Isothermal flow calorimetric investigations of the D/Pd and H/Pd systems

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Abstract

Isothermal calorimetric studies of the D/Pd and H/Pd systems have been carried out at high deuterium (hydrogen) loadings (i.e. [D(H)]/[Pd] > 0.9) at approximately 30°C. Under these conditions, the generation of "excess power" was observed in a series of deuterium-based experiments, but not in a hydrogen-based experiment. The results of these experiments enable several (tentative) conclusions to be reached concerning the conditions necessary for the reproducible observation of this anomalous thermal effect.

1. Introduction

Following the results reported by Fleischmann et al. [1], a considerable amount of effort has been expended in order to test the hypothesis that the electrochemical loading of deuterium into palladium leads to the production of energy in excess of that predicted to arise from known chemical or electrochemical phenomena. Based on the totality of the calorimetric results reported to date, it is evident that the ultimate acceptance or rejection of the original hypothesis will not be determined by calorimetry alone, but only in addition to the confirmed observation of other products of the energy producing process, leading ultimately to the development of supportable new theories. However, because of the potential importance of the energy-related aspects of the phenomenon, calorimetric studies provide the most

appropriate basis from which to undertake a comprehensive investigative programme.

Some of the discrepancies in the results of the various calorimetric studies undertaken thus far may be traced to the different experimental approaches adopted; not all of these may be expected to be equally accurate or reliable. More importantly, perhaps, in accounting for the variety of reported calorimetric results, is the wide range of possible conditions which may be employed (or encountered) in a given experiment, some of which will be difficult to control or reproduce.

This consideration, in particular, may hinder attempts to replicate the original experiments of Fleischmann et al. Nonetheless, it is evident from the calorimetric results reported to date, that the experimental hypothesis referred to in the above paragraph cannot be supported as stated; additional criteria must be satisfied.

An experimental programme was undertaken in order to investigate and, if appropriate, to characterize further the energy production effect described by Fleischmann et al. At the outset it was postulated that anomalous effects previously unobserved, and presently unexplained, in the deuterium/palladium system will occur at deuterium loadings (D : Pd atomic ratios) approaching or exceeding unity. Thus a central feature of the experiments described here is the (electrochemical) control, and continual in situ measurement, of the deuterium (and hydrogen) loading during the entire calorimetric experiment. Further, it was decided that the most accurate, and sensitive, thermal measurements would be obtained using a sealed (thermodynamically closed) electrochemical cell (with knowledge at all times of the composition of the reacting system), in combination with a flow calorimeter. The experimental approach adopted here thus differs significantly from that originally described [1], and from the majority of subsequent calorimetric studies (for reviews of previous work, see refs. [2] and [3]).

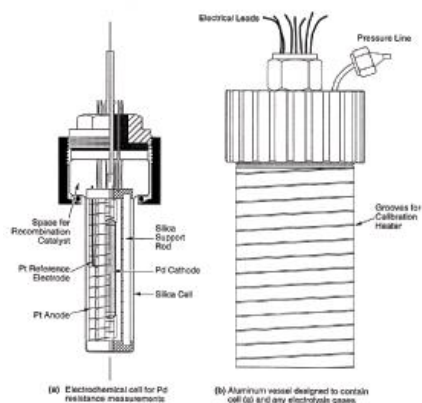The research reported here was carried out during the period August, 1990 to February, 1991.

Fig. 1. (a) Electrochemical cell for Pd resistance measurements and (b) aluminium vessel designed to contain cell (a) and any electrolysis gases.

2. Experimental

2.1. Electrochemical cell design

All the experiments reported here were carried out in thermodynamically closed electrochemical cells which operated at approximately atmospheric pressure. The closed system (Fig. 1) consisted essentially of two components, a PTFE vessel, which housed the electrochemical components, contained within a sealed aluminium vessel.*

*In Fig. 1(a) the electrochemical cell components are shown contained within a silica cell boundary. While this arrangement has been employed in degree of loading (non-calorimetric) experiments, the inner PTFE liner of the aluminium vessel served as the cell boundary in the calorimetric experiments whose results are reported here. The facility to insert a degree of loading cell with its silica cell boundary, directly into the aluminium vessel was employed in several experiments, the results of which will be reported subsequently.

