

Calorimetric Studies of Palladium Alloy Cathodes Using Fleischmann-Pons Dewar Type Cells

Melvin H. Miles
University of La Verne
1950 3rd Street
La Verne, California 91750
909-593-3511 Ext. 4646
mmiles@ulv.edu work

ABSTRACT

My first three experiments conducted at NHE using the Fleischmann-Pons (F-P) Dewar type cells investigated the Pd-Ce-B, Pd-B, and Pd-Ce alloy cathodes. Significant excess power was produced from the cells using the Pd-B and Pd-Ce alloy cathodes. The Pd-Ce-B alloy, in contrast, showed no measureable excess power effects. Previous experiments at China Lake using similar Pd-B alloy cathodes prepared by the Naval Research Laboratory (NRL) produced excess heat in seven out of eight experiments. The same Pd-Ce cathode that was used at NHE also produced significant excess power in previous experiments at China Lake. Due to the controversy over methods of data analysis for the F-P cells (see ICCF-5 Proceedings, 1995, pp. 105-115), I developed my own methods while at NHE. As I refined my methods for evaluating the calorimetric measurements, they approached more closely the methods outlined by Fleischmann and Pons in their Icarus Systems handbooks available at NHE. The method previously developed by NHE for the analysis of the F-P cells showed no excess heat for any of these same three experiments. The major problem with the NHE method is that a single calibration was used in determining the effective radiative heat transfer coefficient for the cell. An incorrect heat transfer coefficient can readily confuse the excess heat effect with the calorimetric error for the system. Calorimetric results for the same experiment using the NHE method, my method, and the F-P method for data analysis are compared. The fact that the alternative NHE method showed no excess heat for F-P cells illustrates the problem in transferring calorimetric methods from one laboratory to another. The second laboratory often fails to follow directions and makes changes that compromise the calorimetry. Similar problems were encountered in the attempt to transfer the China Lake calorimetry to NRL, hence excess heat was not observed.

INTRODUCTION

The New Energy Development Organization (NEDO) of Japan made it possible for me to return to cold fusion and to perform calorimetric experiments for a five-month period as a Guest Researcher at the New Hydrogen Energy (NHE) laboratory in Sapporo, Japan. Two types of isoperibolic calorimeters were used in these studies (1) China Lake type calorimetric cells where the heat transfer is mainly by conduction, and (2) Fleischmann-Pons Dewar type cells where the heat transfer occurs mainly by radiation. The excess power measured at NHE in the China Lake calorimetric cells has been reported elsewhere [1-5]. The focus here will be on three experiments using Pd-Ce-B, Pd-B, and Pd-Ce alloy cathodes in Fleischmann-Pons Dewar type cells. Previous experiments at China Lake using similar Pd-B alloy cathodes prepared by the Naval Research Laboratory produced excess heat in seven out of eight experiments [6,7]. The same Pd-Ce cathode that was used at NHE also produced significant excess power in previous experiments at China Lake [6,7]. The Pd-Ce-B alloy cathode prepared by NRL had never been previously investigated.

EXPERIMENTAL

The Pd-Ce-B and Pd-B (0.5 weight % boron) alloy cathodes were prepared at the Naval Research Laboratory [8], and the Pd-Ce alloy was obtained from Martin Fleischmann. In order to test possible effects of different polishing procedures, the Pd-Ce-B sample was polished using only silicon-carbide paper while the Pd-B sample was polished using normal NHE procedures involving diamond paste. The third sample, Pd-Ce, gave excess heat in a previous study at China Lake [6,7], but now contained a deep, long crack that was difficult to remove. This sample was polished by NHE procedures to remove the crack, while the final polish used silicon-carbide paper. The final dimensions of these three rods were 4.40x20.05 mm for the Pd-Ce-B sample ($V=0.305 \text{ cm}^3$, $A=2.92 \text{ cm}^2$), 4.71x20.1 mm for Pd-B ($V=0.350 \text{ cm}^3$, $A=3.15 \text{ cm}^2$), and 3.16x19.54 mm for Pd-Ce ($V=0.153 \text{ cm}^3$, $A=2.02 \text{ cm}^2$). These cathode rods were each spot welded on the side to platinum lead wires. Quick-setting Epoxy was used to cover the spot weld area, the top of the cathode, as well as the end of the glass tubing containing the platinum lead wire.

