ISOTHERMAL FLOW CALORIMETRIC INVESTIGATIONS OF THE D/Pd SYSTEM

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INTRODUCTION

An experimental program was undertaken to explore the central idea proposed by Fleischmann *et al*.[1] that heat, and possibly nuclear products, could be created in palladium lattices under electrolytic conditions.

Three types of experiments were performed to determine the factors that control the extent of D loading in the Pd lattice, and to search for unusual calorimetric and nuclear effects. It is the purpose of this communication to discuss observations of heat output observed calorimetrically in excess of known sources of input heat.

The central postulate guiding the experimental program was that anomalous effects previously unobserved or presently unexplained in the deuterium-palladium system occur at a very high atomic ratio D/Pd. Emphasis was placed on studying phenomena that provide a fundamental understanding of the mechanism by which D gains access to the Pd lattice, and how very high loadings (near, at, or perhaps, beyond unity) can be achieved and maintained.

Measurements of the interfacial impedance and of the Pd cathode voltage with respect to a thermodynamic reference electrode were made in order to characterize the electrochemical kinetic and thermodynamic processes that control the absorption of D into Pd.

Measurements of the Pd solid phase resistivity were used to monitor on-line, the degree of loading atomic ratios, specifically D/Pd, H/Pd and H/D. Calibration of the resistance ratio - atomic ratio functionality has been made by reference primarily to the works of Baranowski[2-4] and Smith[5-6], but also by volumetric observation of the displacement of gas during loading in a closed system at constant pressure and temperature.

The overall conclusions of this study are that, by careful control of the electrode pretreatment, the electrolyte composition and the current density, it is possible to load Pd to an atomic ratio D/Pd >~ 1, and to sustain this loading for periods of weeks.

Calorimetric experiments were performed in palladium rods, highly loaded with D and/or H, and electrolyzed at substantial current densities (typically 300-600 mA cm^{-2}, but up to 6400 mA cm^{-2}) for considerable periods of time (typically 1000-2000 hours). The application of knowledge gained from the independent loading studies was essential in achieving these conditions.

Our calorimeters were designed with the philosophy that in precise calorimetry, and in the search for unusual reaction products, it is desirable to have a closed system, and a knowledge at all times of the composition of the reacting system. All experiments were performed with closed and sealed electrochemical cells operating from 40 to 10,000 psi above atmospheric pressure. Axial resistance measurements were made to monitor the D/Pd or H/Pd ratio.

Approximately 30 experiments have been performed with flow calorimeters operating at constant power input. The calorimeters were designed and constructed with the following features:

- Conceptually simple system based on the first law of thermodynamics.
- Maintenance of complete control of operating parameters (including cell temperature).
- A large dynamic range of heat input and output (0.1 - 100 W).
- On-line monitoring of all important variables.
- Multiple redundancy of measurement of critical variables *e.g.* temperature.
- High accuracy and precision (the greater of 10 mW or 0.1%).
- Known sources of potential error yield conservative estimates of output heat.
- Steady state operation leading to simple analysis.

EXPERIMENTAL METHODS

Two systems of flow calorimeters were designed in accordance with the principles outlined above. One system accommodated up to four large electrochemical cells (working volume up to 200 cm^3 and power input $\geq$ 100W). The other accommodated three "small" cells (working volume 50 cm^3 and power input up to ~ 30 W).

These two systems had several features in common. In both, a sealed electrochemical cell was fitted with a helically wound compensation (and calibration) heater and sheathed with axially oriented heat exchanging fins. This unit was immersed directly in the calorimeter heat transfer fluid inside an isothermal and insulating boundary (the calorimeter). The isothermal boundary was itself immersed in a well regulated ($\pm$ .003°C) bath of the same fluid. In early experiments this fluid was silicone oil, chosen for its low heat capacity, low corrosivity, and its good electrical insulation properties. In recent experiments the calorimeter fluid was water for which the heat capacity is better known and exhibits smaller dependence on temperature.

The heat transfer fluid was pumped from the bath, past the cell inside the calorimeter volume, using FMI (QV-OSS Y) constant displacement pumps. The mass flow rate was determined by pumping the flow to an auto siphon device placed on a digital balance. The control/measurement computer polled the balance periodically to determine the average mass flow rate as $\delta m / \delta t$

All experiments were performed with thermodynamically closed electrochemical cells at D_2 partial pressures between ambient and ~10,000 psi. In high pressure cells the charging current was sustained by the anodic reaction of $\frac{1}{2} D_2 + OD^- \rightarrow D_2O + e^-$ (in base). At higher anodic current densities or low D_2 partial pressures, O_2 was evolved at the anode. A large area catalyst was provided in the head space of the cells to recombine evolved O_2 and D_2 so that the net reaction in all cells after the Pd rod is loaded is $D_2O \rightarrow D_2O$, for which the thermoneutral voltage is zero.

Constant current or slowly ramped current conditions were used in all cases. Commonly, experiments were performed electrically in series in order to test the effects of different variables *e.g.* D_2O versus H_2O. Under current control, the cathode voltage and cell voltage frequently were observed to fluctuate significantly, particularly at high current densities in low pressure cells where the presence of large D_2 and O_2 bubbles disrupted the electrolyte continuity. Three electrode potentiostatic control, or two terminal voltage control of a series string, in the presence of a fluctuating load (cell resistance) will cause a fluctuation in both the cell voltage and current and make an unmeasured contribution to the input power (that may be interpreted incorrectly as excess heat) unless the *rms* levels are monitored. On the other hand, if the cell current is provided from a source that is sensibly immune to noise and level fluctuations, then the current would operate on the cell voltage (or resistance) as a scalar. As long as the voltage noise or resistance fluctuations are random, no unmeasured *rms* heating can result under constant current control.

The power input to the calorimeter by the electrochemical current was considered to be the product of that current and the voltage <u>at the isothermal boundary</u>. Under experimental conditions this input power changed due to voltage or resistance variations in the cell, or at times when the current was ramped. This had two undesirable consequences. A change in input power changed the cell temperature so that the electrochemical conditions were no longer under control. A change in the temperature also moved the calorimeter from its steady state as the calorimeter contents took up or released heat. To minimize these effects, a compensation heater was used to correct for changes in electrochemical power so that the sum of the heater and electrochemical power input to the calorimeter was held constant. A computer controlled, power supply was used to drive the compensation heater element operated in galvanostatic mode in order to avoid possible unmeasured *rms* heat input. This heater also was used for calorimeter calibration, where the input power was measured as the product of the heater current and voltage at the isothermal boundary.

