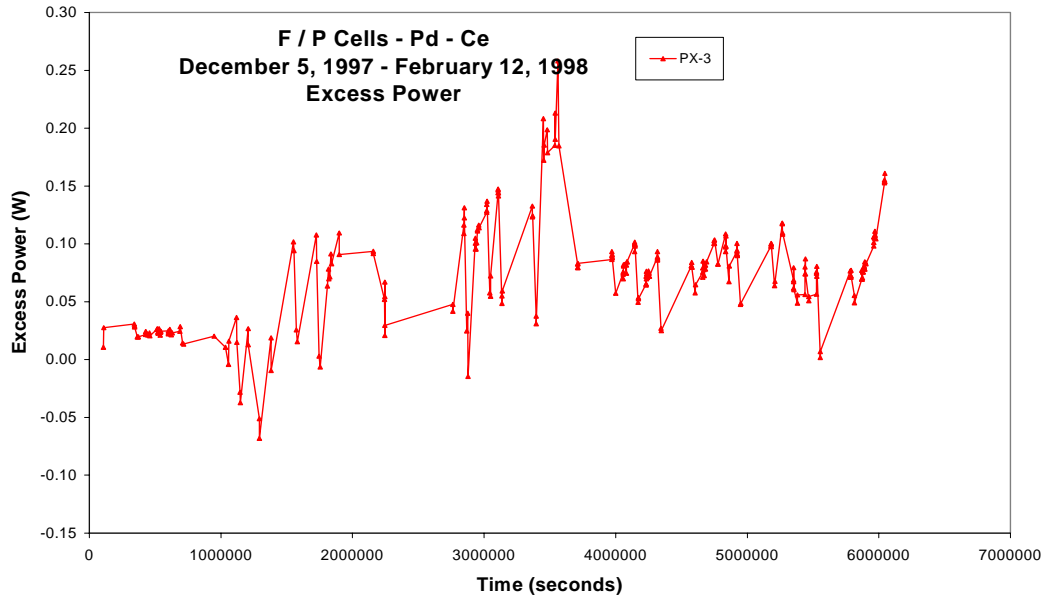


Figure 11. Excess power measurements for the Pd-Ce cathode in Cell A-3.

In contrast to the Pd-Ce-B cathode in Cell A-1, the Pd-0.5B cathode in Cell A-2 and the Pd-Ce cathode in Cell A-3 show periods when the excess power becomes more negative than 50 mW. The presence of excess power during the period of calibrations could result in negative P_X values. Another possibility is changes in the cell constants, thus daily calibrations are necessary for more precise measurements. Preparata et al. (Reference 4) have shown that cell constants determined by heating pulses can increase in systems that are producing excess power. The neglect of this factor would minimize excess power measurements.

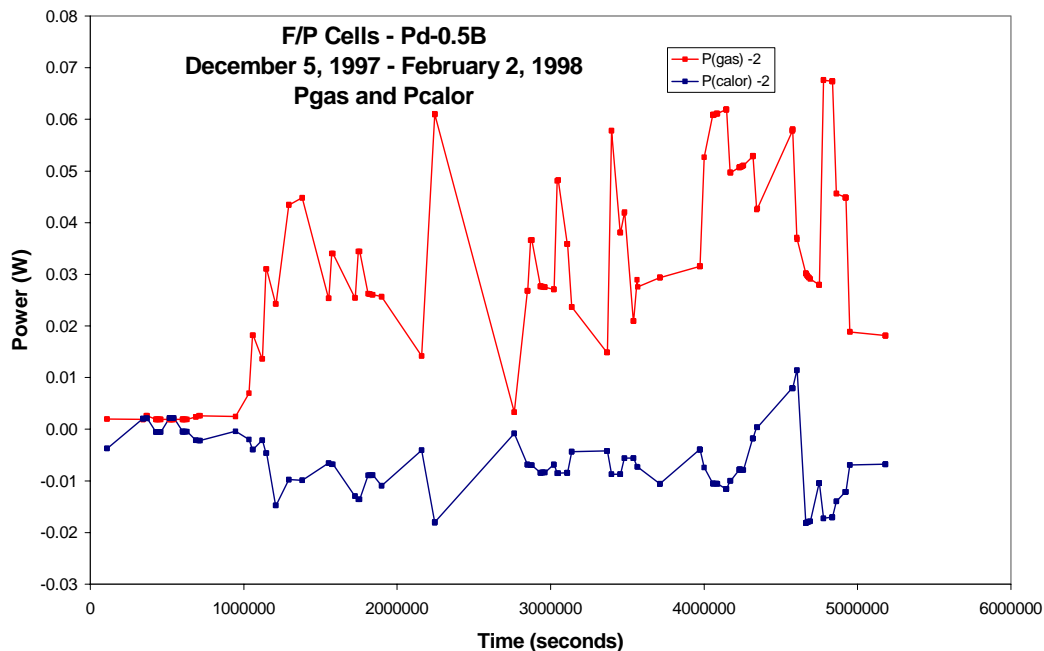


Figure 12. Display of the calorimetric terms P_{gas} and P_{calor} determined from Equations 21 and 22 for the Pd-0.5B study in Cell A-2.

The ratio of output and input power or $X=(P_{\text{out}}+P_X)/P_{\text{EL}}$ also shows that there is a clear difference between the X values for Cell A-1 and the X values for the two cells that produced excess power (Cells A-1 and A-3). However, the percent of excess power is small – typically in the range of 3 – 8%. The mean X-values are 1.002 ± 0.008 for Cell A-1 and 1.03 for both cells A-2 and A-3. Error limits are larger and meaningless for cells that give fluctuating levels of excess power.