These electrodes along with the platinum anode cage structures were assembled in three similar Fleischmann-Pons cells. The platinum wire spiral anode was supported by a thin Kel-F disk containing glass rods at the base of the cell. Each cell also contained a resistive heater and two thermistors (short and long). The long thermistor was positioned in the bottom part of the cell above the electrodes while the short thermistor was located near the mid-point of the cell. The top of each cell contained a special Kel-F plug cap which seals in all of the components which protrude through it. This is to restrict all vapor to exit the cell strictly through the distillation tube also mounted in the cap. For experiments involving boiling of the electrolyte, the vapor is condensed and collected in a flask resting on an electronic balance. The Kel-F caps were sealed to the Dewar cells using clear silicon rubber and cured overnight.

The three Fleischmann-Pons cells were placed in a large water bath containing a glass window that allowed direct observations of the electrolysis. Each cell was filled with 90 cm^3 of 0.1 M LiOD+D₂O. The D₂O used throughout these experiments was from Isotec, Inc. (99.9 atom % D). The Dewar glass dimensions were 25.0 cm in height with the top 8.0 cm silvered. The outside circumference of the Dewar cell was 13.3 cm with an inner diameter of about 2.5 cm. It was determined that 82 cm^3 of the LiOD solution filled each cell to the bottom edge of the silvered portion. This mark was frequently used to determine the amount of D₂O required in refilling the cell. A special port in the cell top sealed with a solid glass rod was used to add D₂O with the aid of a graduated glass hypodermic syringe (5.0 cm^3) fitted with a stainless steel needle. An exact record was kept for all D₂O additions for each cell.

Each Dewar cell was connected to the Icarus 2.00 data acquisition system via eight connections: anode, cathode, short thermistor (2), long thermistor (2), and resistive heater (2). The power to each cell was controlled by its own potentiostat/galvanostat (Hi-Tek DT 2101) while a fourth instrument supplied power to the resistive heaters in each cell. A reading for the cell voltage, two cell temperatures, bath temperature, cell current, and time was recorded every 300 seconds for each of the three cells. These readings were also shown in real-time on the console display. This Icarus 2.00 system was similar to those used in earlier work in the IMRA-Europe laboratory in France.

CALORIMETRIC EQUATIONS AND MODELING

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

$$P_{calor} = P_{EL} + P_X + P_H - P_{out} - P_{gas} \quad (1)$$

where

$$P_{EL} = [E(t) - \gamma E_H] I \quad (2)$$

$$P_{out} = k_R (T_{cell}^4 - T_{bath}^4) \quad (3)$$

$$P_{gas} = (\gamma I / F) \{ [0.5 C_{P, D_2O} + 0.25 C_{P, O_2} + 0.75 (P / (P^* - P)) C_{P, D_2O (v)}] \Delta T + 0.75 (P / (P^* - P)) L \} \quad (4)$$

$$P_{calor} = C_{P, D_2O (l)} [M^\circ - (1 + \beta) (\gamma I t / 2F)] (d\Delta T / dt) - (1 + \beta) (\gamma I / 2F) C_{P, D_2O (l)} \Delta T \quad (5)$$

Excess power is represented by P_X and the power added to the cell via the calibration heater is given by P_H . The silvering of the top portion of the cell results in a radiative heat transfer coefficient (k_R) that is nearly independent of time. The thermoneutral potential (E_H), the heat of evaporation of D_2O (L), each heat capacity value (C_P), and the vapor pressure of D_2O (P) were always calculated based on the measured cell temperature (T_{cell}). The equations for these temperature-dependent calorimetric parameters are presented elsewhere [6]. The faradaic efficiency for the water electrolysis (γ) was always unity based on the D_2O consumption. Equations 1-5 are consistent with those reported previously by Fleischmann and Pons (9).