A large area catalyst was provided in the head space of the PTFE cell to recombine evolved oxygen and deuterium (or hydrogen) such that, after the cathode had loaded, there were no net thermal effects due to electrolysis. All experiments were performed using 0.3 cm diameter × 5 cm length Engelhard palladium cathodes of 99.9% purity. Anodes were coaxial helices of Engelhard CP Platinum STD Grade platinum thermocouple wire formed from 100 cm of 0.5 mm diameter wire wound on a form consisting of six silica rods. In all cases the electrolyte was 1.0 M in lithium hydroxide or

deuteroxide, formed by the reaction of 99.8% purity (natural isotopic ratio) Aesar lithium with light or heavy water. In addition, the presence of approximately 200 ppm of dissolved aluminium (or silicon) in the electrolyte was found to facilitate the reproducible attainment and maintenance of high loadings. A Tecrad model DMO-350 micro-ohmmeter was employed to measure in situ the axial electrical resistance of the palladium cathodes [4]. The associated palladium loading was thus determined from the known resistance-loading variations in the H/Pd and D/Pd systems (Fig. 2). (The data shown in Fig. 2 are compiled from the results of several resistance-loading studies, in particular refs. [5] – [9])
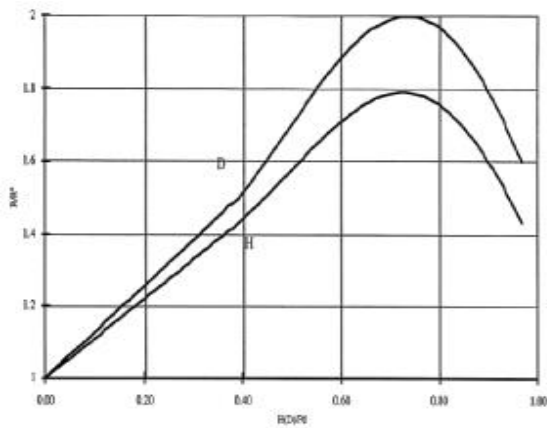
Fig. 2. Resistance ratio-loading variations in the H/Pd and D/Pd systems at room temperature.

To perform an experiment, cathodes first were machined to the correct diameter, and furnished with grooves to receive the four 0.5 mm platinum wire contacts for current supply and axial resistance measurement. The electrodes then were degreased and cleaned. After being annealed for 2 h at 850°C in vacuo and allowed to cool in argon, the four wires for cathode current and voltage contact were mechanically wrapped and spot welded into place. Two surface pretreatments were employed in order to facilitate loading; either rinsing in "heavy" or "light" aqua regia (for heavy or light water experiments respectively), or surface modification by helium implantation to a depth of approximately 3 μm. Following pretreatment, cathodes were carefully mounted inside the pre-prepared anode cage, avoiding contaminant contact. The assembled structure was placed inside the PTFE vessel, freshly prepared electrolyte added, and the aluminium

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vessel sealed. The aluminium vessel was initially pressurized with the appropriate amount of deuterium (or hydrogen) gas (calculated assuming a final loading of unity) in order to recombine the excess oxygen evolved during the initial charging of the cathode.
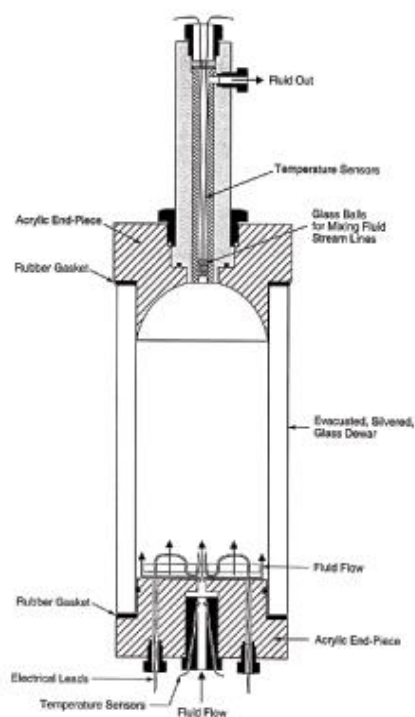
2.2. Calorimeter design

The sealed aluminium vessel was fitted externally with a helically wound compensation (and calibration) heater, and sheathed with axially oriented heat exchanging fins. This unit was immersed directly in the heat transfer fluid of a flow calorimeter (Fig. 3). The body of the calorimeter consisted of an evacuated, silvered glass Dewar, the ends of which were closed with tightly fitting end-pieces made of a PMMA acrylic plastic. Rubber gaskets were used to achieve a watertight seal. The calorimeter was itself immersed in a well-regulated (±3 mK) bath of the same fluid maintained at approximately 30°C. For the majority of experiments reported here, the calorimetric fluid was silicone oil, chosen for its low heat capacity, low corrosivity, and its good electrical insulation properties. A preliminary account [10] of the work reported here contains a mis-statement concerning the identity of the calorimetric fluid.

The heat transfer fluid was pumped from the bath, past the cell inside the calorimeter volume, using FMI (QV-OSSY) constant displacement pumps. The mass flow rate was determined by pumping the flow to an auto-siphon device placed on a Setra model 5000L digital balance.