Figure 12 represents the values for the P_{gas} and P_{calor} terms (Equations 21,22) for the Pd-0.5B study in Cell A-2. The P_{calor} term remains small under the steady state conditions selected for this data ($d\Delta T/dt \approx 0$). As seen from Equation 21, the P_{gas} term will increase with increases in the cell current and cell temperature. It can become quite large when the cell approaches boiling conditions since the vapor pressure of the $\text{D}_2\text{O-LiOD}$ electrolyte (P) will approach the atmospheric pressure (P^*). This cell containing the Pd-05.B alloy was driven to boiling on February 10, 1998. Preliminary measurements indicate that there was no unexplained excess power during this boiling process. As seen in Figure 10, however, the excess power had decreased to near zero prior to this boil-off study. It was impressive, nevertheless, to watch the rapid boiling action with the electrolyte solution vigorously swirling about the Pd-B cathode.

D. DISCUSSION

The polishing procedures used for the cathodes do not appear to be a significant factor for the excess heat affect. The Pd-0.5B cathode polished only by normal NHE procedures using

diamond paste produced excess heat (Figure 10). The Pd-Ce cathode polished by both diamond paste and silicon-carbide paper also produced excess heat (Figure 11). The other cathode (Pd-Ce-B) was polished only using silicon-carbide paper and produced no excess power (Figure 8).

There was no measurable recombination in any of these three cells. The D₂O consumption slightly exceeded that calculated based on Faraday's law as expected due to evaporation. The experimental values of β used in Equation 22 were 0.048 for Cell A-1, 0.081 for Cell A-2, and 0.062 for Cell A-3.

The use of all the experimental points recorded by the data acquisition system and the heating pulse each day, along with extensive averaging techniques should improve the data analysis. These improvements would apparently lead to the same methods of data analysis developed by Fleischmann and Pons. It is recommended that the collected data for these three cells be processed directly by Martin Fleischmann or Stanley Pons or at least be processed by the methods that they have developed. Simpler methods of data analysis will not likely be as accurate.

CO-DEPOSITION OF PALLADIUM AND DEUTERIUM IN FLEISCHMANN-PONS TYPE CELLS

A. INTRODUCTION / EXPERIMENTAL PROCEDURES

The method of depositing palladium from solution onto a copper cathode in the presence of evolving deuterium gas was first reported by S. Szpak et al. in 1991 (Ref. 5). This method is claimed to produce excess heat, tritium, and emanating radiation (Ref. 5, 6). This co-deposition method normally uses a D₂O solution containing 0.05 M PdCl₂ and 0.3 M LiCl, but this was modified at NHE in an attempt to obtain bright palladium deposits. This, however, did not succeed.

A standard electroplating bath for palladium deposition is Pd(NH₃)₂Cl₂ in NH₄Cl+NH₃ (Ref. 7). For the experiments at NHE, the plating solution consisted of 0.025 M PdCl₂, 0.15 M ND₄Cl and 0.15 M ND₄OD in D₂O. This mixing of these chemicals produced an orange solution and the formation of an insoluble precipitate. This precipitate was likely Pd(OD)₂ due to the rather high initial pH of the solution (pH= 9-10). Because of this precipitate, the volume of solution added to each cell had to be measured by a graduated cylinder rather than by a syringe; this volume was 91±1cc. The copper cathodes used in each cell were approximately 4 mm x 25 mm. Based on the amount of PdCl₂ used, the palladium deposition onto the copper cathode should be completed after one day of electrolysis at a current of 0.006 A.

B. EXPERIMENTAL RESULTS

These three co-deposition experiments in Cells A-1, A-2, and A-3 started at 10:00 a.m. on February 18, 1998 using a current of 0.006 A in each cell. The deposition of palladium onto the copper was visible within a few minutes, and the copper was completely covered by a dark palladium deposit within 30 minutes. This deposit was not the bright, adherent palladium desired, but this requires palladium deposition without hydride formation which occurs only in a narrow potential window of about 150 mV (Ref. 7). Within 24 hours, the plating solution was nearly clear and gassing was readily visible at the Pd/Cu cathode. The current was then increased to 0.100 A in each cell. On the second day, the solutions had turned to a pale yellow color. The current was then increased to 0.200 A, but a chlorine gas odor developed in the room, hence the current had to be reduced to 0.020 A for the weekend. The following week the cell currents were increased to 0.100 A, then 0.200 A and finally to 0.400 A without any further problems with the chlorine odor. These experiments were turned off on February 26, 1998.

C. EXCESS HEAT MEASUREMENTS

Assuming the same cell constants as in the previous experiments, the amount of excess power in each cell was calculated using Equation 18. The results are shown in Figure 13. Excess power is apparently present in each cell. During the last two days of this experiment, about 400 mW of excess power was present in both Cells A-2 and A-3 while about 100 mW of excess power was present in Cell A-1. However, recombination of the electrolysis gases (D_2 , O_2) is possible in these cells due to the loose palladium deposits that were formed. In fact, the loose palladium particles floating in the solution in Cell A-2 caused concern about a possible explosion, hence the current was reduced from 0.400 A to 0.300 A for this cell during the last day of this experiment. There were considerable less palladium particles floating in Cells A-1 and A-3. Despite this difference, the excess heat measured in Cell A-3 was nearly identical to that in Cell A-2.