The use of Equations 1-5 to determine any excess power (P_X) requires the accurate determinations of two critical cell parameters: (1) the radiative heat transfer coefficient (k_R) and (2) the water equivalent of the cell ($M^\circ C_{P, D_2O (l)}$) where M° is the moles of D_2O initially present in the cell as well as at the refilled level. The values for M° is 4.97 moles of D_2O for these experiments. The actual value to be used for the water equivalent is increased somewhat by the glass and other components of the cell. The accurate methods for determining these key cell parameters are presented in detail elsewhere [10-12].

Due to the rather long time constants of these Dewar-type cells (90 minutes), the actual temperature of the cell represents a large averaging effect for 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 $\pm 0.01^\circ C$ in a single measurement of either the cell temperature or the bath temperature produces a variation in P_{calor} (Eq. 5) of ± 15 mW. This is due to the large value of $M^\circ C_{P, D_2O (l)}$ (450 J/K) multiplied by $d\Delta T / dt$ ($\pm 0.01 K / 300$ seconds). Another variation results from experimental fluctuations in the cell voltage due to gas bubbles. For example, a change of ± 0.02 V in the measurement of $E(t)$ in Eq. 2 at a cell current of 0.5 A will give an experimental variation of ± 10 mW for the electrochemical power added to the cell. These variations in the cell temperature, bath temperature, and cell voltage measurements can give compound fluctuations of ± 40 mW in any measurement of excess power based on a single point. Data averaging of all these measurements is an absolute necessity for accurate results using the Fleischmann-Pons calorimetry. Generally, an 11 point running average of the cell temperatures and voltages covering 55 minutes is used by Fleischmann [10-12].

RESULTS AND DISCUSSION

Due to the controversy involving NHE over methods of data analysis for the Fleischmann-Pons Dewar type cells [13], I developed my own methods for evaluating the calorimetric measurements. This report is based on my extensive notebook recordings of the cell

temperatures, voltages, and currents from the console display during the workday at the NHE laboratory. This data was further selected for periods of nearly steady state conditions ($d\Delta T/dt \approx 0$) where the P_{calor} term (Eq. 5) is small. This minimizes errors due to the $M^\circ C_{p,D2O(l)}$ term. The NHE method assumes a value of 490 J/K for $M^\circ C_{p,D2O(l)}$ [13]. However, both theoretical and experimental determinations yield a significantly lower value of 450 J/K for the water equivalent of these cells [10-12]. Averaged values of $d\Delta T/dt$ (Eq. 5) were used in all calculations.

The main controversy involving NHE and Martin Fleischmann is the method of determining the radiative heat transfer coefficient (k_R) for these Dewar type cells [10-13]. The NHE method relies on a single determination of k_R based on the very first application of the resistive heater (Day 3 for these experiments). Possible problems for this single determination of k_R is that the cell currents were much lower than normal (0.15 A) during this early stage of the experiments. Cell temperatures, therefore, were also rather low during this period. Another problem is that the time period of six hours for the application of the resistive heater was too short to establish a good baseline due to the long time constant for these cells (90 minutes). Furthermore, any early development of excess power and “positive feedback” would seriously compromise this single determination of k_R . This is indeed the case for the Pd-B study where both excess power and positive feedback are present for the calibration period selected [10-12]. Any error in k_R would produce a shift in the baseline for zero excess power, thus real excess power would be readily confused with errors in the calorimetry.

My method of data analysis for the Fleischmann-Pons calorimetry differs significantly from that reported by either Martin Fleischmann [9-12] or by NHE [13] and is much simpler to understand. It consists of the following steps:

1. Equations 1-5 are used exactly with all parameters calculated for the measured cell temperature. Modern computers make this quite feasible.
2. Experimental values at nearly steady state conditions ($d\Delta T/dt \approx 0$) are selected to minimize errors due to the $M^\circ C_{p,D2O(l)}$ term (Eq. 5). An estimated value of $M^\circ C_{p,D2O(l)}$ is calculated.
3. The pseudo radiative heat transfer co-efficient (k'_R) is calculated from Eq. 1 by assuming that there is no excess power ($P_X=0$).
4. The actual radiative heat transfer co-efficient (k_R) for the cell is determined by averaging over a selected time period where k'_R was high.
5. The value obtained for k_R in Step 4 is used in Eq. 1 to determine the excess power for each measurement. Averaging techniques for the cell temperature and cell voltage improve the accuracy.

