
Excess Energy and Nuclear Products

Improved, Open Cell, Heat Conduction, Isoperibolic Calorimetry

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Abstract

Significant calorimetric improvements have been realized at our laboratory. These improvements include the calorimetric hardware design, theoretical modeling, computerized experimental control, data acquisition, and extensive averaging of experimental measurements. The absolute calorimetric accuracy for operating over the entire temperature range from bath temperature to near boiling temperatures (0 to 5 watts of input power) was better than ± 10 mW or $\pm 1\%$, whichever is larger. This improved calorimetry yielded a short-term precision of ± 0.2 mW or $\pm 0.1\%$ of the input power. The noise level ($\pm 0.1\%$ or ± 0.2 mW, peak to peak) is very low compared to other known calorimetric systems in use. Control experiments consisting of silver cathodes in 0.1 M LiOD showed no excess heat to within experimental error. In live experiments using palladium and palladium-boron alloys as cathodes, the exothermic heat of loading of deuterium into the metal is readily measurable. Small amounts of sporadic excess power were seen in one experiment using a palladium cathode.

1. Introduction

Accurate, sensitive calorimetry that is appropriately scaled to the electrode size and that has sufficient time resolution is essential to the study of the Fleischmann-Pons excess heat effect in the palladium-LiOD + D₂O system. As a general rule, the calorimetry must be capable of readily detecting an excess power level of about one watt per cubic centimeter of palladium that is used.¹ Accurate calorimetry is also needed to show the exothermic loading of deuterium into the palladium.² Finally, Jones et al.³ have suggested possible energy storage in the cell and phase transitions to explain excess heat measurements. Our improved calorimetry shows that there is no energy storage mechanism in the Fleischmann-Pons type experiments.

2. Experimental

Our basic electrochemical calorimetric cell design is described in previous publications.^{4,5} The use of the appropriate equations along with a room temperature correction yields an error range of ± 20 mW or $\pm 1\%$ of the input power (whichever is larger) for our integrating, open isoperibolic calorimetry.¹ Based on our extensive previous experience with this calorimetry, various improvements were made to eliminate or minimize most of the error sources. This new calorimetry and improvements are illustrated in Figure 1. The major new improvements include a copper inner jacket that acts as the integrator and replaces the H₂O jacket used previously. An insulating box over the cell top and bath greatly reduces the effect of changes in the room temperature. Furthermore, the lead wires coming out of the cell top are thermally staked to the bath itself, thereby further reducing the effect of the room temperature. A copper outer jacket contacts the bath and minimizes bath level effects by virtue of its high thermal conductivity. This outer jacket helps form an isothermal outer surface that makes the calorimetry less sensitive to air temperature change over the bath.

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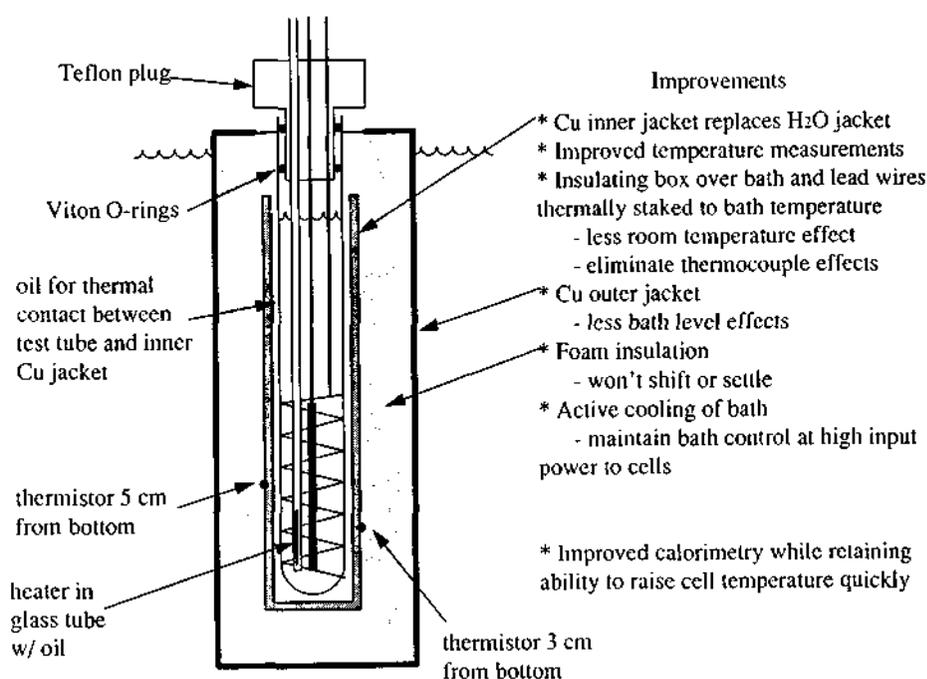


Figure 1. Improved design for integrating, open, isoperibolic calorimeters developed at China Lake.