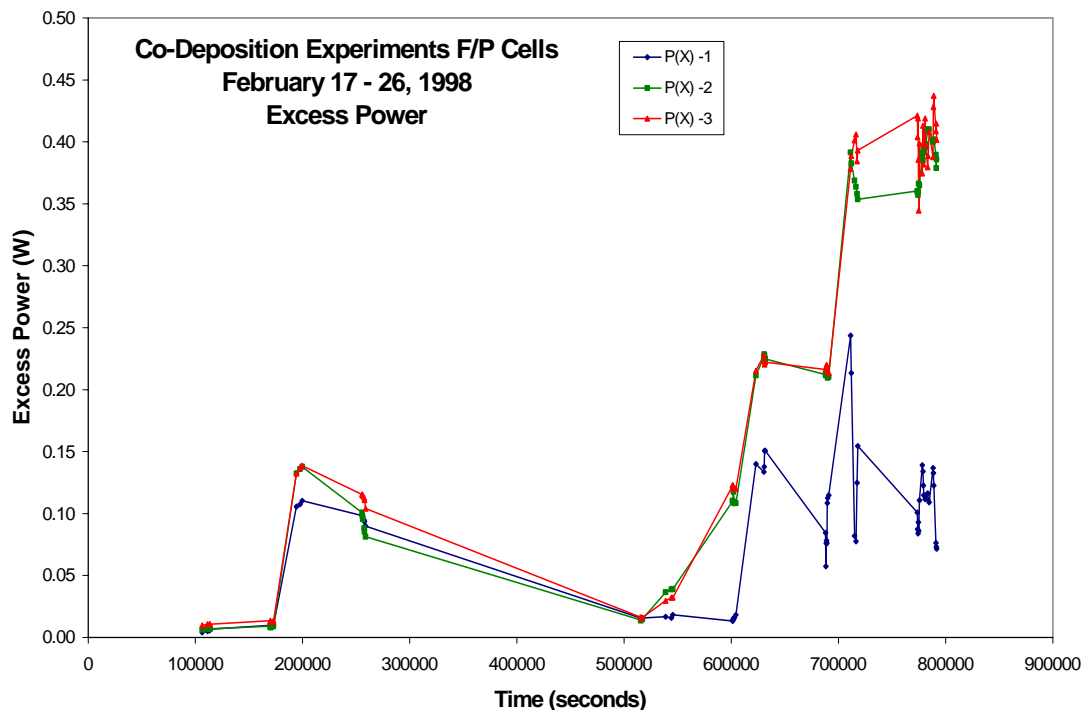


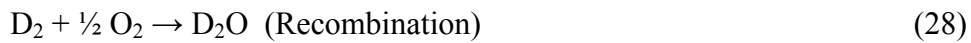
Figure 13. Excess power measurements in co-deposition experiments.

For this experiment shown in Figure 13, the cell current was turned on to 0.006 A at 86100 seconds, increased to 0.100 A at 173100 seconds, increased to 0.200 A at 259200 seconds, and then was reduced due to chlorine evolution. During the following week, the current was increased to 0.100 A at 518700 seconds, then to 0.200 A at 604500 seconds, and finally 0.400 A at 691200 seconds. The larger excess power effects are observed at the higher currents.

In order to address the issue of the possible recombination of D_2 and O_2 gases on the loose palladium particles, the electrolyte volume was carefully measured at the end of these experiments. The amount of D_2O consumed was 7.4 ± 1.0 cc in Cell A-1, 7.7 ± 1.0 cc in Cell A-2, and 8.7 ± 1.0 cc in Cell A-3. The error of ± 1.0 cc is mainly due to the error in measuring the initial volume of solution prior to electrolysis. The consumption of D_2O in each cell was within experimental error of the theoretical amounts based on Faraday's Law (8.1 cc for Cell A-1 and A-3, and 7.2 cc for Cell A-2). Cell A-1 shows about the same or smaller consumption of D_2O as Cells A-2 and A-3, yet this cell showed only small excess power effects in Figure 13. Thus there are no obvious correlation of the excess heat to recombination.

D. DISCUSSION

The analysis of this co-deposition system is complicated by the following possible reactions,



In the plating solution selected, the palladium is also stabilized by the formation of $\text{Pd}(\text{ND}_3)_4^{2+}$ (Ref. 7). It was found that the initial high pH of the solution (pH = 9-10) decreased to pH = 1-2 during these experiments. The electrolysis gases probably remove ND_3 from the solution, shifting Equation 27 to the left. Furthermore, the deposition of palladium gives a net increase in D^+ ions due to the corresponding electrolysis of D_2O to form O_2 (Equation 25). The chlorine evolution took place during the early electrolysis when the solution was basic but decreased as the solution became more acidic. The bleaching of pH paper by the gases from the cell was observed during the early electrolysis but not during the later electrolysis. Any chlorine evolution would only minimize the excess power calculated from Equation 18, since the thermoneutral potential (E_H) is larger for the cell reaction producing chlorine than for D_2O electrolysis.

The co-deposition of palladium and deuterium from D_2O solutions is an area that warrants further research. Anomalous effects apparently occur relatively quickly due to the rapid loading of palladium with deuterium as it is being deposited (Refs. 5, 6). This type of experiment also produces the dynamic conditions at the electrode surface that seem to be essential for the observation of cold fusion effects. Any duplication of these co-deposition experiments should be conducted in a well-ventilated area with proper protection against any possible explosion due to recombination.