This method is based on the fact that any excess power in the cell will cause k'_R to decrease. Time periods where k'_R remain high can then be assumed to represent actual periods of small or zero excess power. This method can only underestimate the amount of excess power since the value of k_R determined will be too small if any excess power were actually present. This value of k_R represents an average of many measurements under typical cell operating conditions and is related to the lower-bound value used by M. Fleischmann [10-12].

The use of this method for the Pd-Ce-B cathode suggests that the excess power, if any, is quite small for this experiment. The average experimental error in k'_R for the entire data set assuming no excess power is only $\pm 0.93\%$. Using the time period between 1033800 to 2159400 seconds (13 days) yields a radiative heat transfer coefficient of $k_R = 8.46 \pm 0.06 \times 10^{-10}$ W/K⁴ for the Pd-Ce-B cell. This time period covers typical operating conditions for the cell (0.3-0.6 A). The value

for k_R was then used in Equation 1 to calculate the excess power for the Pd-Ce-B cell. The results are shown in Figure 1.

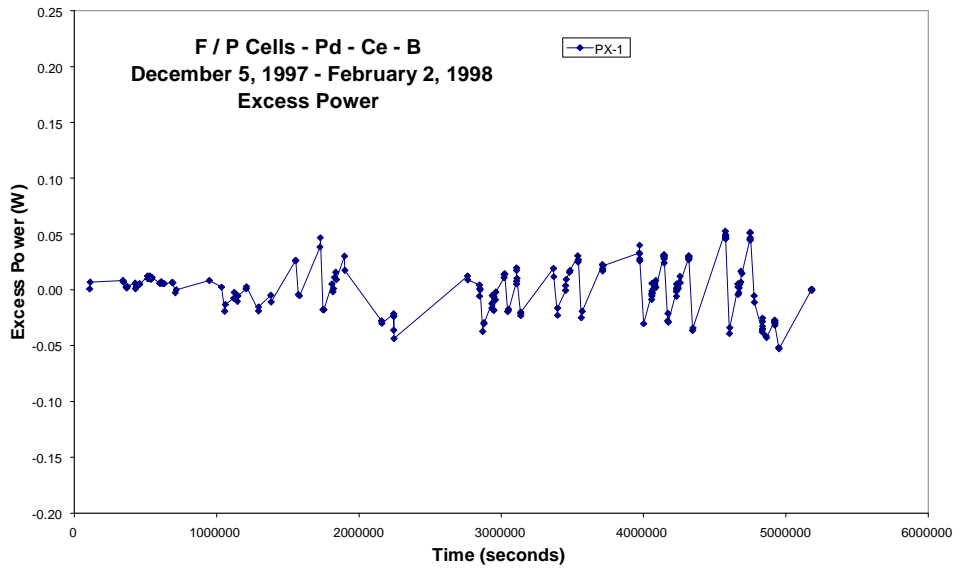


Figure 1. Excess power measurements for the Pd-Ce-B cathode.

The excess power is near zero during the entire 60 days of this experiment. The ratio of the power out ($P_{out}+P_X$) to the power in (P_{EL}) for this experiment is $X=1.002\pm 0.008$, this there is no average excess power effect within an error range of $\pm 0.8\%$. Improvements in this data analysis would require the exact determination of $M^{\circ}C_{p,D2O(l)}$ for this cell as well as further averaging of the cell voltages and the cell and bath temperatures. Extensive use of the daily application of the resistive heater could lead to improved k_R values for this cell, however, the six-hour heater time period used by NHE is simply too short for establishing accurate baselines.

This same method of data analysis was applied to the Pd-B cell. The resulting radiative heat transfer coefficient for the Pd-B cell was $k_R = 8.11 \pm 0.10 \times 10^{-10} \text{ W/K}^4$ using the time period of 2847900 to 3973800 seconds (13 days). The excess power that is calculated from Equation 1 using this k_R value is shown in Figure 2.

