

The Extraction of Information From an Integrating Open Calorimeter in Fleischmann-Pons Effect Experiments

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Abstract

Our first 5 months of investigating the Fleischmann-Pons effect in 1989 experiments produced no significant excess enthalpy. The November 1989 report of the Energy Research Advisory Board to the U.S. Department of Energy listed China Lake with MIT, Caltech, Harwell, and other laboratories as one of the groups not observing excess heat. Later experiments using palladium from another source (Johnson-Matthey), however, produced up to 30% excess power and 1,400 kJ of excess enthalpy. This amount of excess enthalpy is difficult to explain by any chemical reaction. Numerous experiments have shown that there is no recombination of the D₂ and O₂ electrolysis gases when fully-submerged palladium cathodes are used. Recombination can occur when palladium particles are exposed to the gas phase. In this case, our experiments prove that this recombination can be readily detected and easily corrected. In general, only about 20% of our experiments have produced measurable amounts of excess enthalpy. The cathode material used is apparently a major factor since successful experiments cluster around Johnson-Matthey supplied palladium.

1. Introduction

A previous paper has discussed the principles and problems of open isoperibolic electrochemical calorimetric systems (1). This includes the pronounced effect of the electrolyte level when the temperature is measured directly in the electrochemical cell (1,2). The measurement of the temperature in a secondary fluid or solid surrounding the cell provides an integration of the total cell power and minimizes the effect of the electrolyte level within the electrochemical cell itself.

2. Methods

Our first set of experiments in 1989 involved two different types of calorimetric cell designs: 1. the measurement of the temperature within the electrolyte of the cell and 2. the measurement of the temperature in a secondary compartment filled with H₂O and surrounding the cell (2). The second design providing an integrating open calorimeter proved to be more accurate (2). Both types of calorimeters were used in early 1989 experiments to investigate a palladium wire (Wesgo, d = 0.14 cm) and produced no evidence for any excess enthalpy production (2).

An improved calorimetry design involving temperature measurements by two thermistors (± 0.01 K) rather than by a single thermometer (± 0.05 K) evolved from these experiments as shown in Fig. 1. This calorimetric cell design and calibrations are reported in detail in previous publications (3,4).

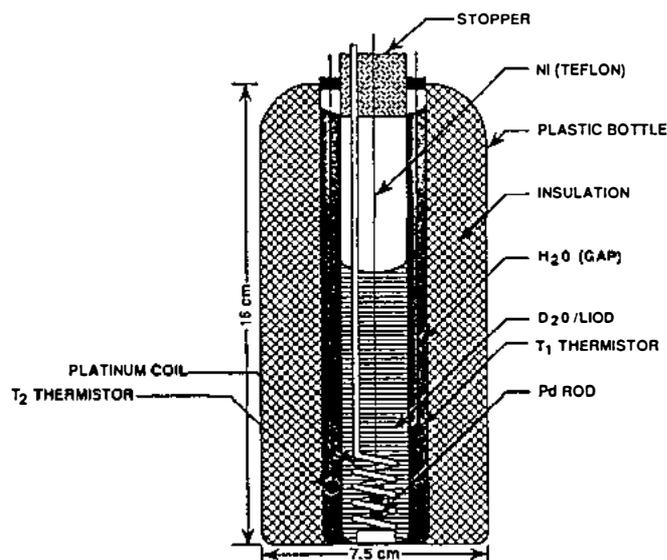


Figure 1. Electrochemical Calorimetric Cell Design.

A summary of general experimental procedures is given in Table I. Low currents (25-100 mA) are typically used for 7-10 days of electrolysis. The cell

Table I. General Experimental Procedures.

Electrodes
Pd polished with #600 silicon-carbide paper (dry)
Pd spot welded to 1 mm diameter Ni wire
Ni lead covered by shrink-Teflon
Epoxy used to mask spot-weld
Pt-coil counter electrode (symmetry important)
Cell
Pyrex glass test tubes (1.8 x 15 cm)
0.1 M LiOD (16 cm ³)
Rubber stopper sealed with silicon rubber
Calorimeter
Vermiculite and Styrofoam insulation (heat conduction)
Isoperibolic (constant surroundings)
Operations
Low currents (25-100 mA) used for 7-10 days
Cell temperatures usually 40-60°C (400-600 mA)

current is then increased to 400-600 mA that raises the cell temperature to about 40-60°C when 0.1 M LiOD is used. Any excess enthalpy will generally be measurable within 2-3 weeks of the start of the experiment. However, some experiments required 6 weeks of electrolysis before any excess enthalpy was detected. Most experiments (80%) failed to produce any significant excess heat effects. The excess power was generally in the range of 1-5 W per cm³ of palladium. The design of any calorimetric experiment should consider the size of the palladium cathode and the expected magnitude of the excess power. This is illustrated by Table II for palladium rods of 1.5 cm lengths. The cathode size should be sufficient to yield an excess power effect that can be readily measured.