FLUIDIZED BED EXPERIMENTS IN CELLS A AND B

A. INTRODUCTION / EXPERIMENTAL PROCEDURES

These experiments were designed to give dynamic electrolysis conditions by using small palladium particles that can be somewhat suspended in solution while still maintaining electrical contact. The movement of these particles due to the D_2 gas evolution continuously produces changing surfaces for the cathodic reaction. To my knowledge, this type of cold fusion experiment had not been performed previously. Platinum particles were tested in Cell A as a control while palladium particles were investigated in Cell B. The platinum and palladium particles had the same dimensions, i.e., 0.6 – 0.65 mm diameter and 0.65 – 0.7 mm length. It could be seen with the aid of a microscope that these particles were actually miniature cylindrical rods. The stated purity was 99.99% for both metals.

Preliminary studies showed that these particles were too heavy to be suspended in solution by the gas evolution and that only the surface layer showed movement during electrolysis. The bottom of the electrochemical cells, therefore, were filled only to a level of 3 – 4 mm with the small metal particles. A platinum wire sealed in shrink Teflon with only a small tip exposed was used to make electrical contact to the metal particles at the bottom of the cell. The same platinum coil anodes as in the previous experiments in Cells A and B were positioned about 0.5 cm above the bed of metal particles. Each cell was then filled with 18.0 cc of 0.1 M LiOD. Thermistors T_1 and T_6 were fixed in position on the outside surface of Cell A while thermistors T_3 and T_4 were similarly placed on the outside surface of Cell B. These positions were 1.9 cm above the bottom of each cell (T_1 , T_3) and 4.5 cm above the bottom on the opposite side of each cell (T_6 , T_4). Cell A that showed evidence of excess heat in the previous experiment now contained the platinum particles where no excess heat would be expected.

In order to investigate variations in calorimetric designs, the secondary compartment outside the electrochemical cell was filled with copper granules in these experiments rather than aluminum foil. The top 2.5–3.0 cm of space in the secondary compartment of each cell was filled with Styrofoam insulation and then sealed with silicon rubber. These changes were designed to facilitate heat conduction between the electrochemical cell and the bath while minimizing heat transfer out of the top of the cell.

The current was first applied to these fluidized bed experiments on February 11, 1998. The initial cell current of 0.100 A was increased to 0.300 A after one day. These cells were typically run at 0.300 – 0.400 A.

B. EXPERIMENTAL CALIBRATIONS

Cell calibrations at 0.300-0.400 A assuming no excess power during the first week of electrolysis yielded the following new equations for the cell constants:

$$K_1 = 0.00299 V_A + 0.03588 \quad (29)$$

$$K_6 = 0.00299 V_A + 0.03638 \quad (30)$$

for cell A (Pt particles) and

$$K_3 = 0.00312 V_B + 0.08608 \quad (31)$$

$$K_4 = 0.00307 V_B + 0.07625 \quad (32)$$

for Cell B (Pd particles). When $V_A=V_B=18.0$ cc, these cell constants are $K_1 = 0.08970$ W/K, $K_6= 0.09020$ W/K for Cell A and $K_3 = 0.1422$ W/K, $K_4= 0.1315$ W/K for Cell B. The difference in cell constants for the two cells was rather surprising since they were similar in design. However, K_3 and K_4 for Cell B were also higher than K_1 and K_6 for Cell A in the prior experiment using aluminum foil in the secondary compartment. The larger amount of air space in the aluminum foil construction accounts for its better insulating properties and lower cell constants. The weight of copper granules in the secondary compartment was 330.1 g for Cell A and 321.4 g for Cell B.

C. EXCESS POWER MEASUREMENTS

The excess power for the fluidized bed experiments was determined using Equation 4. The use of steady-state data where $d\Delta T/dt$ is small allows the neglect of the P_{calor} term (Equation 3) while the P_{gas} term will remain nearly constant and less than 0.050 W for $I = 0.300\text{-}0.400$ A at cell temperatures of 40-60°C. The cell constants were determined by the use of Equations 29-32 using measured and calculated values for the cell volumes.

Figure 14 presents the electrochemical power added to the cell, $[E(t) - \gamma E_H]I$, and the output power of the cell ($K\Delta T$) for the platinum particles in Cell A. On Friday, February 20, 1998 at 12945 minutes the input power to the cell was switched to the pulse power mode and no steady state data was collected until Monday, February 23, 1998 at 17180 minutes (9:20 a.m.). Details of the pulse power experiments conducted jointly with Dr. Tripodi are given in Appendix B. Figure 14 shows that there was no excess power for the platinum particles in Cell A. In fact, the measured output power is often slightly less than the input power. For pulse electrolysis, this could be readily explained by the decrease of P_{gas} due to the low average current of only 0.012 A under the pulse conditions.