Precautions were taken to ensure that fluid was not lost following its transit through the cell, before flow rate determination. In the calorimeter design described here, the incoming fluid was at the same temperature as the bath, and the predominant heat transport was upward. All electrical leads were taken through the bottom insulating boundary across which the temperature gradient (and therefore conductive loss) was a minimum. A pressure pipe (not shown in Fig. 3) extended from the cell, through the top acrylic end-piece, 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. Since the pressure pipe emerged through the top insulating boundary, it was expected to contribute to conductive heat loss from the calorimeter, discussed further below.

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Fig. 3. Flow calorimeter design.

The inlet and outlet heat transfer fluid temperatures were measured with platinum resistance temperature devices (RTDs). Two RTDs were used to sense each temperature; the temperature difference was then calculated from the two independent pairs. The required resistance measurements were made in a four-terminal mode, where all the RTDs were multiplexed sequentially to a single multimeter calibrated against NIST traceable standards. Calorimetric measurements were carried out isothermally, under constant input power conditions, whenever possible. The power input to the calorimeter by the electrochemical current was considered to be the product of that current and the voltage at the isothermal boundary.

Under experimental conditions, this input power changed by voltage or resistance variations in the cell, or at times when the current was ramped. This had two undesirable consequences. Firstly, a change in input power changed the cell temperature so that the electrochemical conditions were no longer under control. Secondly, a change in the temperature also moved the calorimeter from its steady state as the calorimeter contents took up or released heat. Hence, to minimize these effects, the compensation heater was used to correct for changes in electrochemical power so that the sum of the heater and electrochemical power inputs to the calorimeter was held

constant. Computer-controlled power supplies were used for both the electrochemical power and the compensation heater element, both were operated in galvanostatic mode in order to avoid possible unmeasured rms heat input. The heater also was used for periodic calorimeter calibration.

The cell and heater currents were each measured as a voltage dropped across a calibrated, series resistor. 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%.

Apple Macintosh computers (equipped with a IO-tech IEEE-488 interface, Keithley 706 scanner, Keithley 195A DMM, Tecrad DMO-350 micro-ohmmeter, Setra 5000L balance, and a 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.

2.3. Excess power determination

The steady state equation for the power output from the calorimeter is

$$P_{\text{output}} = (C_{\text{p}}\, \delta m/\delta t + k')(T_{\text{out}} - T_{\text{in}}) \tag{1}$$

where C_{p} is the average value of the heat capacity of the calorimetric fluid in its transit through the calorimeter (1.646 J K^{-1} g^{-1} for silicone oil, 4.188 J K^{-1} g^{-1} for air-saturated water), $\delta m/\delta t$ is the fluid mass flow rate, k' is an effective conductive loss constant, T_{in} is the inlet (from bath) temperature and T_{out} is the mean temperature of the emerging fluid.

Similarly, for the power input to the calorimeter,

$$P_{\text{input}} = |I_{\text{c}}V_{\text{c}}| + |I_{\text{h}}V_{\text{h}}| \tag{2}$$

where I is the current and V is the voltage measured at the calorimeter boundary, and subscripts c and h refer to the electrochemical cell and compensation heater. In a closed system, the difference between the output and input powers may be described as an "excess power". In the absence of extensive, time-dependent changes in temperature, pressure or overall

composition within the system, the excess power is expected to be zero (in the absence of anomalous power producing/ consuming processes).

For the cell and heater currents,

$$P_{input} = V_{cr}/R_c \,; \qquad I_h = V_{hr}/R_h \tag{3}$$

where V_r is the measured voltage drop across a calibrated resistance (the subscripts c and h again refer to the electrochemical cell and compensation heater, respectively). The primary temperature measurements were made with RTDs, so that

$$T = T^0 + (R - R^0)/\alpha R^0 \tag{4}$$

where T^o is the temperature at which the device resistance is R^o, and α is the (known) temperature coefficient of resistance of platinum. Hence, we may write

$$P_{excess} = P_{output} - P_{input}$$
$$= (C_p \, \delta m/\delta t + k') (R_{out}/ R^0_{out} - R_{in}/ R^0_{in})/\alpha - V_h V_{hr}/R_h - V_c V_{cr}/R_c \tag{5}$$

The terms in this equation may be divided into three classes: **(i)** measured variables, δm, δt, R_{out}, R_{in}, V_h, V_{hr}, V_c, V_{cr}; **(ii)** predetermined constants, C_p, α, R^o_{out}, R^o_{in}, R_h, R_c; **(iii)** the conductive loss constant, k'.