Figures 1 and 2 show schematic detail of the small and large calorimeter vessels. Different strategies were employed in these two designs to minimize the conductive heat loss through the many wires which enter the vessel for electrical sensing and current control. A simple labyrinth design was used in the small calorimeter in which the electrical leads are taken from the cell by a tortuous path to the outside, and are forced to give up heat in a counterflow of incoming fluid. For the mass flow rates typically used in our experiments (1-2 g s^{-1}), the conductive power loss was of the order of 1-2% of the total input power calculated as above.
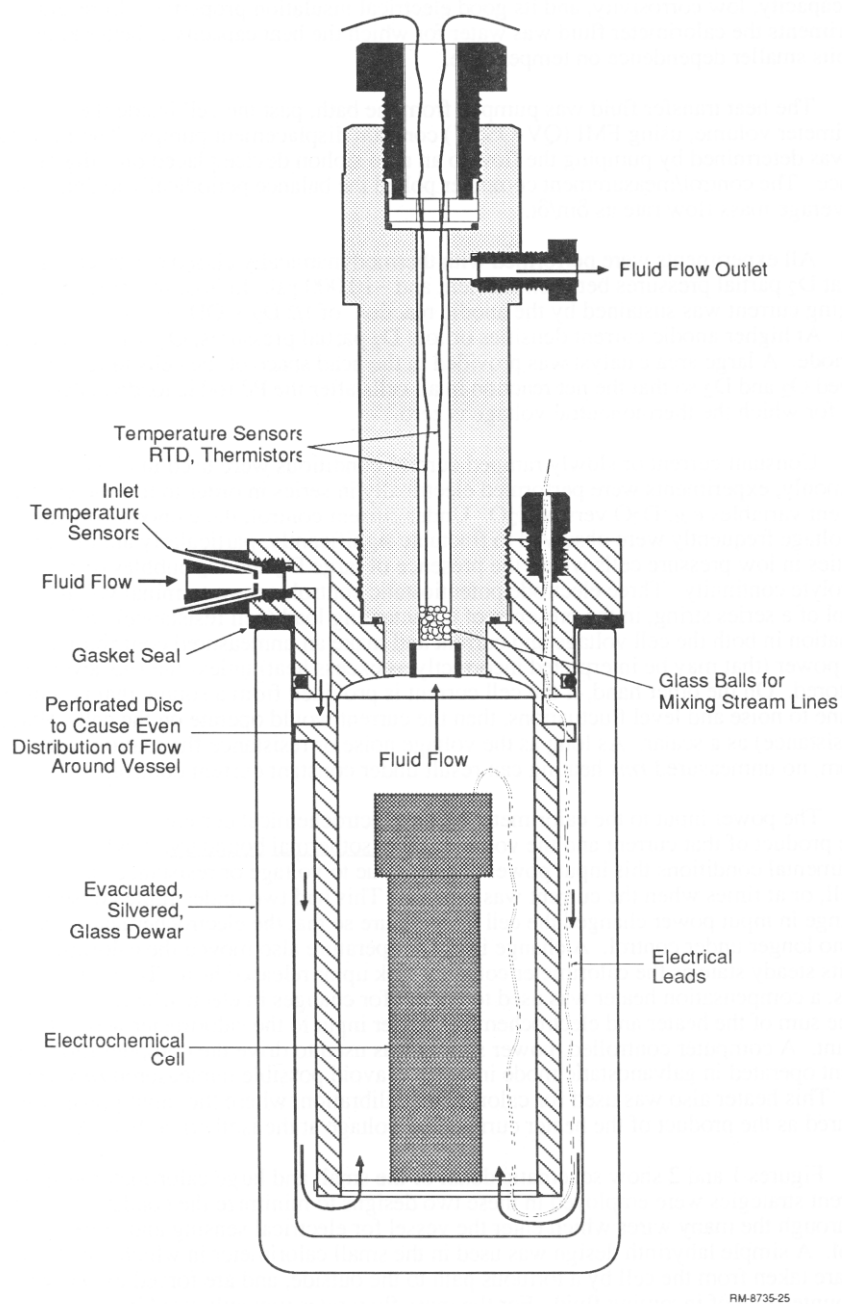
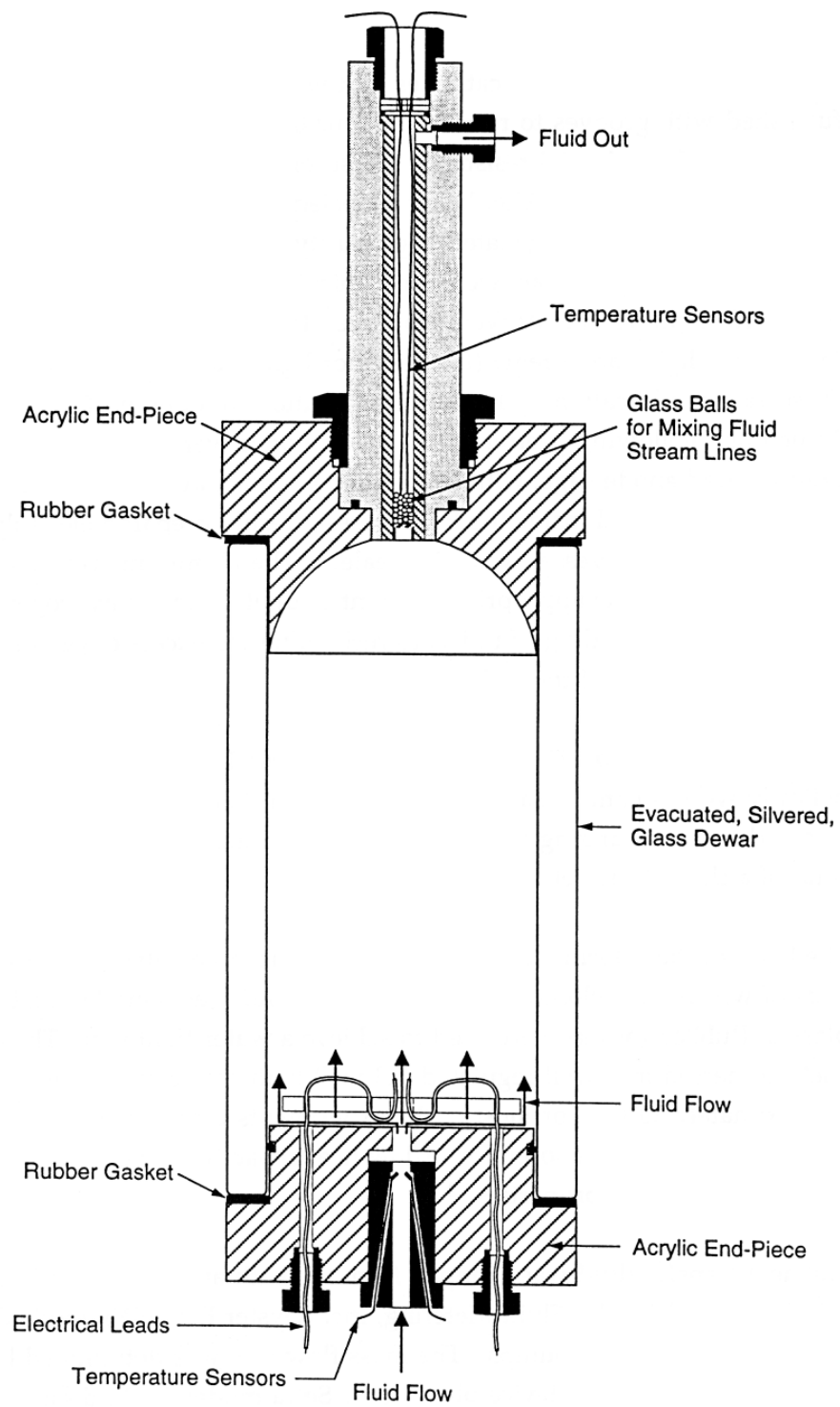**Figure 1. Small flow calorimeter, detail.**

Figure 2. Large flow calorimeter, improved design.

Advantage was taken in the large calorimeters of the fact that the incoming fluid was at the same temperature as the bath, and that predominant heat transport was upward. All electrical leads were taken through the bottom insulating boundary across which ΔT (and therefore conductive loss) was a minimum. An additional feature of the large calorimeters was the pressure pipe which extended from the cell to a pressure transducer above the bath. The pressure pipe also contained a PTFE catheter that was used to insert chemical species into operating cells. For practical reasons the pressure pipe emerged through the top insulating boundary and contributed an additional conductive loss term. For the mass flow rates used, conductive power loss in the large calorimeters represented typically 3-5% of the total input power.

The steady state equation of heat output from the calorimeter can be given as

$$P_{output} = \left(C_p \delta m / \delta m + k' \right)\left(T_{out} - T_{in} \right)$$ (1)

where C_p is the average value of the heat capacity of the calorimeter fluid in its transit through the calorimeter, $\delta m / \delta t$ is the fluid mass flow rate, k' is the effective conductive loss term, T_{in} is the inlet (or bath) temperature and T_{out} is the average temperature of the emerging fluid.

Similarly, for the power input to the calorimeter,

$$P_{input} = \left| I_c V_c \right| + \left| I_h V_h \right| + P_u$$ (2)

where I is current, V is voltage measured at the calorimeter boundary, and subscripts c and h refer to the electrochemical cell and compensation heater. The additional term, P_u, is any unaccounted power source, and may be positive, negative or zero.

Currents were measured as a voltage dropped across a calibrated, series resistor;

$$I_c = V_{cr} / R_c ; I_h = V_{hr} / R_h$$ (3)

and the primary temperature measurements were made with platinum resistance temperature devices (RTD's), so that

$$T = T° + \left(R - R° \right) / \alpha R°$$ (4)

where $T°$ is the temperature at which the device resistance is $R°$, and α is the temperature coefficient of resistance of platinum.

In examining potential sources of error, it is useful to express P_u in terms of the directly measured variables. Combining equations we obtain:

$$P_u = P_{output} - P_{input} = \left[C_p \frac{\delta m}{\delta t} + k' \right]\left[\frac{R_{out}}{R°_{out}} - \frac{R_{in}}{R°_{in}} \right]\left[1/\alpha \right] - \frac{V_h V_{hr}}{R_h} - \frac{V_c V_{cr}}{R_c}$$ (5)

This equation has three different classes of variables and constants, with different potential sources of error.

Measured variables: δm/δt, R^out, R_in, V_h, V_hr, V_c, V_cr
Predetermined constants: C_p, α, R°_out, R°_in, R_h, R_c
Calibration constant: k´

Efforts were made to maintain the accuracy of each parameter at better than 0.1%, and also to ensure that potential sources of error result in an underestimate, not an overestimate, of P_u.