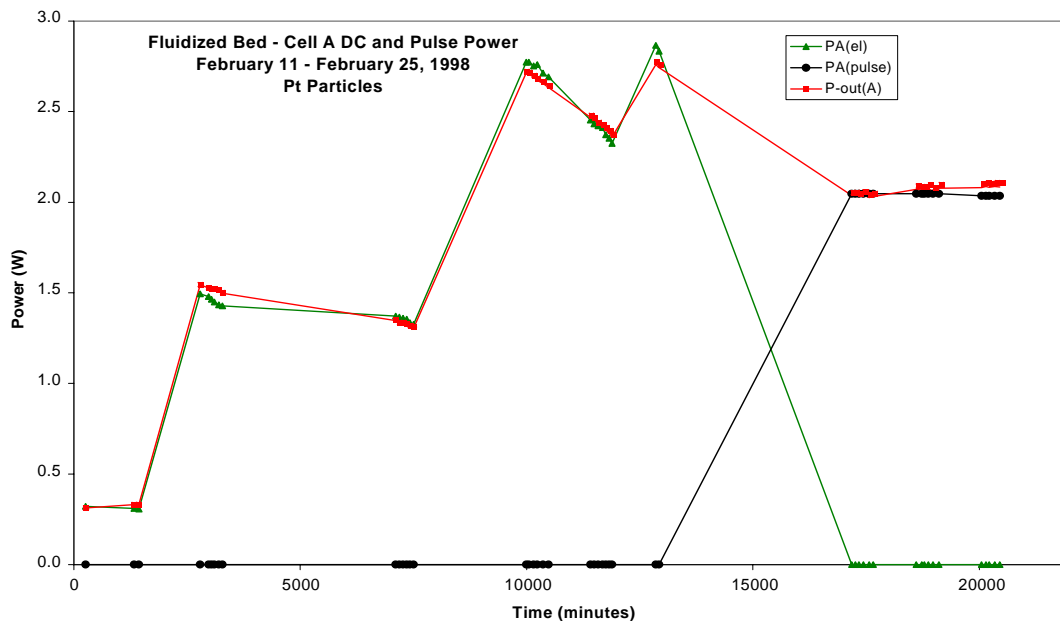


Figure 14. The electrochemical power and output power for the platinum particles in Cell A.

Figure 15 shows the electrochemical power added to Cell B along with the output power of this cell containing palladium particles. After about a week of electrolysis, the output power begins to slightly exceed the input power to the cell. This excess power reaches a peak of about 90 mW for direct current electrolysis on February 23, 1998 (17180 minutes). The electrochemical input power was switched to the pulse method on February 25, 1998 (20490 minutes). As shown in Figure 15, even larger amounts of excess power were observed. Further discussions of this pulse method are given in Appendix B.

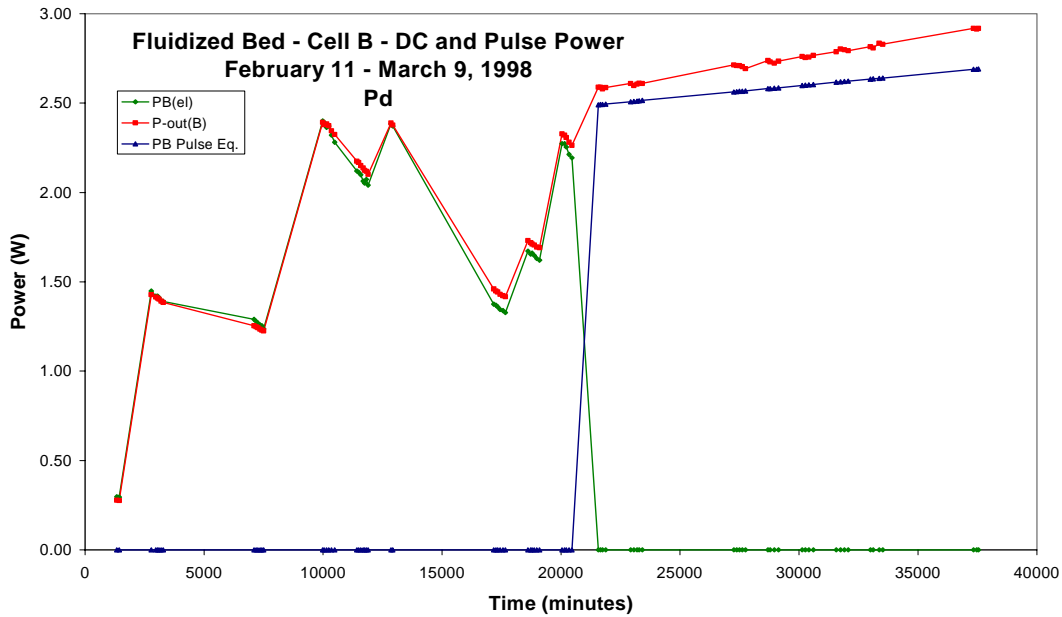


Figure 15. The electrochemical power and output power for the palladium particles in Cell B.

D. DISCUSSION

These novel fluidized bed experiments provide dynamic conditions that are believed to be important for the observation of excess heat in cold fusion experiments. Preliminary studies showed that the small metal particles jostle about during electrolysis, hence new surface areas are continually exposed to the metal/electrolyte interface where the main electrolysis occurs. The many tiny metal particles make these experiments less sensitive to the unknown hidden variables that produces excess heat in one palladium rod but not in another similar rod. The probability for the excess heat effect is increased by the many particles of palladium metal in the cell as well as by the dynamic conditions produced by these experiments.

ELECTROMIGRATION EXPERIMENTS IN FLEISCHMANN-PONS TYPE CELLS

These experiments were conducted jointly with Dr. Tripodi during the last week of experiments at the NHE laboratory. These results are reported in Appendix C of this report. Preliminary analyses show an excess power of about 150 mW in Cell A-2 during electrolysis in 0.1 M LiOD+D₂O. For the volume of the 50 μ diameter wire (50 μ x 40 cm), this yields 190 W/cm³ of palladium. Power densities of 3 kW/cm³ of palladium have been reported for electromigration experiments using thin palladium wires (Ref. 4).