The use of a conductive loss constant, k', requires further discussion. Conductive heat transport occurs because the electrochemical cell, its contents, and the contents of the insulating, isothermal boundary of the calorimeter vessel, are at a temperature different from that of their surroundings. An added complexity is heat transported through the pressure pipe that emerges through the top insulating boundary. Thus, depending on the ambient and cell temperatures, heat may be conducted in or out of the calorimeter. In view of the potential importance of conductive loss, the constant k' has been the subject of extensive analysis (not reported here), which indicates that, although several heat sources exist within the aluminium vessel, the value of k' is negligibly influenced by the spatial distribution of these sources or the anticipated variations in the bath and air temperatures. Thus k' was treated as a constant, its value determined during the calibration procedure, described below. For the calorimetric fluid flow rates used (approximately 1 g s^{-1}), conductive power loss represented typically 3% − 5% of the total input power.

2.4. Calibration and general operating procedures

Calibration was required in order to determine R^o values for the RTDs

and the conductive loss constant, k'. This was performed at the outset of the calorimetric experiment. The values of R^o were determined 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 times (approximately 6 h) of at least twenty calorimeter time constants to reach a steady state. The quantities δm, δt, R_{out}, R_{in}, V_h, V_{hr}, V_c, V_{cr} were measured on line and the steady state values were used with eqn. (5), assuming $P_{\text{excess}} = 0$, to determine k'. It should be noted that this method of calibration determines k' in terms of the other externally calibrated constants: C_p, R^o_{out}, R^o_{in}, α, R_h, R_c and the voltage calibration of the multimeter. In this way the cumulative inaccuracy of the determination of k' was greatly reduced.

In order to confirm that the value of k'determined during calibration was time invariant, a second procedure was undertaken occasionally during the routine operation of the calorimeter. It entailed variation of the total input power (by stepping the heater power at constant electrochemical cell current), together with observation of the resulting excess power response (at times when the excess power was zero). For a properly calibrated calorimeter, the excess power should, of course, not change as the result of such a power step. This procedure, together with the use of redundant temperature sensors, served to check continually the results of the initial calibration procedure. Further, it enabled the validity of eqn. (5) to be verified at very high total input powers, a procedure which was found to be more time efficient when carried out in this manner than when undertaken at the outset of the experiment.

In general, two different experiments were performed simultaneously in the same bath; the electrochemical cells were connected electrically in series, but the calorimetric systems were connected hydraulically in parallel. Separate pumps were provided for each calorimeter and the flows from the two cells were multiplexed to a single mass balance. All measurements were multiplexed to a single multimeter that was periodically interchanged with another precalibrated meter. In this way, one series cell effectively acted as a standard for the other; if P_{excess} was observed not to be zero in one cell while zero in another, then this was unlikely to be an artifact due to the current source or voltmeter mis-calibration. Further, the current-measuring

resistors were interchanged, replaced, and removed and recalibrated during periods of excess power production, reducing the likelihood that errors were associated with the measurement of current.

Typically, constant current or slowly ramped current conditions were employed. As stated above, the calorimeter was run under conditions of constant power. Thus, during a current ramp, the heater power was reduced slowly while ramping up the electrochemical power, thereby maintaining approximately constant total power. Under current control, the cell voltage frequently was observed to fluctuate significantly, particularly at high current densities where the presence of large deuterium (or hydrogen) and oxygen bubbles disrupted the electrolyte continuity. By providing the cell current from a source that is sensibly immune to noise and level fluctuations, the current operates on the cell voltage (or resistance) as a scalar. Hence, as long as the voltage noise or resistance fluctuations are random, no unmeasured rms heating can result under constant current control, provided that the average voltage is measured accurately,

2.5. Fixed errors, uncertainty propagation and transient effects

While it is impossible to eliminate all the fixed (or bias) errors in a given experiment, it is possible to reduce the magnitude of such errors and, more importantly, their time dependence, by suitable system design and data acquisition procedures, as described extensively above. Clearly, problems will occur if new fixed errors arise during the course of an experiment, or if those fixed errors present during the initial calibration procedure are able to vary at a later time.

For a closed electrochemical cell, the expected value of the excess power is zero, in the absence of anomalous processes and large variations in the cell temperature, pressure and/or internal composition. Clearly, in order to assess the significance of a measured deviation in the excess power from its "expected" value, an estimate of the uncertainty in the excess power measurement is required. Since the magnitude of the excess power at a given time may not (at present) be predicted, excess power determinations are considered to be examples of single sample measurements [11]. The uncertainty in the excess power is related to the uncertainties in the variables which enter into eqn. (5), by

$$\delta P_{\text{excess}} = \left(\sum |\partial P_{\text{excess}}/\partial X|^2 \, \delta X^2 \right)^{1/2} \tag{6}$$

where the quantities X and their uncertainties are as follows: C_p (0.002 J K^{-1} g^{-1}); $\delta m/\delta t$ (0.0001 g s^{-1}); R (0.002 Ω); α (0.00002 K^{-1}); input healer power (0.2% of power); input electrochemical power (0.2% of power). Uncertainties are ascribed to C_p and α since the (small) temperature dependences of these quantities are not explicitly included in eqn. (5). The uncertainties in the input powers were determined from the scatter in the measured power data during periods of nominally constant input power. The uncertainty in the RTD resistance was determined from the difference between the temperature readings for two sensors in the same constant temperature bath. Since mass flow measurements are an average taken over a relatively extended time period, the quoted uncertainty is an estimate. Where determined empirically, the quoted uncertainties are at the 95% confidence level (or higher); it is assumed that this confidence level applies to the derived value of δP_{excess}.