Errors in temperature measurement may be attributed to errors in the ratio's R/R° or to α. Resistance measurements were made in a four terminal mode where all RTD's were multiplexed sequentially to a single multimeter calibrated against NIST traceable standards. Since temperature was measured from a resistance ratio, absolute calibration was not of primary importance, although multimeter drift must be avoided Two RTD's were used to sense the inlet and outlet temperatures; the temperature difference was then calculated from the two independent pairs. The inlet sensors were held at the bath temperature, and the bath was held constant with respect to a calibrated thermistor. The inlet RTD's can thus be regarded as secondary resistance standards, referenced to the temperature set by the control thermistor. In this way any trend in resistance due to change in multimeter calibration could be observed.

In some experiments the outlet temperature was sensed with an additional two thermistors to guard further against range-specific resistance calibration drift.

The temperature coefficient of resistance, α, is easily calculated from the Calendar -Van-Dusen equation, the constants of which for platinum are well known. White not independent of temperature, α is effectively constant within a small temperature range. This value was considered unlikely to change with time. Inlet and outlet temperatures each were measured with an accuracy of ± 0.001K.

Outlet power was determined primarily by the temperature difference and the product C_p δm/δt. In all experiments reported here, high purity, air saturated H_2O was used as the calorimeter fluid, for which the thermal capacity was taken to be 4.188 ± 0.004 J g^{-1} K^{-1} in the interval $30 \leq T \leq 40°C$.

Mass flow rates were measured using a Setra model 5000L digital balance with an accuracy of better than 0.01% (200 ± .01g / 240 ± .01 seconds). This accuracy reflects the determination of the mass delivered to the balance. Precautions were taken to ensure that fluid was not lost following its transit through the cell before flow rate determination. This was checked, and assured, by employing a ¼" line with Swagelok® fittings from calorimeter to pump, and pump to mass balance. The calorimeter vessel was placed on the negative pressure side of the constant displacement pump so that potential leaks from the bath into the calorimeter would be of fluid conveyed past the outlet temperature sensors. Beyond this point leaks would have allowed air into the system; this would not have produced errors in flow rate determination (although this may influence the flow rate).

A schematic diagram of the placement of the large calorimeters in their constant temperature bath is shown from a top view and in profile in Figures 3 and 4; Figure 5 shows the hydraulic flow system for two cells in the large bath. The cells were placed on legs to be above the bottom of the bath and in the well-mixed water. The water supplied to the bath was purified first by ion exchange and then by reverse osmosis. The rate of supply was approximately twice that withdrawn by the calorimeter pumps so that level of the bath was maintained by overflow.

In the large bath, electrochemical cells were connected electrically in series, but the calorimeter systems were hydraulically in parallel. Separate pumps were provided for each calorimeter and the flows were multiplexed for two cells to a single mass-balance. Mass flow rates were measured for one cell during the filling of the auto-siphon vessel (capacity ~ 3500 cc).

When the computer sensed that the auto-siphon was operating ($\delta m/\delta t < 0$) the output of both pumps was sent to waste. After a predetermined time, flow from the previously unmeasured cell was sent to the vessel and the cycle repeated. The constant displacement pumps used were relatively immune to a flow rate variation with small changes in head. Nevertheless, care was taken to ensure that the flow rate during the measurement period was the same as that during the eclipse when flow was sent directly to waste. This was done by ensuring that the hydraulic resistance and static heads from the pump to the point at which the flow emerges to the siphon vessel were the same as those from pump to waste. In a number of experiments the flow rate was continuously monitored volumetrically using a rotameter for each cell, to further insure against errors.

Input power was determined for both the cell and the heater as the product of two measured voltages normalized by a precalibrated resistance. Voltages were measured using a Keithley 195A 5-1/2 digit digital multimeter with 0.01% dc volt accuracy and 0.015% resistance accuracy. Resolution was 1 ppm (Ω) and 10 ppm (dcV). Each 5-1/2 digit measurement was averaged 32 times before being recorded. Resistance standards were calibrated periodically against NIST traceable standards using NIST traceable calibration-instruments yielding an accuracy of ~ 0.1 %

It is important to note that experiments typically were run with a single controlled current passing through two or more electrochemical cells in series. All measurements were multiplexed to a single multimeter that was periodically interchanged with another precalibrated meter. In this way, a series cell effectively acted as a standard for the others; if P_u was observed not to be zero in one cell while zero in another, then its origin was unlikely to be an artifact of voltmeter miscalibration. Monotonic calibration drift was monitored by multimeter interchange. The current was monitored independently in each of the cells in series so that R_c for each cell acted as a standard for other series cells. The resistors were interchanged, replaced, and removed and recalibrated during periods of excess power production ($P_u > 0$), reducing the likelihood that errors were associated with the measurement of current.
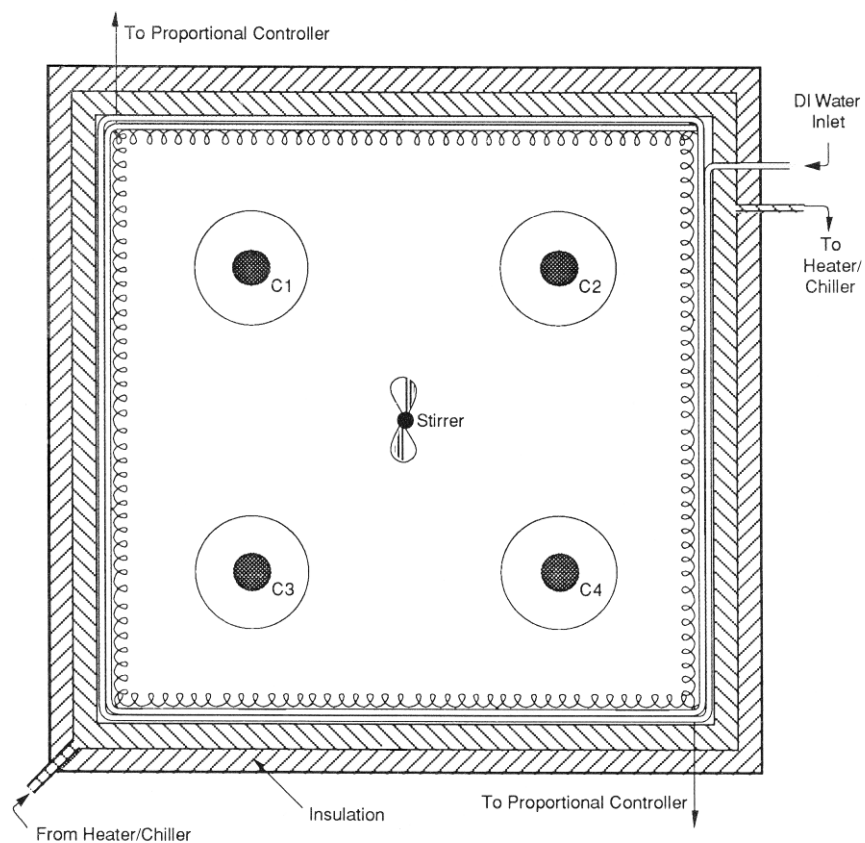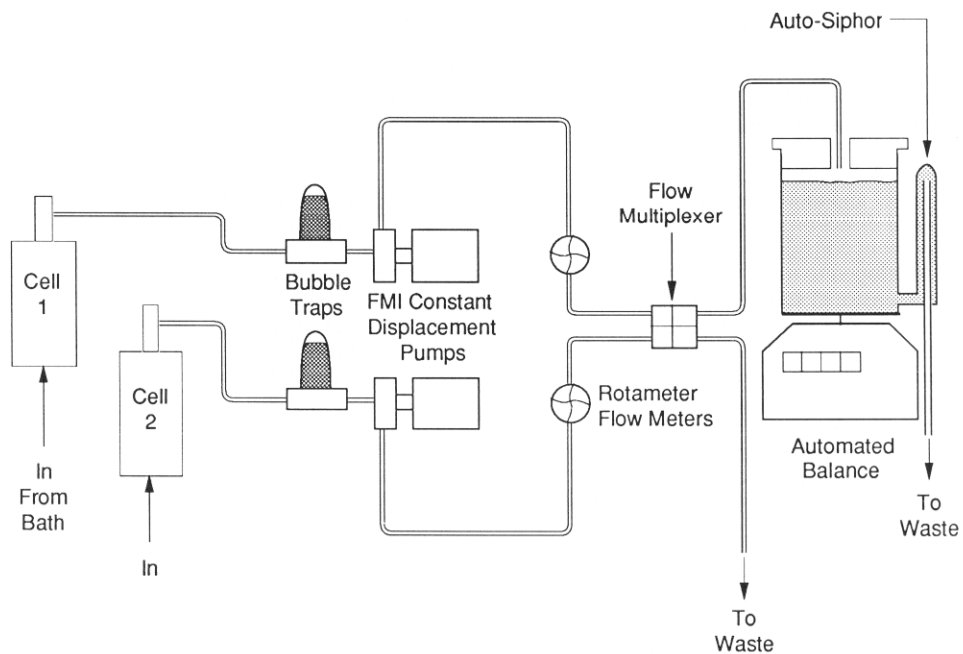
Figure 3. Large bath for calorimetric experiments, top view.
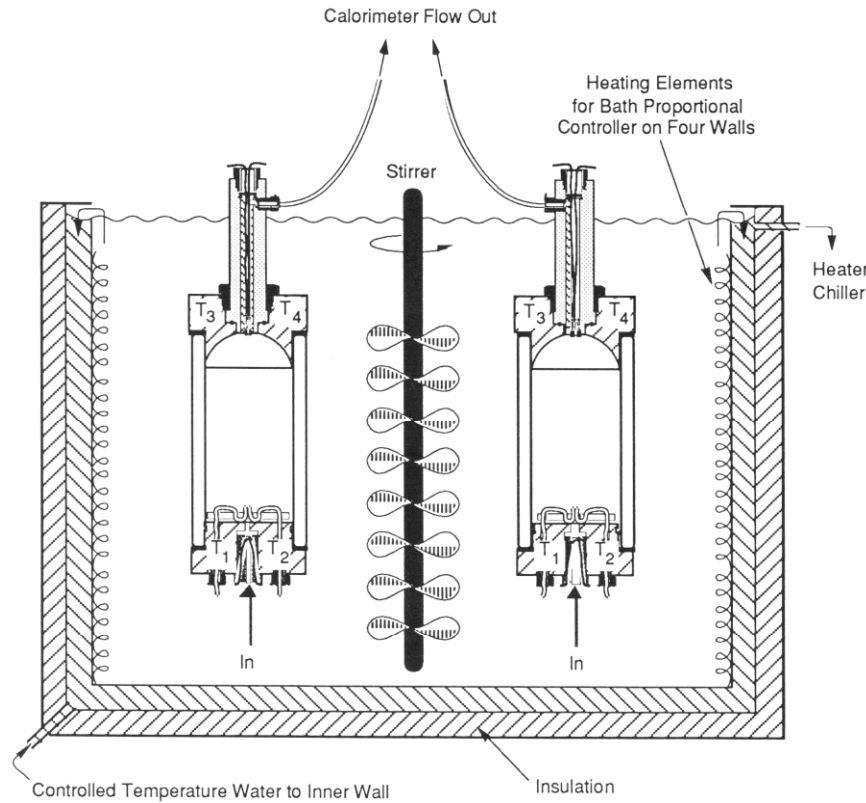
Figure 4. Large bath for calorimetric experiments, side view.