TRITIUM RESULTS

Tritium measurements were made on the final electrolyte solutions after adjusting the D₂O levels to the initial volumes. The results are given in Table I where the tritium activity is given in units of disintegrations per minute per mL (dpm/mL).

TABLE I. Tritium Results for NHE Experiments

Experiment (Dates)	D ₂ O Consumption (cc)	Tritium (dpm/mL)	a(t)/a(o) (Experimental)	a(t)/a(o) (Theoretical for S=1.6)
Cell A – Pd (Nov. 7, 1997 - Feb. 3, 1998)	161.0	361.26 ± 1.12	1.615	1.597
Cell B – Pd (Nov. 7, 1997 – February 9, 1998)	175.0	347.02 ± 1.11	1.551	1.598
F/P A-1 – Pd-Ce-B (Dec. 5, 1997 – February 12, 1998)	248.5	336.92 ± 1.08	1.506	1.483
F/P A-3 Pd-Ce (Dec. 5, 1997 – Feb. 12, 1998)	258.0	334.92 ± 1.07	1.497	1.490
F/P A-1 Co-Deposition (Feb. 18 – Feb. 26, 1998)	7.4 ± 1.0	217.24 ± 0.89	--	--
F/P A-2 Co-Deposition (Feb. 18 – 26, 1998)	7.7 ± 1.0	212.62 ± 0.87	--	--
F/P A-3 Co-Deposition (Feb. 18 – 26, 1998)	8.7 ± 1.0	214.21 ± 0.88	--	--
Control Sample (No electrolysis)	--	223.74 ± 0.89	--	--

The fluidized bed experiments and the electromigration studies were completed too late for tritium measurements of the electrolyte. The D₂O in Cell A-2 (Pd-05B) was lost, of course, in the boil-off study.

The expected increase in tritium during D₂O electrolysis is given by

$$a(t)/a(o) = S - (S - 1)e^{-tI/2FSnV} \quad (33)$$

where a(o) and a(t) are the activity of tritium initially and at time t, respectively, and S is the isotopic separation factor (Ref. 1). This equation assumes a constant current (I) a constant electrolyte volume (V) and that the isotopic separation factor (S) remains constant throughout the

experiment. The electrolyte volume was 18.0 mL for Cells A and B and 90.0 mL for F/P cells. Assuming $S = 1.6$ and using $n = 0.055$ mol/mL for D_2O gives reasonable agreement between $a(t)/a(o)$ calculated from Equation 33 and the experimental measurements (Table I). There was no large production of tritium in any of these experiments. In fact, for the co-deposition experiments the measured tritium activity was less than that measured in the control sample where no electrolysis was performed.

There is an interesting difference between Cell A and Cell B with respect to tritium. The amount of tritium measured in Cell A is significantly larger than that in Cell B despite the fact that more D_2O electrolysis occurred in Cell B. This difference yields a twelve sigma significance level ($14.24 / \pm 1.12 = 12.7$). The only other long term electrolysis experiments was in the Fleischmann/Pons cells and gave tritium results within a two sigma error range (Table I).

SUMMARY

Excess heat effects were observed in Cell A using a palladium cathode that previously produced positive results. No excess heat was found in Cell B with a palladium cathode that previously failed to give any excess power production. Later experiments produced excess heat in Cell B using small palladium particles in a novel fluidized bed approach. These palladium particles produced larger amounts of excess power under pulse electrolysis conditions. No excess heat was observed, as expected, for platinum particles in Cell A.

Fleischmann-Pons type cells gave excess heat effects for Pd-0.5B and Pd-Ce cathodes, but no excess power was observed for the cell using a Pd-Ce-B cathode. Experiments involving the co-deposition of palladium and deuterium from the D_2O solution produced excess power in all three cells. However, recombination cannot be completely ruled out as an explanation for this excess heat. An electromigration experiment also produced evidence for excess heat.

Although these excess power effects are small (400 mW or less), they cannot be explained away by experimental errors. They contribute to the body of scientific evidence for the presence of anomalous effects in deuterated metals.

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APPENDIX A

TEMPERATURE-DEPENDENT CALORIMETRIC PARAMETERS

$$C_{P,D_2} = 28.9778 - 1.49226 \times 10^{-3} T + 4.14779 \times 10^{-6} T^2 + 0.26544 \times 10^{-5} T^{-2} \text{ (J mol}^{-1}\text{K}^{-1}\text{)}$$

$$C_{P,O_2} = 23.1436 + 18.2628 \times 10^{-3} T - 6.605 \times 10^{-6} T^2 + 1.2118 \times 10^{-5} T^{-2} \text{ (J mol}^{-1}\text{K}^{-1}\text{)}$$

$$C_{P,D_2O(g)} = 26.7006 + 21.2897 \times 10^{-3} T - 2.66774 \times 10^{-6} T^2 + 1.2907 \times 10^{-5} T^{-2} \text{ (J mol}^{-1}\text{K}^{-1}\text{)}$$

$$C_{P,D_2O(liq)} = 200.13 - 495.9 \times 10^{-3} T + 573.07 \times 10^{-6} T^2 - 16.765 \times 10^{-5} T^{-2} \text{ (J mol}^{-1}\text{K}^{-1}\text{)}$$

$$L_{,D_2O(liq)} = 85263.9 - 173.429T + 0.2586 T^2 - 1.91913 \times 10^{-4} T^3 - 1805569 T^{-1} \text{ J mol}^{-1}\text{)}$$