When the calorimeter, or its contents, departs from a steady state, a transient departure from power balance will occur. Such departures result principally from changes in the enthalpy of the cell contents, via fluctuations in temperature, pressure and composition. Assuming that the observed pressure fluctuations (which are typically less than 1 lbf in^{-2}) during an experiment are due to non-constant recombiner operation, a correction to the derived value of the excess power may be calculated. It is typically a few milli-watts. We are at present unable to make a corresponding temperature-related correction; however, its effect is presumably included in the short-term "scatter" in the measured excess power data, and thus its magnitude may be estimated. Further, it is important to note that, although affecting the measured value of the excess power, such transient effects will not affect the excess energy over a time period for which the initial and final states of the cell contents are identical.

In addition, apparent departures from the steady state behavior described by eqn. (1) will result since the input variables (inlet temperature, electrical power and flow rate) are measured essentially instantaneously, whereas the output variable (outlet temperature) can respond only with the time constants of the (conductive) transfer of heat from the cell to the calorimetric fluid and the (convective) transfer of the heated fluid to the outlet temperature sensor. In the range of mass flow rates employed in the experiments described here, the calorimeter was observed to exhibit a single

(exponential) time constant of approximately 15 min, dominated by the convective terms. A correction has been applied to the excess power data reported here according to this time constant.

3. Results

Results are presented here from a series of five experiments performed in sequence, designated P12 – P16. Experiment P12, a heavy water experiment which was the prototype for the sequence of experiments described here, was performed alone in the calorimeter bath. P13 was prepared as a light water replica for P12, and replaced P12 in the calorimeter; P13 was run, initially alone, using the same electronics as had been used for P12. P14, a heavy water replica 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 helium implanted as part of the electrode surface pretreatment.

In the space available it is not possible to present the data for the complete duration of any one of the experiments reported. What is presented here primarily are results of excess power determinations. 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.

For each of the cells P12 through P16, there were occasions when, for nominally identical current ramps, similar average cathode loadings 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 approximately 50 mW of zero excess power production.

Figure 4 shows the time evolution of the current density, together with the calculated excess power and its associated uncertainty, for P12 for the time period 1222 – 1558 h (associated reference voltage and cathode resistance ratio data are given in ref. 10). At the beginning of this period, the calorimeter was operated at a constant input power of 10 W. During this time, the current was held constant at 0.1 A (approximately 20 mA cm^{-2}) and 2.0 A (400 mA cm^{-2}) and ramped and stepped between these limits. At the initial current density, the resistance ratio attained a value of about 1.75, decreasing (corresponding to increasing loading) slightly with time, while

the calorimeter maintained a power balance. As the current was increased, the resistance ratio fell to about 1.67 at approximately 100 mA cm^{-2}, indicating that the electrode was loading further. The increase in current density and absorption of deuterium were accompanied in this case by the production of excess power. The excess power responded apparently monotonically to the current density, above a certain threshold value. At each instance of a step in the current density, the excess power responded apparently with the time constant 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.
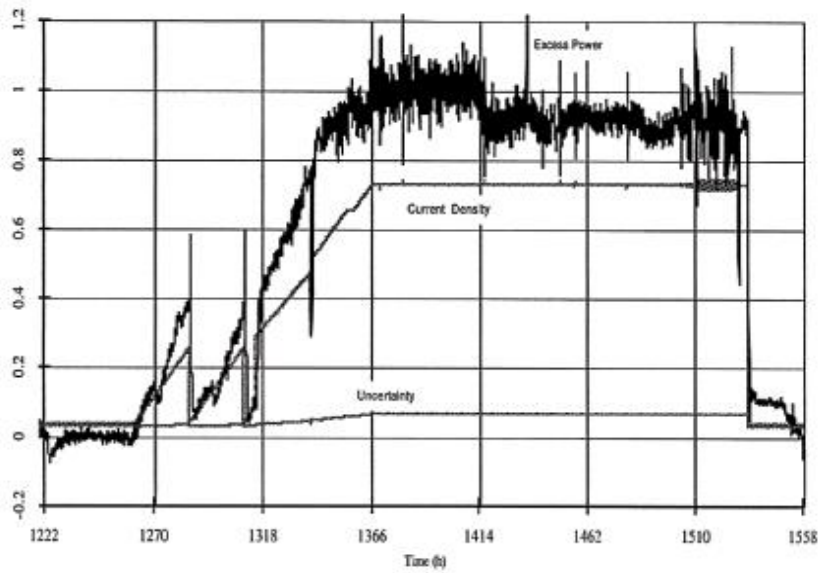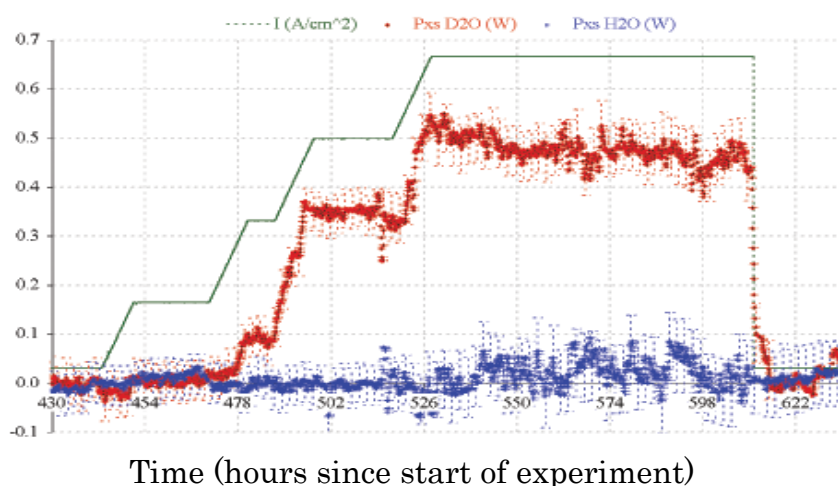