Figure 5. Hydraulic flow system for calorimetric experiments

The remaining term in equation [5] for discussion, is the "effective" conductive loss term, k'. This term is special, and has been the subject of considerable analysis that is not reported here. Conductive heat transport occurred because the electrochemical cell, its contents, and the contents of the insulating, isothermal boundary of the calorimeter vessel, were at a temperature different from that of their surroundings. By submerging the calorimeter vessels in a well-mixed, well-controlled and constant temperature bath, the environment of primary significance was that of the fluid bath . This fluid entered the vessel; in the small cell by a convolved path, in the large cell at the bottom, on the cylindrical axis. Once the flow approached the cell or the conductors contacting the cell it was heated. A conductive loss therefore occurred with respect to the bath.

An added complexity with the large calorimeter was heat transported through the pressure pipe that emerged through the top insulating boundary. This pipe contacted the bath fluid but terminated in the air above the bath. Depending on the ambient and cell temperatures, heat could have been conducted in or out of the calorimeter.

A number of distributed heat conduction paths were therefore present which we have analyzed at three levels of complexity. In a lumped parameter model the cell and heater inside the enclosing metal boundary were treated as a point source that was represented by the average properties: mass, heat capacity and temperature. This point source was considered to give up heat to the flowing fluid and exchange heat conductively with the environment through the pressure pipe, and with the bath through the conductive cables. The emerging fluid may exchange heat with the bath through the walls and top of the calorimeter vessel.

In a distributed parameter model, we have determined the heat balance with sources and sinks distributed in one dimension along the axis of the calorimeter. We considered separately the inlet plenum (elements of flow after the inlet sensor and before the cell), along the length of the cell, and in the outlet plenum (up to the outlet sensors at the calorimeter boundary).

These two approaches made use of the metallic boundary provided by the pressure vessel and axial heat fins to approximate a heat source that was isothermal in the radial and axial directions, (lumped parameter) or just the radial dimension (distributed parameter), without consideration to the distribution of sources inside. A finite element model is being developed to more accurately represent the various distributed heat sources: the two dimensional sources at the anode and cathode interfaces, the three dimensional source of the electrolyte volume, the three dimensional source of the recombiner at the top of the cell, the approximately two dimensional source of the helical compensation heater, and the roughly linear sources of current flowing to the cell in the conductive cables inside the calorimeter boundary.

The lumped parameter model has been analyzed for both the steady state and transient response of the calorimeter. The distributed parameter model has been developed to obtain a steady state solution, while no results have yet been obtained from the finite element model.

On the basis of the modeling, thus far, we are able to draw a number of useful conclusions:

- It is meaningful to define an effective loss term, k', composed of several different heat flows from distributed sources.
- The value of k' is negligibly influenced by the distribution of the heat source within the pressure vessel.

- Within the variations of bath and room temperature experienced and expected, k' may be considered to be constant within the limits of experimental error.
- Within the range of mass flow rates used, the calorimeter response could be represented by a single exponential response, with time constant varying approximately inversely with mass flow rate. Using water as the calorimeter fluid at 1 g s^{-1} the time constant was approximately 16 minutes.

The data that we present here are based on a simple lumped parameter model with k' taken to be a constant determined by calibration. In the results presented, no correction was made for departures from the steady state condition. However, failure to consider deviations from steady state would yield transient errors in P_u, but no error in its average value or in excess energy.

There was one further point of concern in the determination of ΔT and hence k' and P_{out}. It is important that the temperatures measured accurately represent the average values at the inlet and outlet. This was of little concern for the inlet temperatures since the fluid issues from a well-mixed tank. Significant errors could result in the determination of ΔT, however, if the outlet sensors were not placed in a region where the fluid flow was well mixed. Several solutions to this problem were employed: porous plugs and packed beds to promote turbulence, fluidized beds of glass spheres, and imposition of turbulent flow through a Venturi orifice.

Calibration was performed first by determining the values of R° *in-situ,* under flow conditions at known bath temperature and zero or low input power. The total input power was then stepped to successively higher values using the heater (in the presence of low electrochemical power), allowing at least 20 time constants (~ 6 hours) to reach a steady state. The quantities $\delta m/\delta t$, R_{out}, R_{in}, V_h, V_{hr}, V_c, V_{cr} were measured on line and the steady state values were fitted to equation [5], assuming $P_u = 0$, to determined k'. It should be noted that this method of calibration determines k' in terms of the other externally calibrated constants: C_p, R_{out} and R_{in}, α, R_h and R_c, and the voltage calibration of the multimeter. In this way the cumulative inaccuracy of the determination of k' was greatly reduced. From this time on, only changes in calibrated values would have given rise to error.

As stated above, the calorimeter was run under conditions of constant power. This was achieved in a stepwise fashion. First, a maximum desired input power was established. Then the heater was allowed to slowly turn off by ramping the electrochemical power while maintaining the total power constant. In many experiments, and in all experiments for which the D/Pd ratio was less than ~ 0.9 or the duration of electrolysis was ≤ 300 hours, the substitution of electrochemical power for heater power yielded no excess power. That is, $P_u = 0 \pm 50$ mW for $P_{total} \le 18$ W.