The electrochemical cell shown in Figure 1 is a Pyrex test tube with an 18-mm outer diameter and a 15 cm length. The cell top consists of a machined Teflon plug with Viton O-rings. The 1-mm nickel lead wires are covered with double-walled shrink Teflon tubing. Spot-welding was always used to join the lead wires and electrodes. The shrink Teflon tubing extends over the spot weld and prevents any exposure of the nickel lead wire to the solution. The cathodes tested were 1-mm and 2-mm diameter wires and rods consisting of palladium, palladium-boron, and silver (for calibrations) ranging from 4 to 4.3 cm in length. The counter electrodes were made from 0.5 mm diameter platinum wire, 100 cm in length and coiled to 5 cm from top to bottom of the coil. The cell volume was 19 mL of 0.1 M LiOD + D₂O when full, while 10 mL was the smallest volume allowed during calorimetric measurements.

The inner copper jacket shown in Figure 1 is a very important improvement. This jacket consists of 3/4 inch copper plumbing pipe cut to 12 cm in length. The use of this jacket greatly reduces the electrolyte level dependence of heat conduction through the sides of the calorimeter. Ideally, the inner copper jacket makes an isothermal surface whose dimensions do not change with the changing electrolyte level. Mineral oil is used for the thermal contact between the glass electrochemical cell and the inner copper jacket. Two thermistors are set in groves in the inner copper jacket for temperature measurements. This has several important advantages over calorimeters that measure the temperature in the electrolyte. First, the temperature is smoothed over time so that any rapid fluctuations in cell temperature are integrated to yield lower noise and more accurate temperature readings. The noise in the temperature measurements is typically about 0.001°C for the calorimetry shown in Figure 1. This allows very smooth and accurate derivatives of the cell temperature versus time to be calculated. Second, mixing of the electrolyte is no longer an issue when the temperature is measured in the isothermal jacket. Although local temperatures in the cell may be of interest for understanding heat production within the cell, the temperature of the isothermal jacket remains the only temperature of interest for calorimetric measurements. The only exception to this is for very rapidly changing cell temperatures such as during D₂O additions or changes in the cell input power.

Common foam tubing insulation for plumbing pipe is used for insulation between the inner and outer copper jackets shown in Figure 1. An appropriate size for a tight fit is selected so that no

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shifting is possible. This allows these calorimeters to be disassembled and reassembled without any change in dimensions.

A 100-ohm constantan wire is used for an additional calibration and temperature control heater in the cell as seen in Figure 1. This heater wire is coiled in a 3-mm outer diameter Pyrex tube containing mineral oil for thermal contact. These heaters were carefully constructed to provide good thermal contact and accurate voltage measurements.

Two calorimetric cells were always connected in series. These cells were also connected in series with two resistors that provided accurate and redundant measurements of the cell current. These resistors were a 10-ohm constantan wire with Teflon insulation and a 1-ohm commercial power resistor. Voltage measuring leads were attached and the connections sealed. These resistors were immersed in the bath to maintain them at constant temperature in order to minimize errors from resistance changes due to temperature. This provided for very accurate current measurements ($\pm 0.01\%$). The heaters for the two cells were also connected in series. Furthermore, they were also connected in series with another pair of resistors, identical to those described above, that provided accurate measurements of the current through the heaters.

The two calorimetric cells connected in series were immersed in a constant temperature bath set to approximately 22°C. Active cooling of the bath allows the controller to operate with a more uniform power load that provides better bath temperature control and keeps the bath temperature from rising during high cell input powers. Short term (1 hour) fluctuations in the bath temperature were less than $\pm 0.01^\circ\text{C}$.

The thermally insulating box built over the bath to control the air temperature above the bath contained a small fan to circulate the air. This box was continually purged with a low flow rate of nitrogen gas that was conditioned to bath temperature by passing it through a coil of copper tubing immersed in the bath. This served to reduce the humidity in the box as well as providing a safety measure to prevent deuterium and oxygen gases from accumulating in the box in the event of a leak in the cell gas discharge tubes. This insulating box reduced the air temperature fluctuation to 1/8 of the normal daily fluctuation (1-3°C) of the air temperature in our laboratory.