Fig. 4. Variation of excess power (W), current density (A cm-2) and calculated measurement uncertainty (W) with time (since start of experiment) for P12.

Time (hours since start of experiment)

Fig. 5. Variation of current density (A cm-2) for P13 and P14, excess power (W) for P14 and excess power (W) for P13, with time (since start of P13). [Note: this version of this figure taken from a later paper, McKubre, M.C.H. *Review of experimental measurements involving d-d reactions (PowerPoint slides).* in *Tenth International Conference on Cold Fusion.* 2003. Cambridge, MA: LENR-CANR.org.]

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 about 200 mA cm-2. At higher current densities the loading appears to decrease somewhat, while the excess power increases.

During the sustained hold at high current density from approximately 1366 to 1534 h, the cell voltage slowly increased, presumably as a result of loss of conductive species from the liquid phase in the cell. Towards the end of the current plateau, the input electrochemical power exceeded 10 W, so that the system departed further from its steady state, and the quality of data was reduced. At approximately 1534 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 obtain excess power.

Following termination of P12, P13 was placed in the calorimeter using the same hardware, electronics and flow system. An attempt was made to achieve nearly identical conditions to those of P12, excepting only that the electrolyte was prepared from light water 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 no excess power was observed, to within approximately 50 mW.

P13 was operated alone in the calorimetric bath for about 290 h, at which time P14 was added, connected electrically in series and hydraulically in parallel with P13. The current was ramped through the two cells in series, twice, with no observation of excess power in P13 or P14, despite the fact that both cells had apparently achieved loadings greater than 0.95. Figure 5 shows the results of the third occasion on which P13 and P14 were jointly subjected to current ramps. The excess power recorded for P13 was essentially flat and zero, while that for P14 departed significantly from zero at current densities above approximately 200 mA cm^{-2}, and apparently increased with increased current density. In this comparative experiment, 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 extremely unlikely that the difference in results can be accounted for in terms of an instrumental artifact.