$$\text{Log } P^{\circ}_{D_2O} = 35.47686 - 3343.93 T^{-1} - 10.9 \log T + 0.0041645 T + 9.14056/(197.397 - T)$$

$$P = (0.98 P^{\circ}_{D_2O}) P^*$$

$$E_H = 1.5318346 - 0.0002067 (T - 273.15) \text{ (V)}$$

APPENDIX B

PULSE ELECTROLYSIS STUDIES

These studies were conducted jointly with Dr. Tripodi of Italy. The first pulse experiment involved the palladium cathode in Cell A. The pulse power was applied to this cell on January 22, 1998. The pulse width was 10 μ sec at a frequency of 5 kHz. The measured peak voltages and peak current were 16 V and 4 A, respectively, and the average input power to the cell was calculated from the equation

$$P = \sum (E_i - 1.52) I_i \Delta t_i \cdot f \quad (\text{B.1})$$

where f is the frequency of the pulse (Hz). On January 27, 1998, the average pulse power was measured as 1.164 ± 0.006 W while the calorimetric output power was 1.236 W, thus the excess power for Cell A was 0.072 W. The average cell current based on this measurement was 0.108 A. This effect is similar to the excess power level obtained using direct current electrolysis. Later that same day, the polarity of the pulse was switched so that the palladium electrode was the anode for calibration purposes. However, these results were difficult to interpret due to considerable corrosion of the palladium cathode. The addition of KCl to this cell a few weeks earlier to lower the cell voltage likely contributed to this palladium corrosion.

The pulse was applied to Cell B on January 30, 1998 using a shorter pulse (2 μ sec) and higher voltage (40 V). The excess power measurements were near zero or somewhat negative in these studies. For example, on February 6, 1998 the pulse power was measured at 1.872 ± 0.005 W while the calorimetric power measured during that same day averaged 1.873 ± 0.003 W. The average current for the pulse studies in Cell B was 0.060 A. Other measurements on Cell B, however, gave excess power values ranging from -0.044 W to $+0.011$ W. Negative P_x values of -0.020 W can be explained by the decrease in the P_{gas} term due to the lower cell current during pulse electrolysis.

The most striking effect of pulse electrolysis was found in the studies of the palladium particles. This is illustrated in Figure 15. The excess power became noticeably larger under pulse electrolysis conditions. There were no similar effects for studies using platinum particles (Figure 14). The voltage and current for a typical pulse used for the palladium and platinum particles are shown in Figure B.1. The peak voltage is nearly 100 V for this pulse while the peak current is 6 A. The pulse width is 1.0 μ s and the pulse frequency is 5 kHz. The average electrolysis current was only 0.012 A for the pulse conditions used for the platinum and palladium particles, hence the electrolyte volume changes were very gradual.

The pulse electrolysis studies produced irreversible changes in the platinum particles in Cell A. A fairly stable voltage difference existed between the platinum anode and the platinum particles at open circuit. Short circuiting these electrodes gave a current of about 5 mA for a few seconds. The cell voltage was very erratic when it was switched back to normal direct current electrolysis. These changes indicate the possibility of deuterium injection into platinum under these dynamic pulse conditions.

APPENDIX C

ELECTROMIGRATION EXPERIMENTS

These studies covered the last week (March 6 – 12, 1998) before all experiments were terminated at the NHE laboratory and were conducted jointly with Dr. Tripodi. Thin palladium wires (50 μ x 40 cm) were spirally wound on a support of nickel wire sealed in Teflon. This was formed into a coil to fit into the Fleischmann-Pons type cells with a central Pt wire (1 mm x 6 cm) as the anode. The thin palladium wire had connections at both ends for applying the electromigration current. Dynamic conditions are produced by the voltage change along the Pd wire as well as by the electrolysis. The resistance of the Pd wire prior to electrolysis was 24 ohms for Cell A-1, 20.6 ohms for Cell A-2, and 21.6 ohms for Cell A-3. The applied electrolysis current was initially 0.050 A, then 0.100 A (March 6), 0.300 A (March 9) and then 0.400 A (March 10). An electromigration current of about 0.4 A was applied to Cell A-1 on March 10 (1819200 seconds) and the electrolysis current was reduced to about 0.050 A.

Excess power measurements for this short experiment are shown in Figure C-1. There was a problem with the cell top for Cell A-3, hence the measurements for this cell were not reliable. The results for the other two cells suggest an excess power effect in Cell A-2 beginning on March 9 when the electrolysis current was increased to 0.301 A. This excess power averaged about 150 mW for the rest of the experiment. Surprisingly, there was no excess power observed in Cell A-1 where the electromigration current was applied. The calculations of the power added to this cell, however, is much more complicated than for the case of application of only electrolysis current. For example, gas bubbles produced by electrolysis were still visible even when the electrolysis current was turned off in this cell. This was due to the large voltage change along the thin palladium wire. Our calculations of the power added to Cell A-2 used to determine the excess power shown in Figure C-1 is given by

$$P = I_m E_m + I_{el} (E_{el} - 1.52) \quad (C.1)$$

where the first term is for the electromigration current and the second term is for the electrolysis current. Typical values were $I_m = 0.4065$ A, $E_m = 11.90$ V, $I_{el} = 0.0520$ A, and $E_{el} = 4.80$ V, hence $P = 5.01$ W from Equation C.1.