Table II. Excess Power as a Volume Effect
($P_x \approx 1 \text{ W/cm}^3$).*
(Palladium rods length = 1.5 cm)

Diameter (mm)	Area (cm ²)	P _x (W)
1	0.48	0.012
2	0.97	0.047
3	1.48	0.106
4	2.01	0.188
6	3.11	0.424

Caltech Study: $V = 0.073 \text{ cm}^3$ (0.21 x 2.1 cm)
MIT Study: $V = 0.071 \text{ cm}^3$ (0.1 x 9 cm)

* Must scale cathode to yield P_x of 3 σ or larger above calorimetric error. (NAWCWPNS, 1 $\sigma = \pm 0.020 \text{ W}$).

3. Results

Our first set of experiments conducted over a 5-month period (April-September 1989) produced no significant evidence for any excess enthalpy production. For example, a palladium cathode (Wesgo, $d = 0.14 \text{ cm}$) in D₂O-LiOD produced a ratio (X) of power out/power in of $X = 1.00 \pm 0.04$ while a platinum cathode control in a similar solution yielded $X = 0.97 \pm 0.06$ (2).

The early experiments at China Lake were listed in the Energy Research Advisory Board report to the U.S. Department of Energy as one of the groups not observing excess heat (5). The groups from MIT, Caltech, and Harwell also reported no evidence for excess heat (5) and discontinued their experiments after a few months of investigation. We continued to investigate other palladium samples and eventually observed significant evidence for excess enthalpy from the use of Johnson-Matthey palladium rods (3, 4). In fact, for electrodes cut from one particular palladium rod, 7 out of 8 experiments produced the excess enthalpy effect. The level of excess power observed in our experiments (1 W/cm³ Pd) was very similar to that reported by Fleischmann and Pons for the current densities (100-200 mA/cm²) that were used (3, 4, 6).

Most experiments have failed to produce any significant evidence for excess enthalpy production. A typical experiment producing no excess enthalpy is shown in Fig. 2. For the two cells run in series, the mean X-values were 0.993 ± 0.014 for cell A and 0.982 ± 0.022 for cell B. We have encountered long time periods lasting almost a year (January 1991 to December 1991) where no significant excess enthalpy was detectable. This makes progress very slow in this field. Approximately 20% of our experiments have produced significant levels of excess enthalpies.