3. Data Acquisition and Control System

The data acquisition and control system consisted of a 486 PC computer connected via GPIB connections to a Keithley Model 7002 switch system, a Keithley model 193, 6 and 1/2 digit digital multimeter (DMM), an EG&G PAR 273 Potentiostat/Galvanostat (cell power source), and a Keithley 228 voltage/current source (heater power source). The Keithley Test Point software was used and extensively programmed to provide complete instrument control, data acquisition, and display of data in real time, both digitally and graphically. The Keithley switch system was used to connect the various electrical connections to the K193 DMM. This included 10 temperature channels (1—air, 2—box air, 3—bath, plus two temperature measurements for each cell) and 8 voltage channels. Thermistors were used in all temperature measurements. Their resistances were measured directly with the K193 DMM which were then converted to temperatures. There was negligible self-heating of the thermistors. Extreme care was taken so that all quantities (temperatures, cell voltage, cell current) could be measured to four digits of accuracy. This is very important when attempting to measure 1 mW accuracy at 5 W input power. This was our goal for this new calorimetry.

Computer averaging and appropriate data collection are very important for this calorimetry. Under constant current conditions, cell voltages vary erratically and often quite widely during electrochemical experiments due to bubble formation and release.¹ This is especially true for the high current densities ($\geq 100 \text{ mA/cm}^2$) required for excess heat effects.⁶ These voltage fluctuations often

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exhibit a periodicity on the order of a minute. It is extremely important that the cell voltages are sampled often and averaged over a sufficiently long time period in order that the cell input power is measured accurately. The input power measurements limit the performance of many calorimetric systems, both in accuracy and noise.

For our system, data is collected as fast as the switch and DMM settling time allows. The measurements of cell voltages and currents are made 14 times as often as the other 14 measurements (10 temperatures, 2 heater voltages, and 2 heater current resistor voltages). The measurements are averaged and recorded to disk every five minutes. During this 5-minute period, there are typically 112 measurements of each cell voltage and current along with 8 measurements of the other calorimetric quantities such as temperature. This provides sufficient averaging for smooth and accurate input power measurements.

4. Calorimetric Modeling

Heat conduction, isoperibolic calorimeters are generally modeled with a $K\Delta T$ term for heat conduction from the cell to the bath.^{1,4,5} However, for the new calorimeter shown in Figure 1, it was found that the use of a $K_{3/2} (T_{cell}^{3/2} - T_{bath}^{3/2})$ term provided a better fit of the experimental data over a wide temperature range for the cell. The foam insulation used in this calorimetric system (Figure 1) approximates heat conduction through a motionless gas. The heat conduction for a motionless gas is proportional to $T^{1/2}$ which yields the $T^{3/2}$ term when integrated through the thickness of the wall of the calorimeter.⁷ Therefore, the set of equations used for modeling the calorimeter shown in Figure 1 are as follows:

$$P_{\text{excess}} = P_{\text{out}} - P_{\text{in}}$$

$$P_{\text{in}} = (V_{\text{cell}} - E_h(T))I_{\text{cell}} + V_{\text{heater}}I_{\text{heater}}$$

$$P_{\text{out}} = P_{\text{conduction}} + P_{\text{Cp}} + P_{\text{evap}}$$

$$P_{\text{conduction}} = K_{3/2} (T_{\text{cell}}^{3/2} - T_{\text{bath}}^{3/2}) \quad \text{-heat conduction through foam insulation}$$

$$+ K_2 (T_{\text{cell}} - T_{\text{bath}})^2 \quad \text{-additional term added experimentally for improvement}$$

$$+ K_{\Delta L} \Delta L (T_{\text{cell}} - T_{\text{bath}}) \quad \text{-changing heat conduction through lead wires with electrolyte level}$$

$$+ C$$

$$P_{\text{Cp}} = C_{p(D2O)}(T) dT/dt (M_0 + \Delta M) \quad \text{- heat capacitance term, - power required to change the temperature of the calorimeter}$$

$$P_{\text{evap}} = L_{(D2O)}(T) (0.75 I/F) (P_{D2O}/(P_{\text{atm}} - P_{D2O})) \quad \text{- latent heat of evaporation}$$

where

ΔM = molar loss of electrolyte (due to electrolysis and evaporation) since the cell was last filled

ΔL = distance of electrolyte level below full level

dT/dt = derivative of Temperature with respect to time, calculated from the previous, current, and next points

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The temperature dependence of the terms $L_{(D_2O)}(T)$, $C_{p(D_2O)}(T)$, P_{D_2O} , $E_h(T)$ is given elsewhere.¹ The constants, $K_{3/2}$, K_2 , K_{AL} , M_0 , C are calculated from calibration run data. Typical constants for cell 1 are $K_{3/2} = 0.0027295 \text{ W}\cdot\text{K}^{-3/2}$, $K_2 = 0.000060611 \text{ W}\cdot\text{K}^{-2}$, $M_0 = 2.0819 \text{ mol}$, $K_{AL} = 0.00069436 \text{ WK}^{-1}\text{cm}^{-1}$, and $C = -0.0020172 \text{ W}$.