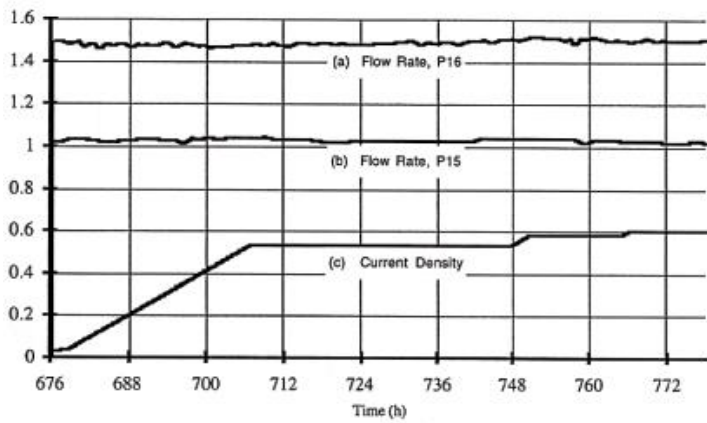
Fig. 6. Variation of calorimetric fluid flow rate (g s^{-1}) for P16, calorimetric fluid flow rate (g s^{-1}) for P15 and current density (A cm^{-2}) for P15 and P16, with time (since start of experiment).
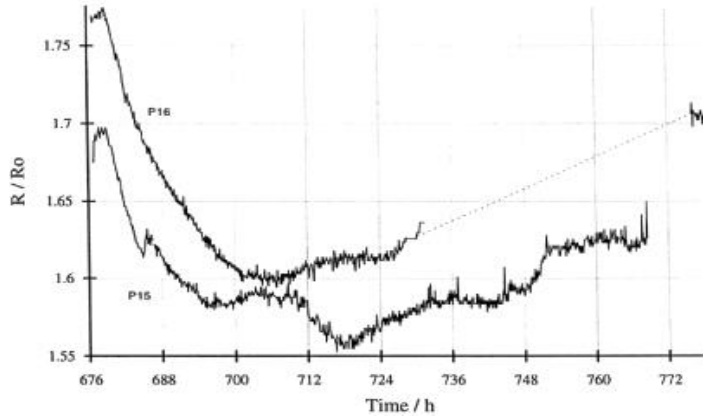
Fig. 7. Resistance ratio variations for P16 and P15, with time (since start of experiment).
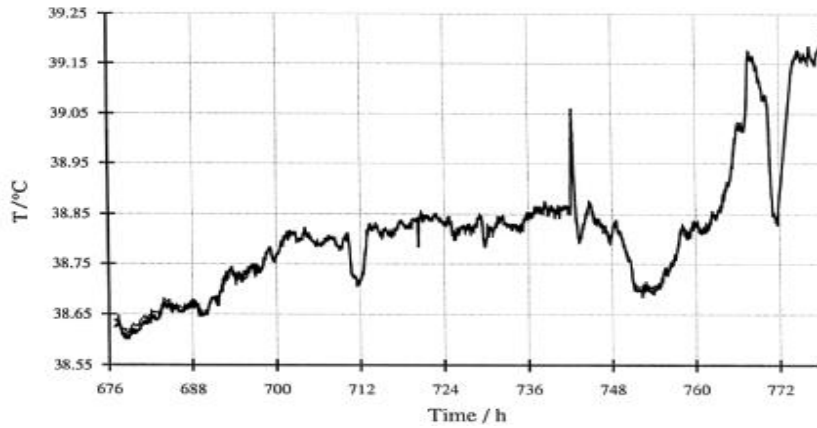

Fig. 8. Variation of outlet temperatures with time (since start of experiment) for P15.

Experiments P13 and P14 were replaced with P15 and P16, both heavy water cells, nominally identical, and varying only in the electrode surface pretreatment. In part because of this, the response of the loading of the two cathodes to the ramped current density differed. Figures 6 are the calorimetric fluid flow rates. (The broken line in Fig. 7 interpolates a region where data were not recorded for P16.) It is clear that both electrodes absorbed deuterium in response to the current ramp. For P16, the resistance ratio decreased from about 1.77 ([D]/[Pd] $\approx$ 0.91) at a current density of approximately 33 mA cm^{-2} to a minimum of about 1.6 (corresponding to a maximum loading of approximately 0.97) at a current density of approximately 500 mA cm^{-2}. For P15, the resistance ratio was always lower, corresponding to higher loadings, and decreased from about 1.69 ([D]/[Pd] $\approx$

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0.94) to a minimum of approximately 1.56 ([D]/[Pd] $\approx$ 0.99).

For P15, during the time interval shown, the mass flow rate, the inlet temperature and the total input power all were sensibly constant; thus, in the absence of excess power, the outlet temperatures should have remained constant. Figure 8 shows the measured temperature profiles for both the RTDs in the outlet plenum of the P15 calorimeter. For this experiment, two thermistors were also present in the outlet flow stream. All four sensors recorded essentially the same temperature response, and these were not constant, varying by as much as 0.6°C with a measurement accuracy of a milli-degree (for the RTDs, less for the thermistors), indicating the presence of excess power.
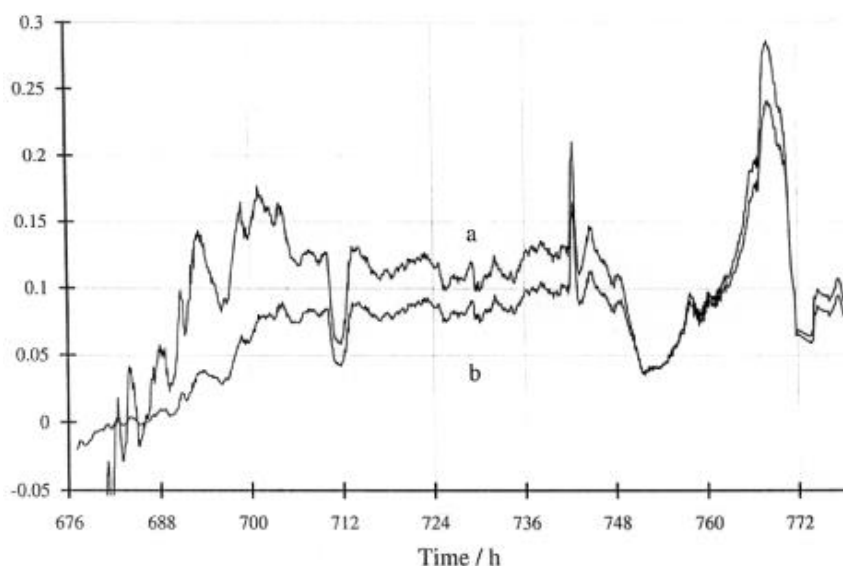
Fig. 9. Variation of excess power for P15 with time (since start of experiment), expressed (curve a) as a fraction of the electrochemical power, and (curve b) as a fraction of the total input power.