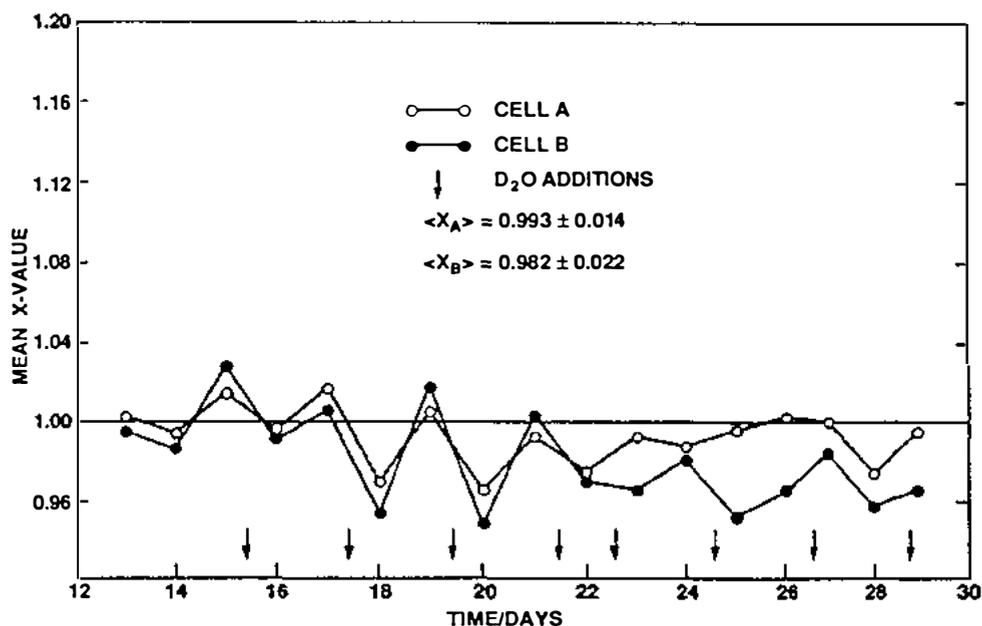


Figure 2. Calorimetric Studies Showing No Excess Power (3-19 August 1992)

Many experiments have proved that the recombination of D_2 and O_2 electrolysis gases does not occur to any significant level for experiments using a fully-submerged palladium cathode (4, 7). Some scientists, however, ignore this evidence and continue to claim that the excess heat effect can be explained by recombination (8). The extent of any recombination can be determined by measuring the rate of evolution of the $D_2 + O_2$ electrolysis gases (4). In addition, the volume of D_2O added to replenish the cell each day provides a secondary check of any significant recombination effect. We have never detected any significant recombination of the D_2 and O_2 electrolysis gases when fully-submerged palladium cathodes are used.

There are completely different types of electrolysis experiments where recombination can occur such as the co-deposition of palladium metal and deuterium from a D_2O - $PdCl_2$ - $LiCl$ solution onto a copper substrate. This method reported by Szpak et al. (9) provides for a high-purity palladium deposit that is simultaneously loaded with deuterium. However, this palladium deposit is often dendritic in nature, hence the palladium becomes detached from the electrode, floats in the solution, and adheres to the cell wall above the D_2O electrolyte level. This

finely-divided palladium acts as an excellent catalyst for recombination and sometimes yields loud explosions. Recombination in the gas phase is quite likely in this co-deposition experiment. The extent of this recombination can be readily determined by measuring the current efficiency (γ) for the D_2O electrolysis. This is determined by the rate of evolution of the $D_2 + O_2$ electrolysis gases. The resulting γ can be easily applied to the calorimetric equations (1) to correct for any apparent excess enthalpy produced by recombination.

A typical co-deposition experiment where significant recombination occurs is shown in Fig. 3. The apparent excess power reaching levels up to 18% could be readily corrected for recombination by the simultaneous measurement of the rate of evolution of the $D_2 + O_2$ electrolysis gases used to determine the current efficiency (γ). The corrected values for X were then close to unity, and the overall ratio of power out/power in was $X = 1.0005 \pm 0.022$; i.e., no significant excess power was observed after applying the correction for recombination. The results in Fig. 3 show that recombination can be readily detected and easily corrected.

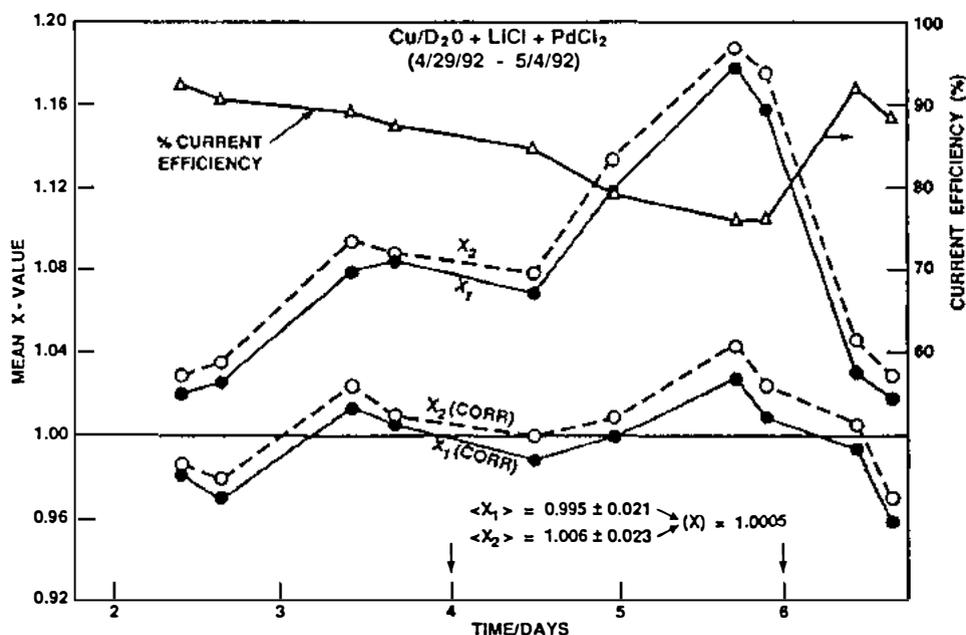


Figure 3. Effect of Deuterium-Oxygen Recombination in a Palladium Deposition Experiment.