Apple Macintosh computers equipped with an IO-tech IEEE-488 interface, Keithley 706 scanner, Keithley 195A DMM, Tecrad DMO-350 micro-ohmeter, Setra 5000L balance, black box COS/4 serial port multiplexer were used to record the parameters of the experiment. The Macintosh interface controlled a Kepco BOP 20-20M power supply to apply cell current and a Kepco BOP 50-2M power supply to control compensation heater power. The power supplies were controlled using internal IEEE-488 interfaces. In addition to the parameters necessary for calorimetric determinations, a number of variables are measured to monitor the physical and electrochemical conditions of the experiments. A list of parameters follows:

Parameters Measured

Voltages: Cell at calorimeter boundary
Heater at calorimeter boundary Reference electrode

Currents: Cell
Heater

Temperatures: Bath (RTD)
Inlet (2 RTD)
Outlet (2 RTD+ 2 thermistor) Room ((RTD)
Room (RTD)

Transducers: Cell pressure
Volumetric flow (rotameter)
Gravimetric flow (multiplexed)

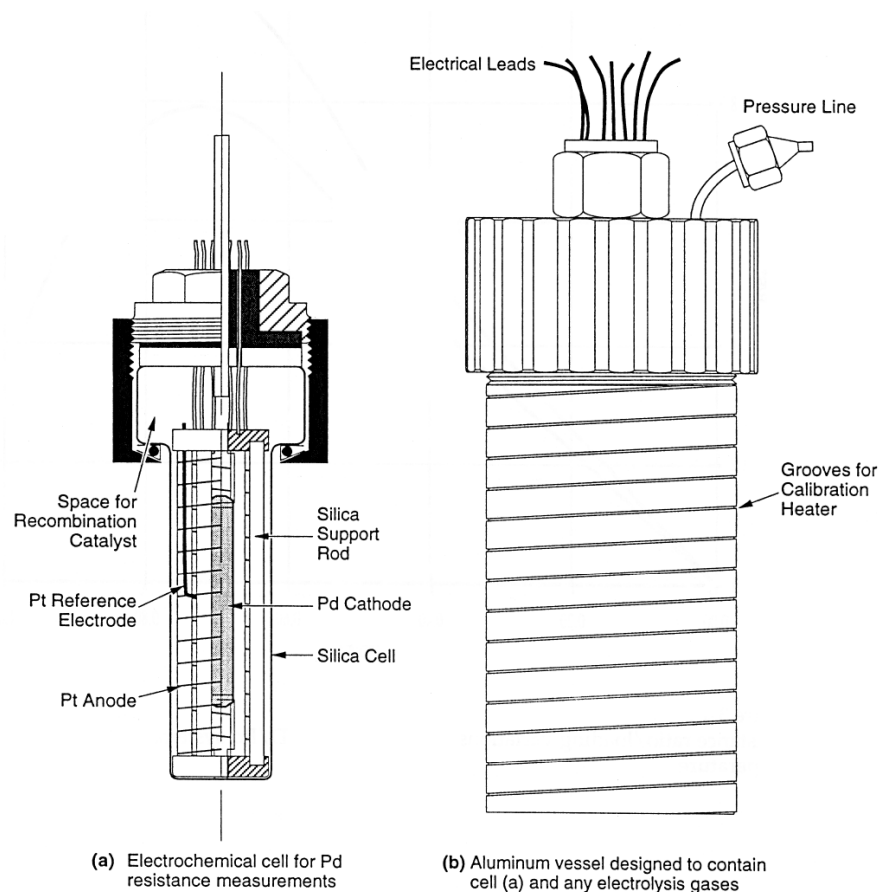Palladium resistance   (multiplexed to Tecrad DMO-350)

Figure 6. Electrochemical cell and pressure vessel for electrochemical experiments.

A Tecrad model DMO-350 micro-ohmeter was employed in a multiplexed mode to monitor the axial resistance of Pd cathodes and thus determine the D/Pd loading. A Solartron model 1250, 1254 or 1260 Frequency Response Analyzer, interfaced to an Apple Macintosh microcomputer was used periodically during experiments to determine the Pd/electrolyte interfacial impedance and thus assess the electrochemical condition of the interface.

Results are presented here from a series of five experiments performed in sequence, designated P12-P16. This series of near-ambient temperature experiments was chosen to demonstrate the features of internal consistency and experiment-to-experiment repeatability, the necessity for high loadings and long times, the need for D_2O and the use of H_2O controls, and the effect of current density on loading and excess heat production.

All experiments were performed using 0.3 cm diameter × 5 cm length Engelhard Pd cathodes of 99.9% purity. Anodes were coaxial helices of Engelhard CP Platinum STD Grade Pt thermocouple wire formed from 100 cm of 0.5mm diameter wire wound on 6 quartz rods. In all cases the electrolyte was 1.0 molar in Li, formed by the reaction of 99.8% purity (natural isotopic ratio) Aesar Li with H_2O or D_2O.

To perform an experiment, cathodes first were machined to the correct diameter with grooves to receive the four 0.5 mm Pt wire contacts for current contact and axial resistance measurement. Electrodes were then degreased and cleaned and the four wires mechanically wrapped then spot welded into place. This assembly was annealed for 2 hours at 850°C in vacuo allowed to cool in argon, rinsed in "heavy" or "light" aqua regia (for D_2O or H_2O experiments), rinsed repeatedly in the appropriate water, dried, and carefully mounted inside the pre-prepared anode cage avoiding contaminant contact. The assembled structure was placed inside the sheathed pressure vessel, freshly prepared electrolyte added, and the vessel sealed (and pressurized with D_2). The pressure vessel was then installed in the calorimeter, charging current applied and monitoring begun.

For the experiments described here, the large calorimeters were used; initial charging and calibration were performed contemporaneously, as described in the previous section.

Experiment P12, which was the prototype for the sequence of experiments described here, was performed alone in the large calorimeter bath. P12 was a heavy water experiment, and exhibited output power in apparent excess of the known sources of input power. Pl3 was prepared as a light water blank of P12, and replaced P12 in the calorimeter. Pl3 was run, initially alone, using the same electronics as had been used for P12. After a period of ~ 600 hours, P14, a heavy water replicate of P12 was run electrically in series with P13, multiplexed to the same electronics.

Experiments P15 and P16 were started simultaneously, electrically in series, following the termination of P13 and P14. P15 and P16 both were heavy water cells. The cathodes in experiments P12, P14 and P16 were implanted with helium following the 850°C annealing step, and instead of the aqua regia etch, as an alternative electrode pretreatment. Typically 5×10^{16} atoms of helium were implanted to a depth of approximately 3 μm; [4]He was used in P12 and P14, [3]He was used in P16. The act of implantation also resulted in a layer of metallurgical damage or restructuring at the surface, < 1 μm thick.

RESULTS

In the space available it is not possible to present the data for the complete duration of the experiments reported, or even of all the parameters measured in a single time interval. What is presented here primarily are results of excess power, being the difference between the output and known sources of input power, determined from equation [5].

A single episode of excess power is presented each for P12, P14 and P15; these are intended to exemplify particular features of the apparent excess power production. In these examples, Pl3 and P16 function as blanks, concurrent with Pl4 and P15, and sequential to P12.

For each of the cells P12 through P16, there were occasions when, for nominally identical current ramps, similar average D/Pd ratios were obtained but with no manifestation of excess power within the sensitivity of the calorimeter. For the full duration of the P13 experiment, the calorimeter was observed in the steady state to be within $\pm$ 50 mW of thermal balance.

Figure 7 shows the electrochemical parameters together with the measured axial resistance ratio and the calculated excess power for P12. Zero time on this plot represents a total time of charging of 1300 hours. The results presented allow examination of the dynamic response of the cathode voltage (measured with respect to a Pt pseudo-reference electrode), the resistance ratio, the excess heat and the cathodic current density.

From 0 to ~280 hours, the calorimeter was operated at a constant input power of 10 W. During this time the cell current was held constant at 0.1A (~20 mA cm^{-2}) and 2.0A (~400 mA cm$^{-2)}$ and ramped and stepped between these limits. The reference voltage and the Pd resistance ratio exhibit a response to the current density. At the initial current density, the resistance ratio attained a value of ~1.75, decreasing (corresponding to loading) slightly with time as the reference voltages slowly increased, white the calorimeter maintains a thermal balance. As the current increased, the reference voltage rose in part due to IR and kinetic effects, but the resistance ratio fell to ~1.67 at ~100 mA cm^{-2} indicating that the electrode was absorbing deuterium.

The increase in current density and absorption of deuterium was accompanied in this case by an apparent evolution of excess power. The top curves in Figure 7 show raw data taken from the two independent pairs of temperature sensors converted to excess power using equation [5]. Departures from steady state can be seen at times when the current was abruptly stepped at 60, 80, 90, 110 and 310 hours. Apart from this effect, the excess power responded essentially monotonically with the current density, above a certain threshold value. At each instance of a step in the current density, the excess power responded with a time constant indistinguishable from that of the calorimeter. That is, the phenomenon that gave rise to this effect itself had a time constant of a few tens of minutes or less.

It should be noted, however, that the resistance ratio did not decrease monotonically with increasing current density; a maximum in loading apparently being achieved in this experiment at current densities as low as ~200 mA cm^{-2}. At higher current density the loading appears to decrease, while the excess power increases.