Figure 9 shows the excess power normalized with respect to the measured electrochemical input power and the (controlled) total input power. A very irregular profile of excess power is seen with a threshold at approximately 200 mA cm^{-2}. The high frequency fluctuations of period $0.1 - 1$ h are probably due to non-constant recombination catalyst operation. Superimposed on the ramped response to current also are apparently spontaneous fluctuations with substantially greater amplitude and period (some $3 - 6$ h) that are not correlated to variations in pressure or any other of the measured parameters

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of the system. It is important to note that during this time interval, and subjected to the same current, P16 did not exhibit the excess power production that was detected (with the same instruments) for P15. P16, however, did exhibit excess power on other occasions, which are not described here.

4. Discussion and conclusions

In this paper, we have described the observation of an (at present) unexplained power generation process occurring in an electrochemical cell employing a deuterated palladium cathode. Representative examples of results have been given from which a number of observations and conclusions may be drawn. Before describing these conclusions, however, it is useful to discuss what constitutes, in the context of the work carried out here, a "control" experiment, i.e. an experiment for which the outcome may be predicted in advance. Firstly, since, as a consequence of the results presented here, the origin of the excess power production process may not be elucidated (be it a real physical phenomenon or the result of a measurement artifact), a light water experiment does not constitute a control. The fact that no excess power was observed in the light water experiment performed here constitutes a result of equal importance to the observation of finite excess power production in the heavy water experiments.

In this work, the role of a control experiment is to demonstrate that, during the course of an experiment (and under certain reproducible conditions, the converse of which are described in detail below), a calorimeter will detect accurately the absence of excess power production, thereby reducing (but not eliminating) the probability that the observation of finite excess power production is due to a time-dependent variation in the calorimeter function. All the experiments reported here contain such "control" periods; in fact, in all cases they exceed in duration the periods of excess power production.

For the thermodynamically closed and intentionally isothermal systems described here, excess power was observed to be as much as 28% above the electrochemical input power or 24% above the total input power. When excess power was present, it was more typically in the range 5% – 10%.

Excess power generation was observed when a minimum of three criteria were met: an average deuterium loading in the vicinity of unity; the

maintenance of high loading for considerable periods of time relative to the time scale of the diffusional processes involving deuterium within the metal (several hundreds of hours for 3 mm diameter cathodes); the application of a current density in excess of a certain critical value. It should not be supposed that these criteria are completely independent. Thus, the threshold current density appeared to decrease with time, up to the point that, as a result of interfacial or external effects, high values of loading could no longer be attained or maintained.

With appropriate control of the interfacial conditions, it has been shown to be possible to load both hydrogen and deuterium into palladium to atomic ratios of approximately unity. Electrode surface pretreatment apparently plays a significant role in the ability to attain and maintain high loading under electrochemical conditions. Although helium implantation provides a suitable means of surface activation to facilitate loading, this process is not clearly superior to that involving an aqua regia rinse. Further, the presence of helium is not obviously implicated in the generation of excess power.

Negative excess power (i.e. time periods during which the measured total input power exceeded the measured output power) was never observed, except for times when a calorimeter was caused to depart significantly from its steady state condition (for example, following an increase in total input power or during periodic fluctuations introduced by non-constant recombination catalyst operation). As demonstrated in the P13 – P14 and P15 – P16 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 excess power in one cell but not in the other. It is very difficult to attribute such an observation to an instrumental artifact.

Subject to satisfying the three criteria listed above, a level of experimental repeatability has been demonstrated, both within and between individual cells. All the heavy water experiments which have met the three criteria produced excess power (data for P16 are not shown here). It is worth noting, however, that excess power in these four experiments was not 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, loading, or the interfacial impedance. Clearly there are issues of interfacial contamination which arise

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in experiments with sustained high current electrolysis that await resolution.

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