Table III presents the total excess enthalpy observed in various experiments. These values range from 248 kJ for the shortest excess enthalpy period (11 days) up to 1,400 kJ for the longest period of excess heat (83 days). The complete combustion of all palladium within the cell to PdO and all the absorbed deuterium to D_2O would only yield about 6-7 kJ for the mass of palladium used (4.3 g). Thus chemical reactions cannot explain the total excess enthalpy that was measured. There was also evidence for 4He production in the 1990, 1991, and 1993 experiments (4, 10, 11).

Table III. Total Excess Enthalpy in Various Experiments.

Year	Cathode	Excess enthalpy	Days/cell	Comments
1989	JM Pd (6.35 mm)	210 kJ	26/B	
1989	JM Pd (6.35 mm)	220 kJ	26/A	
1989	JM Pd (6.35 mm)	300 kJ	38/A	
1990	JM Pd (6.35 mm)	1,400 kJ	83/A	Helium, glass flasks, U or Texas
1991	JM Pd (6.35 mm)	48 kJ	11/B	Helium, glass flasks, Rockwell
1993	JM Pd (1 mm)	290 kJ	66/B	Helium, metal flasks, DOI ^a



^a Helium analysis by Department of Interior Laboratory, Amarillo, Texas.

4. Discussion

The palladium material used in the Fleischmann-Pons effect experiments seems to play a major role in the success rate. Some palladium sources yield a high ratio of experiments that produce excess enthalpy while other palladium sources yield no excess enthalpy in any experiments.

Table IV provides a summary of China Lake experiments for various sources of palladium. The diameter (d) and volume (V) of the palladium cathode is also shown. The first three sources (JM, F/P, JM) are all Johnson-Matthey palladium and yield a combined success rate of 12 out of 17 experiments. Many other palladium sources produce no experiments that show the Fleischmann-Pons excess enthalpy effect. This polarization of successful experiments would be very difficult to explain by random errors. These results indicate that the metallurgical preparation of the palladium is a major factor for observation of the excess enthalpy effect. Possible variables include the palladium metal grain size and the levels of impurities.

The small amount of palladium used in the co-deposition experiments would yield only 2 mW of excess power at 1 W/cm³ of palladium. This small level of excess power would not be detectable by our calorimetry. Two of the 34 experiments, however, produced significant excess power levels that remained even after correcting for recombination. Excess enthalpy, tritium production, and the presence of some form of radiation has been reported for co-deposition experiments (9).

Table IV. Palladium Materials (March 1994 Summary).

Source ^a	d (cm)	V (cm ³)	P _x /V (W/cm ³)	Success ratio
JM	0.63	0.36	1.3	9/14
F/P	0.20	0.038	1.6	2/2
JM	0.10	0.016	2.5	1/1
Tanaka (Japan)	---	0.05	1.2	1/3
JM	0.40	0.20	0	0/1
IMRA (PdAg)	0.40	0.20	0	0/1
NRL	0.40	0.25	0	0/4
JD	---	0.04	0	0/2
Pd/Cu	(0.63)	0.02	0	0/2
Wesgo (1989)	0.14	0.09	0	0/6
Co-Deposition (1992)	(0.63)	0.002	75	2/34

^a JM = Johnson-Matthey, F/P = Fleischmann/Pons,
NRL = Naval Research Laboratory, JD = John Dash,
Pd/Cu = palladium-plated copper.

5. Conclusions

Our experiments show that the patience to continue experiments over long time periods is essential to observing the excess enthalpy effect reported by Fleischmann and Pons. Our 1989 results were very similar to the reports by Caltech, Harwell, and MIT, and others over the April-September time period, i.e., no excess heat was detected. The major difference is that we continued to investigate palladium from other sources and eventually observed significant excess enthalpy production. The ratio of successful experiments, nevertheless, remains low. Apparently, some metallurgical property of palladium is a major factor for producing the Fleischmann-Pons effect.

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