During the sustained hold at 2A from ~160 to 280 h, the cell voltage slowly increased due to loss of conductive species from the liquid phase in the cell At ~ 280 h the product $I_c * V_c$ exceeded 10 W so that the system departed further from its steady state, and the quality of data

was reduced. At ~303 h the total power was raised to 12 W, and at ~309 h the current was reduced to 0.1 A. At this point it was clear from the resistance ratio that the electrode had de-loaded. In subsequent experiments it was found not to be possible to re-load the electrode with deuterium, or to observe excess heat. Following termination of P12, Pl3 was placed in the calorimeter using the same hardware, electronics and flow system. This experiment was intended as a blank, and an attempt was made to achieve nearly identical conditions to those of P12, excepting only that the electrolyte was prepared from H_2O and the cathode was not implanted with helium. This experiment was operated for a total of 815 h and exercised over the same range of current densities and loadings as P12, during which time the steady state response of the calorimeter maintained a thermal balance, and within ± 50 mW no excess power was observed.
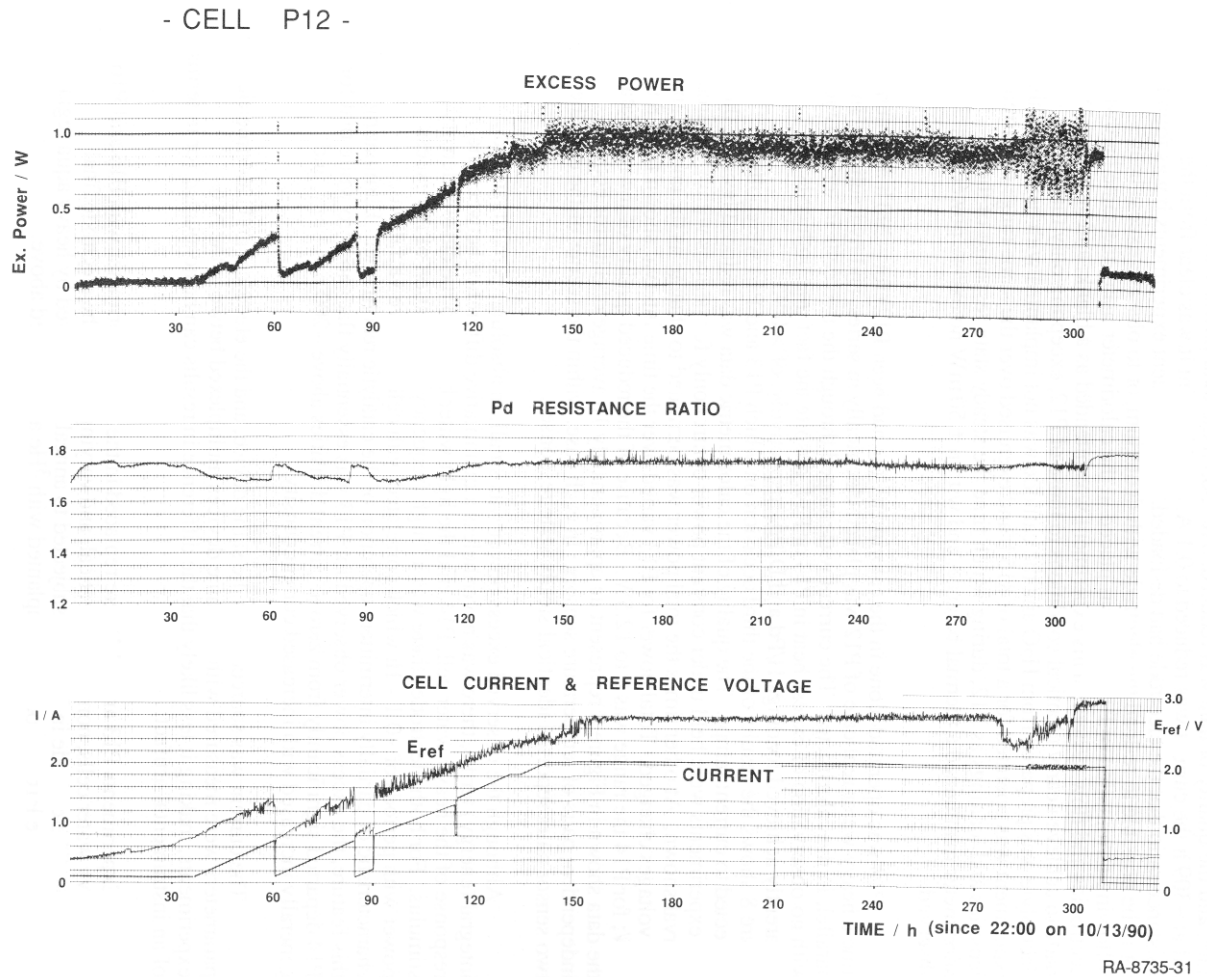

Figure 7. Experiment P12; cell current, reference voltage, resistance ratio and excess power.

P13 was operated alone in the calorimeter (as had been P12) for ~290 h at which time a heavy water replicate of P12 was placed electrically in series, and hydrallically in parallel, in the calorimeter. The current was ramped through the two cells in series, twice, with no observation of excess heat in P13 or P14, despite the fact that both cells had apparently achieved loadings

H/Pd and D/Pd, respectively, of > 0.95. Figure 8 shows the results of the third occasion on which P13 and P14 were jointly subjected to current ramps. The quality of the calorimetric data was reduced because the two experiments were held under constant power control only for periods within the time interval shown. At other times the total power was permitted to change as the current and cell voltages changed. Total power for P13 varied over the time interval shown from 8 to 15W; for P14 the range was 8 to 12.5W. Because of the reduced quality of the raw data, the data shown in Figure 8 represent an approximately 1h average of data for both independent pairs of temperature sensors. In each case, within the scatter of the data the two sensor pairs reported identical steady state responses.

Although the observed excess power was small, in absolute, percentage and integral (energy) terms, there was nevertheless a quantitative difference between the response of the heavy water cell, P14, and the light water blank, to the current density stimulus. For both electrodes there was a "high frequency" fluctuation of the excess power with periods of ~0.1 - 1h which correlated with cell pressure variations, characteristic of partially intermittent operation of the catalytic recombiner. Eliminating this feature, the excess power observed for P13 was essentially flat and zero while that for P14 departed significantly from zero at current densities above ~200 mA cm^{-2}, and generally increased with increased current density.

The current was sourced from the same device, and the electrical and calorimetric parameters were measured with the same devices multiplexed between the two experiments, making it less likely that the difference in results can be accounted for in terms of an instrumental artifact.

Experiments P13 and P14 were replaced in the large calorimeter with P15 and P16, both heavy water cells, nominally identical, and varying only in the electrode final treatment. The cathode in P15 was subjected to annealing followed by heavy aqua regia rinse, while the P16 cathode was implanted with ^{3}He as described above.
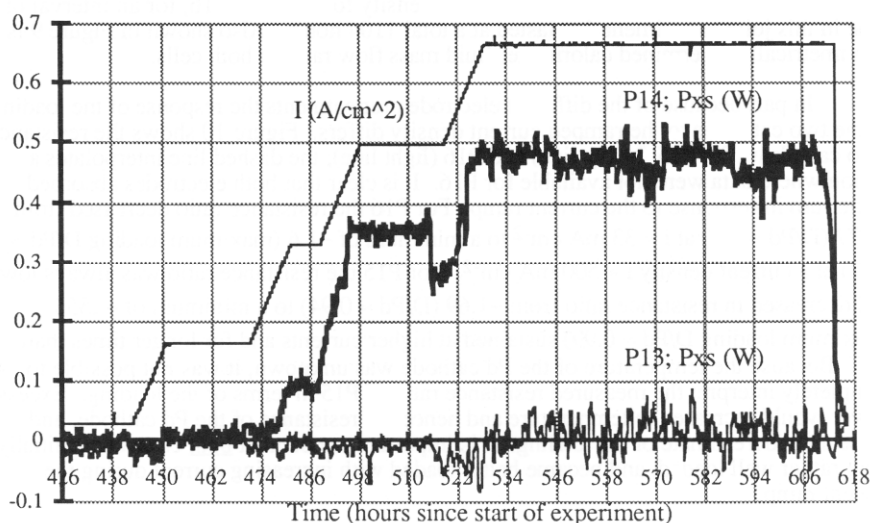

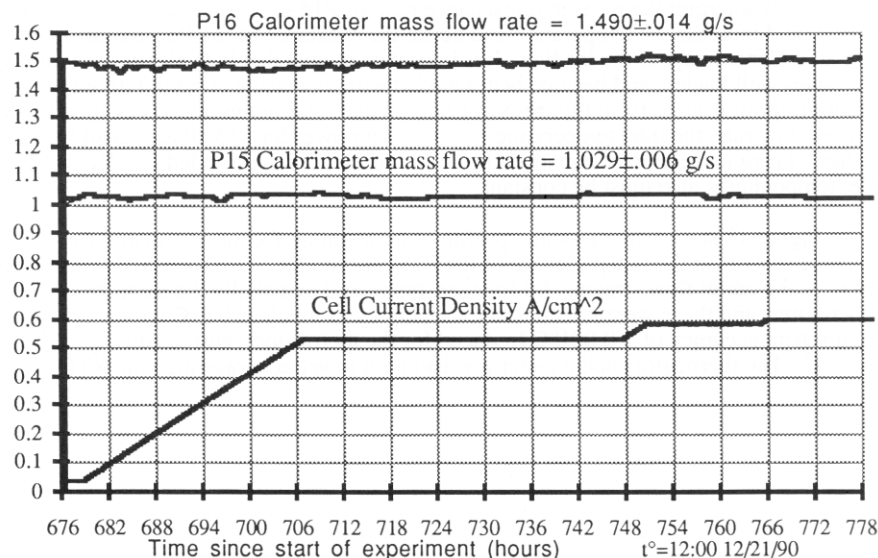**Figure 8. Current density and excess power for experiments Pl3 and P14.**

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Figure 9. Current density and mass flow rate for experiments Pl5 and P16.