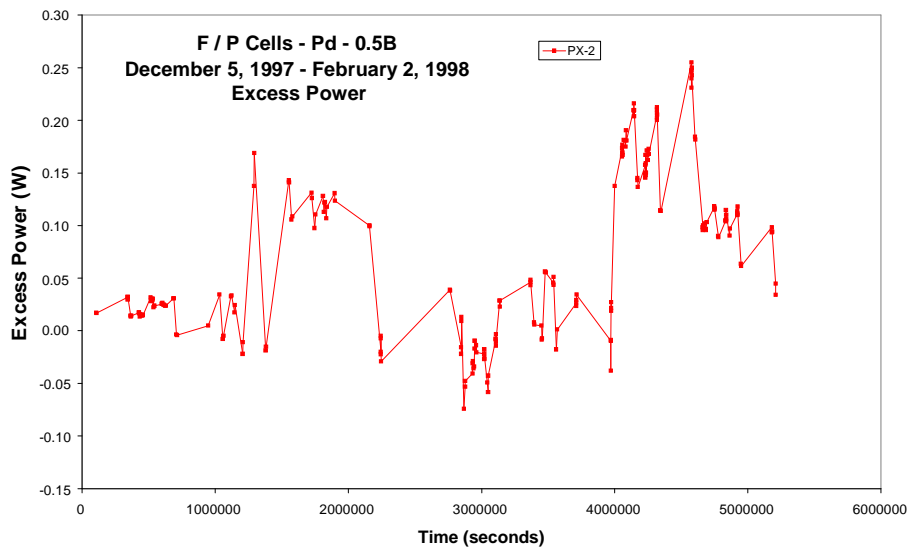


Figure 2. Excess power measurements for the Pd-B cathode.

Figure 2 shows two different episodes of significant excess power production for the Pd-B cell. The excess power reaches levels exceeding 200 mW or 0.6 W/cm^3 . For the first significant episode of excess power near 1500000 seconds, the applied cell current was typically near 0.5 A with an input power of 2.6 W and a cell temperature of 50°C . For the second large episode of excess power at 4500000 seconds, the applied cell current was again near 0.5 A, but the input power was now 3.7 W with a cell temperature of 60°C due to the passivation of the electrodes. The cell currents were generally in the range of 0.4 – 0.6 A during these experiments. This study indicates that the NHE polishing procedures do not hinder the production of excess heat.

The Pd-B results in Figure 2 show periods where the excess power becomes more negative than 50 mW. The presence of excess power during the period selected for the evaluation of the radiative heat transfer coefficient would result in a k_R value that is too small, thus negative P_X values would be expected. A detailed evaluation of the experiment by Martin Fleischmann using the entire data set yields a value of $k_R = 8.5065 \times 10^{-10} \text{ W/K}^4$ with $M^\circ C_{p,D20(1)} = 450 \text{ J/K}$ [10-12]. The use of these cell parameters eliminates negative results for the excess power. Furthermore, the actual excess power shows the same general trends as in Figure 2, but the excess power is significantly higher [10-12]. The boil-off phase for this experiment yields large excess power effects in the range of 3 to 27 W/cm^3 [10-12].

The flawed NHE method [13] applied to the Pd-B data yields a value of $k_R = 7.93504 \times 10^{-10} \text{ W/K}^4$ that is much too small. This produces large oscillations in the excess power centered around zero that are confused with errors in the Fleischmann-Pons calorimetry. This single determination of k_R based on the first application of the resistive heater is obviously incorrect. Numerous serious errors in the NHE method for this experiment are documented elsewhere [10-12].

The same method of data analysis applied to the Pd-Ce cell also shows the presence of excess power. The radiative heat transfer coefficient obtained for this cell was $k_R = 8.00 \pm 0.08 \times 10^{-10} \text{ W/K}^4$ using the time period of 1033800 to 1381800 seconds (4 days) involving cell currents of 0.3 to 0.6 A. The excess power that is calculated from Equation 1 using this k_R value is shown in Figure 3.