If this equation is correct, then there was no excess power effect in Cell A-2 despite the application of the electromigration current. Current measurements at both ends of the palladium wire were similar; for example, 0.4070 A where electrons enter the wire and 0.4065 A where electrons exit the wire. The amount of the electromigration current lost to electrolysis, therefore, is small.

Due to the small diameter of the palladium wire, its volume is quite small (0.00079 cm³) compared to its area (0.63 cm²). Therefore, the excess power of 0.150 W from Figure C.1 yields

a rather high excess power density of 190 W/cm^3 . Much higher values for excess power densities have been reported for electromigration experiments (Ref. 4).

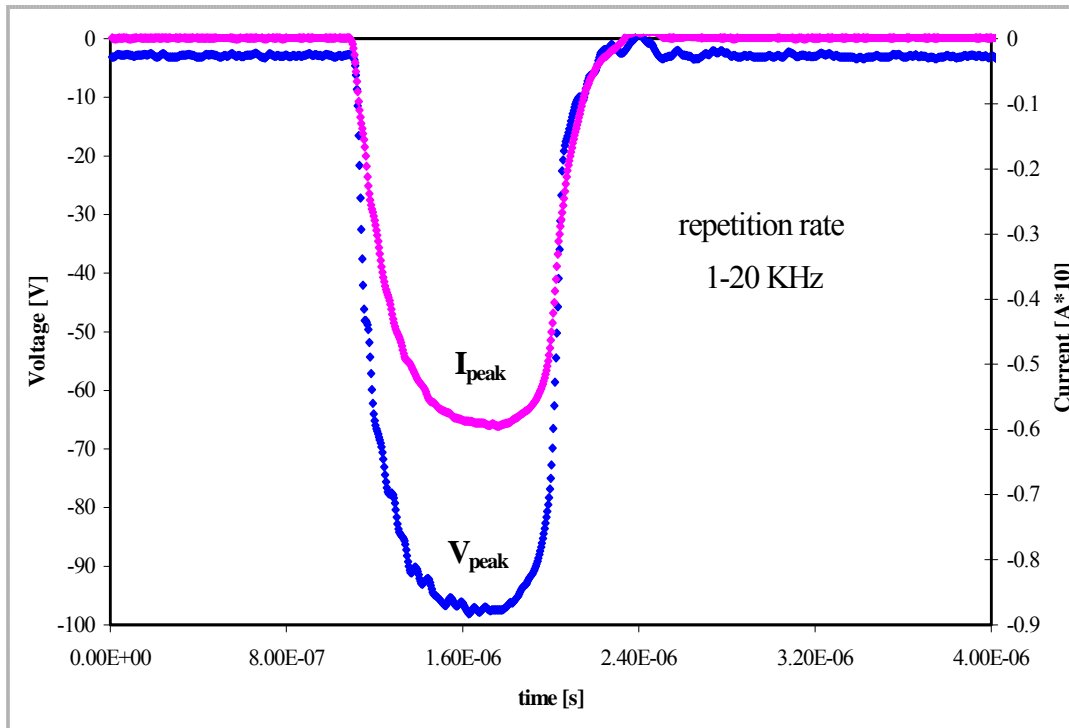


Figure B-1. The voltage and current for a typical pulse.

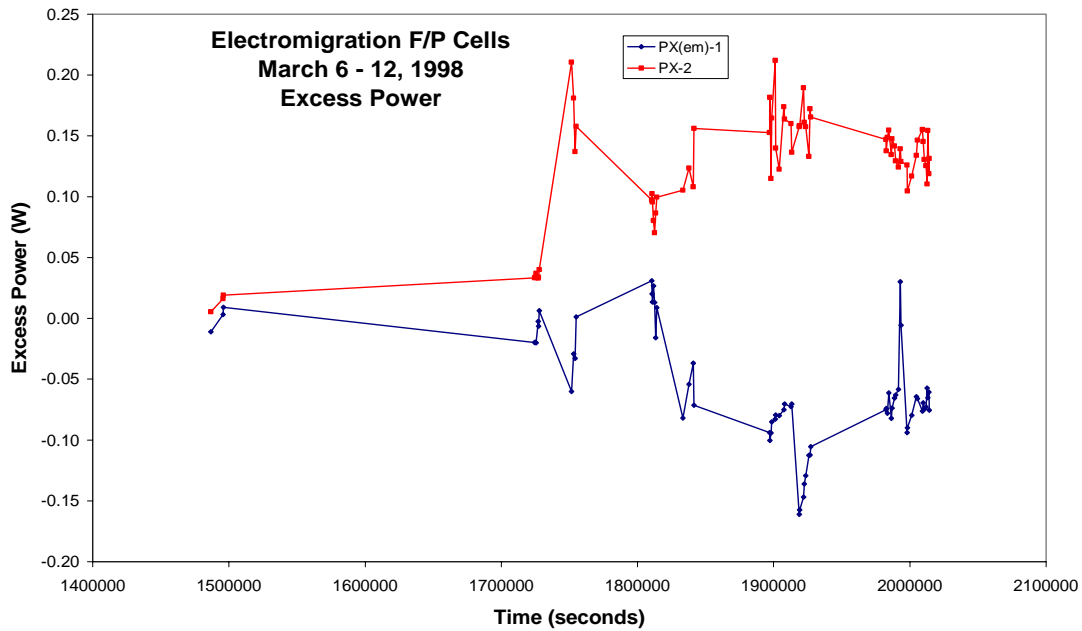


Figure C-1. Excess power measurements for thin palladium wires in electromigration experiments.