Figure 9 shows the profile of current density for P15 and P16, for an interval of time in this joint experiment that lasted at a total 1104 hours. Also shown in Figure 9 is the gravimetrically determined calorimeter fluid mass flow rate for both cells.

In part because of the different electrode pretreatments the response of the loading of the two cathodes to the ramped current density differs. Figure 10 shows the resistance ratio calculated for P15 (heavy line) and P16 (light line); the dashed line interpolates a region where data were not available for P16. It is clear that both electrodes absorbed deuterium in response to the current ramp. For Pl6 the resistance ratio decreased from ~1.77 (D/Pd $\approx$ 0.9) at i = 33 mA cm^{-2} to a minimum of ~1.6 (maximum loading D/Pd $\approx$ 0.97) at a current density i $\approx$ 500 mA cm^{-2}. For P15 the resistance ratio was always lower and decreased in resistance ratio from ~1.69 (D/Pd ~ 0.94) to a minimum of ~ .555 (maximum loading D/Pd $\approx$ 0.99) sustained at higher currents and for longer times than P16. Because the temperature of the Pd cathode was unknown, it was not possible to completely interpret the measured resistance ratio of P15 in terms of the loading. Excess power would increase the temperature and hence the resistance of the Pd cathode, and cause an underestimate of the loading. It is important to note that <u>both</u> electrodes initially were rather well loaded, and became better loaded with increasing current during the current ramp.

Figure 11 shows the temperatures registered by the inlet sensors of P15. Figure 12 shows the total measured input power, initially controlled at 10 W and then stepped to 12 W as the cell voltage rose at constant current. Also shown is the power in the heater used to compensate for changes in the electrochemical input power due to the current ramps or temporal drift. Because the temperature of the Pd cathode was unknown, it was not possible to completely interpret the measured resistance ratio of P15 in terms of the loading. Excess power would increase the temperature and hence the resistance of the Pd cathode, and cause an underestimate of the loading. It is important to note that <u>both</u> electrodes initially were rather well loaded, and became better loaded with increasing current during the current ramp. It is clear from Figures 9, 11 and 12 that, within the interval of time shown, the mass flow rate, the inlet temperature and the inlet

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power for P15 all are sensibly constant. From inspection of equations [1] - [5] it is clear that, provided that P_u is zero, the outlet temperatures also must be constant.

Figure 13 shows the measured profile of temperature for the two platinum resistance sensors in the outlet plenum of the P15 calorimeter. Two thermistors also were present in the outlet flow stream. All four sensors record essentially the same profile of temperatures, and these were not constant, varying by as much as 0.6°C with a measurement accuracy of ± 0.001°C (reduced for the thermistors) and sensitivity of 0.0001°C. The thermistors had a better precision but lower accuracy than the RTD's.
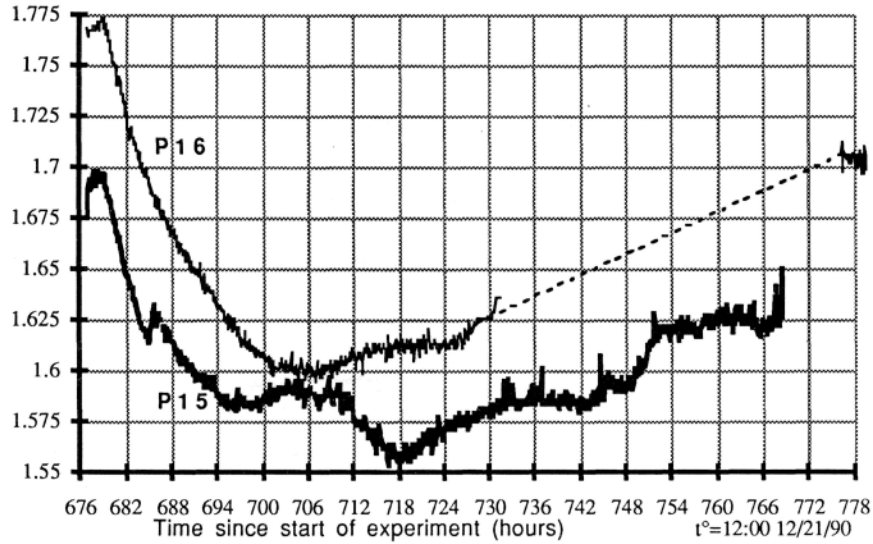

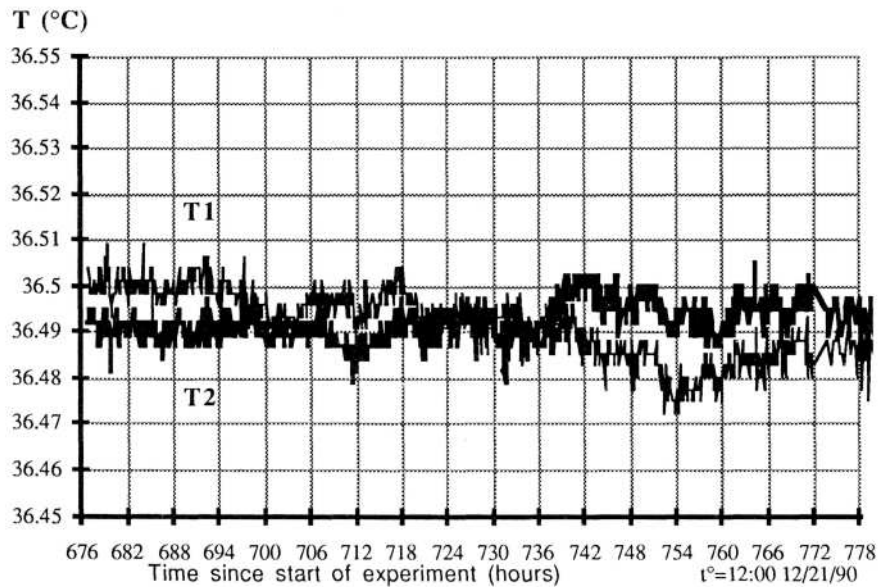**Figure 10. Resistance ratio for experiments Pl5 and P16.**

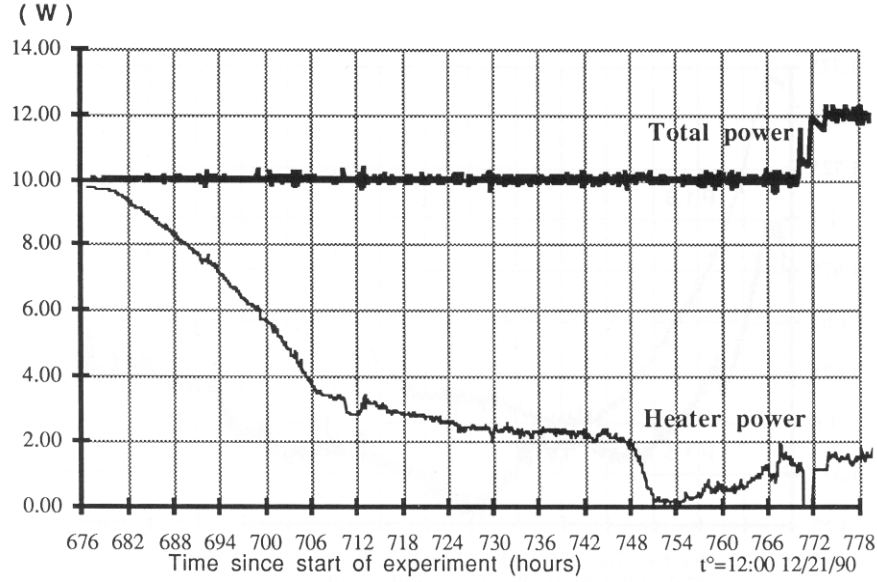**Figure 11. Temperatures in the inlet plenum for experiment P15.**