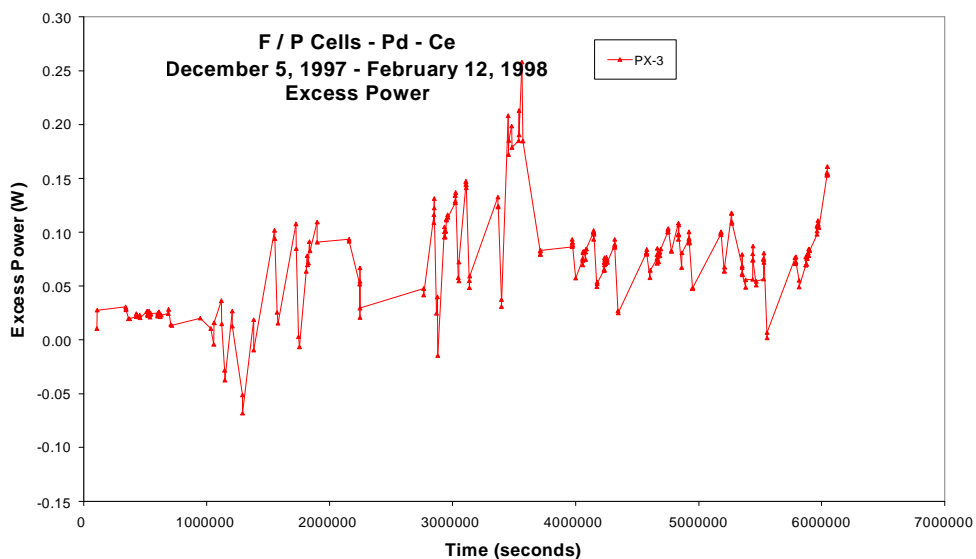


Figure 3. Excess power measurements for the Pd-Ce cathode.

The Pd-Ce alloy began producing significant excess power after fifteen days of electrolysis and

gave a fairly steady level of about 100 mW with a peak of 250 mW (1.6 W/cm^3). A negative episode of excess power exceeding 50 mW suggests that the value for k_R and hence the excess power is actually larger. The flawed NHE method [13] applied to this same data again shows no excess power and large calorimetric errors. An incorrect determination of k_R has once again confused the excess heat effect with calorimetric errors. The precise analysis of this data by Martin Fleischmann is in progress [14].

The fact that the alternative NHE method [13] shows no excess heat for the F-P cells used in these experiments illustrates the problem in transferring calorimetric methods from one laboratory to another. The second laboratory generally does not understand the system, fails to follow directions and makes changes that compromise the calorimetry. Similar problems were encountered in the attempt to transfer the China Lake calorimetry to the Naval Research Laboratory. The NRL laboratory scaled up the size of the system, added extra lead wires for loading studies, failed to average the data, and had poor room temperature control, thus their calorimetric error soared ten-fold to $\pm 200 \text{ mW}$ [8]. The excess power for the Pd-B (Fig. 2) and the Pd-Ce (Fig. 3) cathodes would not be detectable using a calorimeter with an error of $\pm 200 \text{ mW}$. A general rule for excess heat measurements is that the calorimeter must be capable of detecting 1 W/cm^3 based on the volume of the cathode. Typically, the calorimetric error must be less than $\pm 20 \text{ mW}$ for these studies.

SUMMARY

The Fleischmann-Pons calorimetry requires the accurate determination of the radiative heat transfer coefficient, k_R , and the water equivalent of the cell, $M^{\circ}C_{p,D2O(l)}$. The alternative NHE method [13] is a complete failure in the accurate determination of k_R , thus excess heat is confused with the calorimetric error for the system. These new experiments using palladium alloys in F-P Dewar type cells show significant excess power for Pd-B and Pd-Ce alloys. Previous China Lake experiments [5] also showed excess heat for these materials. My simplified method of data analysis for the Pd-B experiment shows the same general pattern for excess power as found in the more detailed and more accurate methods used by Martin Fleischmann [10-12].

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