5. Calorimetric Results

Results using this new calorimetric system are presented elsewhere.^{1,2} For example, Figure 1 of Reference 2 presents the measurement of the exothermic heat of absorption of deuterium into a palladium wire. This yields 5 mW of power over a two-hour period which can be readily measured to within $\pm 0.2 \text{ mW}$ using the new calorimetry. The measured exothermic heat of absorption correlates very well with that calculated for the palladium volume used assuming loading to $\text{PdD}_{0.6}$. This accurate calorimetry proves that there is no energy storage or phase transitions in the cell as suggested by Jones et al.³ to explain excess heat measurements.

Figure 2 shows a fluctuating excess power effect for a 1-mm Johnson-Matthey wire cathode (1 mm x 4.3 cm) that was apparently triggered by a change in the cell temperature. About 50 mW of excess power was measured. This corresponds to 1.5 W per cubic centimeter of palladium which is approximately the level of excess power expected.^{1,8} This result demonstrates how this more sensitive calorimetry can be used to study events that may trigger or kill the excess-power effect.

Four experiments were conducted using palladium-boron alloy electrodes with this new calorimetric system. Despite previous studies which showed a high success rate for excess heat with these alloys,⁸ no excess power was measured. However, these alloy electrodes had swaged, folded-over metal regions and had to be machined prior to use to remove these defects. The poor quality of these palladium-boron cathodes may explain the lack of excess heat.

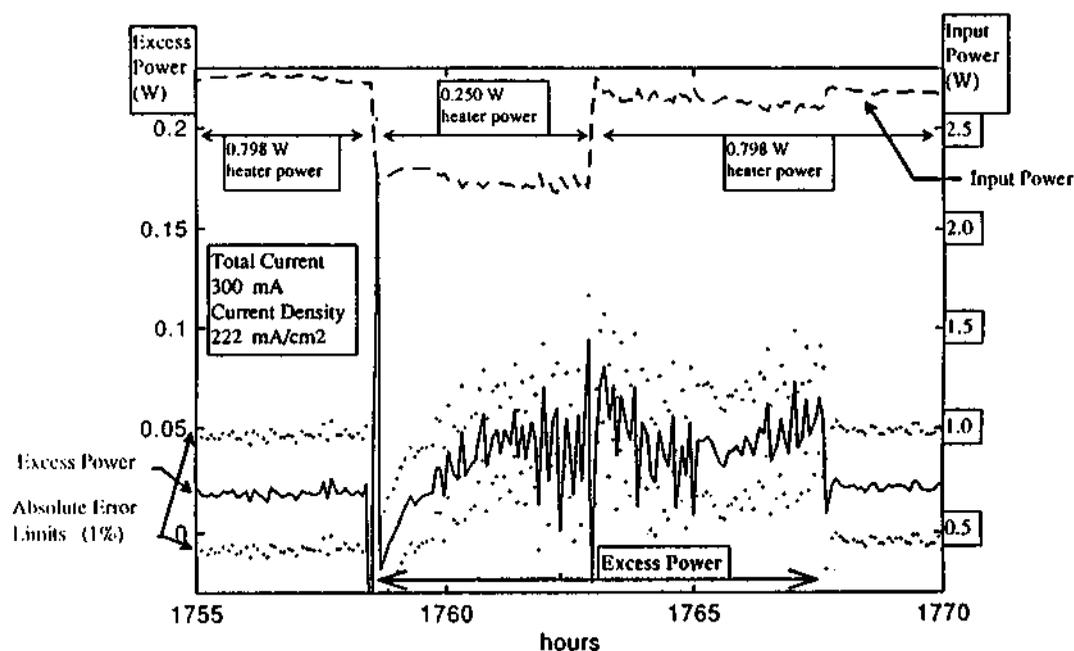


Figure 2. Fluctuating excess power effects for a 1-mm Johnson-Matthey wire cathode (1 mm x 4.3 cm). The onset of excess power began shortly after the reduction in the heater power which changed the cell temperature.

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6. Conclusions

The following specifications were realized for this new calorimetric system: The absolute accuracy is better than $\pm 1\%$ or ± 10 mW over the entire operating temperature range (bath temperature to near boiling temperatures). The short term precision is better than $\pm 0.1\%$ or ± 0.2 mW. The peak-to-peak noise level is less than $\pm 0.1\%$ or ± 0.2 mW. The percent limit is based on the input power and is always used when it becomes larger than the mW limit. The time resolution is 5 minutes point-to-point. Numerous readings are always averaged per point. The heat of absorption of deuterium into the palladium is always observed and is readily measurable with this calorimetry. Small amounts of sporadic excess power was observed in one experiment using a palladium cathode.

7. References

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