Figure 12. Total power and compensation heater power for experiment Pl5.
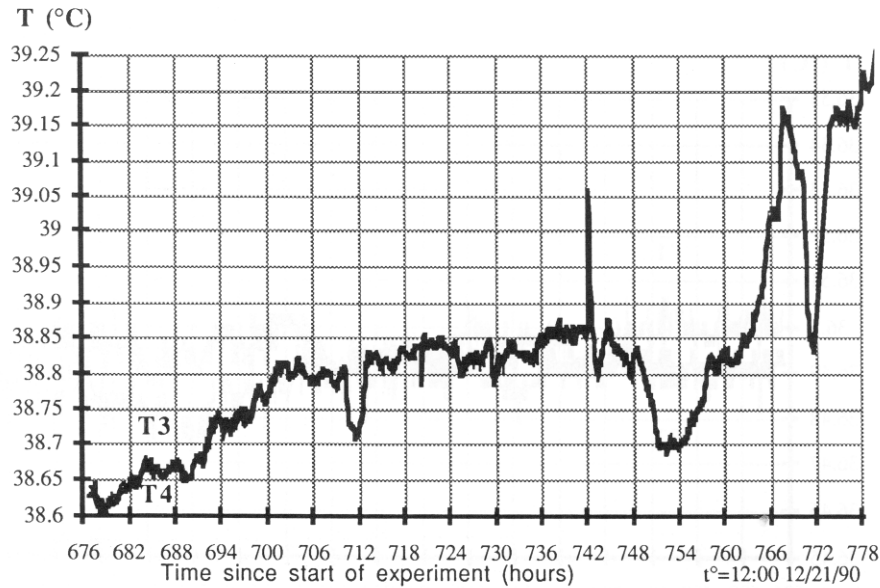

Figure 13. Temperatures in the outlet plenum for experiment P15.

One interpretation of the observed temperature variation is that there is an unknown power source within the calorimeter of an amount that we can quantify using equation [5]. Figure 14 shows the "excess power" normalized with respect to the measured electrochemical input power ($I_c * V_c$) and the controlled total power ($I_c * V_c + I_h * V_h$). A very irregular profile of excess power is seen with a threshold at ~ 200 mA cm^{-2}. The high frequency fluctuations of period 0.1 - 1 h are present due to inconstant recombiner operation. Superimposed on the ramped response to current also are apparently spontaneous fluctuations with substantially greater amplitude and period (~ 3-6 h) that were not corrected to variations in pressure or any other of the measured parameters of the system. It is worth noting that during this time interval, and

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subjected to the same current, P16 exhibited no departure from the thermal balance that was detected with the same instruments as for P15.
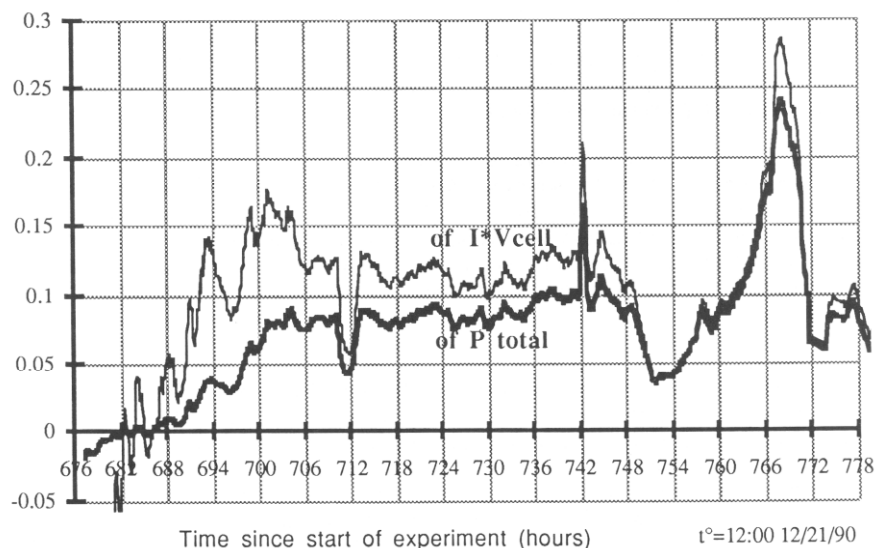

Figure 14. Excess power for experiment P15, expressed as a fraction of the electrochemical and total power input.

DISCUSSION AND CONCLUSIONS

In this paper we have described a calorimetric tool for use in observing the characteristics of unexplained thermal processes in the D/Pd system. Representative examples of results have been given from which a number of observations and conclusions may be made.

We have observed unexplained excess heat in palladium cathodes when a minimum of three criteria were met: an average loading (D/Pd) approaching or exceeding unity; this high loading was maintained for considerable periods of time (100's of hours for 3 mm diameter cathodes); the interfacial current density exceeded a certain critical value.

With appropriate control of the interfacial conditions it has been shown to be possible to load both H and D into Pd to molar ratios of approximately unity. Electrode preconditioning apparently plays a significant role in the ability to attain and maintain high loading under electrochemical conditions, and the appearance of unaccounted heat in deuterium loaded systems. Helium implantation provides a suitable means of surface activation to facilitate loading; the presence of helium is not obviously implicated in the generation of excess power.

For the thermodynamically closed and intentionally isothermal systems described here, output power was observed to be as much as 28% in excess of the electrochemical input power or 24% above the known total input power. When excess power was present, it was more typically in the range 5-10%, in a calorimeter that was accurate to ±0.1%.

In the examples given the largest observation of excess energy corresponded to 1.08 MJ, or 45.1 MJ/mole or ~450 eV/atom normalized to the Pd lattice or to the deuterium in the palladium at a presumed loading of ~1.

The experiments reported here demonstrate that internal repeatability is possible when the three criteria above are achieved. Apparent excess heat was observed under these conditions

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when the current density reached a critical value, and excess heat was not observed when the current density was reduced below the critical value. Furthermore, the threshold current density appeared to decrease with time, up to the point that, due to interfacial or external effects, high values of loading could no longer be attained or maintained.

There appeared also to be some degree of experimental reproducibility between cells. Experiments P13-P16 were attempts to replicate P12 with only minor variations in electrode and electrolyte treatment. All the heavy water experiments (P14, P15, P16) produced excess heat, reproducing in general form the observation in P12 (excess heat data for Pl6 are not shown here). It is worth noting, however, that excess power in these four experiments was <u>not</u> produced in exactly the same amounts, or at exactly the same times, in response to the same stimuli. However, we could not reproduce exactly the electrochemical conditions of cathodic overvoltage, the loading (resistance ratio), and the interfacial impedance. Clearly there are issues of interfacial contamination which arise in experiments with sustained high current electrolysis, that await resolution.

Except for times when the calorimeter was caused to depart significantly from its steady state condition, and during periodic fluctuations introduced by nonconstant recombiner operation, "negative excess" was never observed. In terms of equation [5], P_u was observed always to be positive or zero. Always, where significant quantities of H_2O were used in the electrolyte, P_u was zero. Also, no excess was observed before a critical "initiation time", even in cells that subsequently yielded values of $P_u > 0$.

As demonstrated in the P13/P14 and P15/P16 twin, series experiments, excess power was observed asynchronously in series cells. That is, cells subjected to the same current from the same source and monitored in a multiplexed manner to the same electronics were observed to yield in one cell P_u while in the other $P_u > 0$. It is very difficult to attribute such an observation to an artifact of the common instrumentation.

The association of apparent excess power with a set of necessary conditions for the D/Pd system implies a degree of reproducibility. These conditions are not easy to attain, a fact which may explain the irreproducibility of the phenomenon of excess heat. Examined separately the three criteria may be taken as normal conditions of reacting systems (chemical or nuclear). The criterion of loading is of a thermodynamic driving force; a measure of the activity or chemical potential of a possible reactant species. The need to maintain loading for considerable periods of time before the onset of excess heat suggests a mass transport constraint, possibly involving nucleation and growth of an active region within the volume of the bulk Pd lattice. The final requirement of large interfacial current density suggests a kinetic criterion. Because of the intimate coupling between electron flux and the creation of adsorbed D, and a very facile equilibrium between D_{ads} and D_{abs}, current density can be viewed as the means by which absorbed D are given the energy to undergo reaction.

As a final note, we are unable to account for the observed excess temperature by any artifact known to us and are forced to conclude, tentatively, that the source of the excess power is a property of the D/Pd system. Further, we cannot account for the measured excess heat by any chemical or mechanical process with which we are familiar.

ACKNOWLEDGEMENT

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