

Calorimetric studies of highly loaded deuterides and hydrides of palladium

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Abstract

A search for excess heat production from highly loaded deuterides of palladium was carried out using a closed isoperibolic calorimeter. The main aim of these studies was to test the hypothesis that the production of excess heat from electrolytically prepared deuterides of palladium only occurs when (amongst other conditions) the D/Pd loading ratio exceeds a value of about 0.85–0.90, as estimated by resistance ratio measurements. However, despite the achievement of D/Pd loading ratios in excess of 0.90, no excess heat was observed in any of the experiments within the estimated experimental error of $\pm 1.5\%$.

Keywords: Cold fusion; Palladium hydrides; Palladium deuterides; Calorimetry

1. Introduction

Since Fleischmann et al. [1] reported the production of ‘excess’ heat during the electrochemical loading of deuterium into palladium cathodes, there has been a world-wide effort to verify these claims. However, while a number of research groups appear to have observed excess heat production [2,3], such claims are still viewed sceptically by the scientific community. This scepticism has arisen largely because of the poor reproducibility of the alleged phenomenon and also the failure of a large number of research groups to observe any excess heat [4]. However, in an attempt to address these difficulties, a number of workers [5–9] have suggested that the amount of deuterium absorbed by the cathode must exceed a critical value before excess heat production can be observed. In most instances, a loading ratio (i.e. the D/Pd atom ratio) of between 0.85 [5] and 1.0 [6–9] has been suggested as a prerequisite for excess heat production. A failure to observe excess heat [10] could then be rationalized in terms of an insufficient loading ratio, while occasional reports of heat production might be attributed to the deliberate or adventitious attainment of high D/Pd loading ratios. As noted earlier [11], the lack of reliable loading ratio meas-

urements in most calorimetric studies has hindered attempts to prove or disprove this hypothesis. However, more recently, some experimental evidence has been presented [12–17] which appears to support the ‘high loading’ hypothesis.

For example, McKubre and coworkers [12–14] have recently reported reproducible excess heat production during the electrolysis of D_2O at palladium cathodes provided that the D/Pd loading ratio attained exceeds about 0.85–0.90 and that certain other experimental criteria are also met. These measurements were performed using high precision flow calorimeters with in-situ and on-line measurements of the cathode D/Pd ratio. Excess power levels of around 0.1–2.0 W were typically reported when Pd rods of volume about 0.3 cm^3 were employed. A particularly interesting finding of this work was the apparent correlation between the amount of excess heat produced and the D/Pd loading ratio. In one experiment excess heat generation commenced at a D/Pd loading ratio of 0.85 and increased in an approximately second-order fashion with loadings in excess of this value [13].

Loading ratios in the above experiments were determined by measurement of the electrical resistance of the cathodes. This method has the advantage that it measures directly the amount of deuterium loaded interstitially into the palladium lattice. Other methods based upon volumetric [15] or pressure [16,17] measurements do not discriminate between deuterium contained interstitially in the lat-

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tice and that trapped in voids or dislocations in the metal, and therefore may overestimate the actual extent of interstitial loading. However, the resistance method is usually calibrated against volume and pressure measurements so that such an error may already be implicit in any calibration. Despite this potential complication, resistance measurements are still considered a useful diagnostic in excess heat studies [12].

The other requirements for reproducible excess heat production identified by McKubre's group included (i) the application of substantial current densities (in excess of $100\text{--}200\text{ mA cm}^{-2}$) [12] and (ii) the use of a sufficiently long electrolysis time (typically, hundreds of hours [12,13]). The above three requirements have been identified empirically and their exact mechanistic significance is not yet understood [13]. For example, it is unclear why an initiation period of hundreds of hours should be necessary for excess heat production, particularly when a palladium cathode of the dimensions used can be loaded to $D/Pd > 0.9$ in a few tens of hours [12]. Nevertheless, these findings are important in that they provide a phenomenological model for excess heat production which can be tested experimentally.

Of the three criteria mentioned above, the loading requirement appears to be the most difficult to realize experimentally [12,13]. However, the results of McKubre and coworkers [12,13] and the results of an earlier loading study performed by the present group [11] indicate that attainment of such high D/Pd loadings ratios is possible under certain conditions. One requirement appears to be the prevention of surface cracking of the cathode. Such cracks leads to a loss of deuterium and hence lowering of the D/Pd ratio [13]. The maintenance of high loading ratios for extended periods of time also appears difficult, but McKubre and coworkers [11,13] have recently reported that this can be achieved by adding small amounts (typically 200 ppm) of Al or SiO_2 to the electrolyte [12–14]. In addition, McKubre and coworkers have periodically subjected the cathode to partial unloading and reloading cycles, and this procedure was frequently found to cause significant enhancements in the D/Pd loading ratio [14]. This latter approach has also been successfully employed by Will et al. [15] to prepare highly loaded palladium deuterides and hydrides.

The recent calorimetric and loading studies of Hasegawa and coworkers [16,17] also appear to demonstrate the importance of the D/Pd loading ratio and current density in initiating excess heat generation in the Pd + D system. These workers observed that excess heat was not produced for D/Pd loading ratios of less than approx. 0.80–0.85, or for current densities below approx. $100\text{--}200\text{ mA cm}^{-2}$ [16,17]. Although an initial experiment [16] appeared to show that the amount of excess heat increased rapidly with loading in excess of the threshold, subsequent experiments [17] indicated that the relationship between excess heat production and the D/Pd was highly variable. Neverthe-

less, despite the general lack of any systematic relationship between excess heat and loading, these results support the existence of a loading threshold (albeit at values lower than those observed by McKubre and coworkers [12–14]) and stress the importance of attaining high D/Pd loading ratios if excess heat is to be observed.

The principal aim of the present study was to test the hypothesis [5–9] that excess heat production in the Pd + D system only occurs when the D/Pd loading ratio exceeds a threshold value of about 0.85–0.90. To facilitate this, a calorimetric system was developed that allowed in-situ and on-line measurements of the D/Pd loading ratio. This enabled the relationship (if any) between the loading ratio and the production of excess heat to be examined. In addition, particular attention was paid to the replication of the experiments reported by McKubre and coworkers [12–14] and by Hasegawa and coworkers [16,17] as these probably provide the most substantial evidence for the existence of the excess heat phenomenon.

2. Experimental

2.1. Experimental design

The calorimeter used in the present study was a 'modified' isoperibolic type [18]. In this particular design, the heat flux from the electrolysis cell is integrated by a surrounding metal sleeve and then transferred via an intermediate thermally conductive layer to a metal block maintained at a constant temperature. The power dissipation in the electrolysis cell is then inferred from the steady-state temperature difference between the two metal blocks. This particular design has the advantage [18] that it avoids calorimetric errors caused by temperature gradients in the electrolysis cell.

A schematic diagram of the isoperibolic calorimeter used in the present investigation is shown in Fig. 1. Essentially, the calorimeter consisted of two heavy aluminium cylinders separated by a well-defined thermally conductive layer. The inner aluminium cylinder, which housed the electrochemical cell, was mounted concentrically inside the outer cylinder and held firmly in position by two Perspex support rings. The gap between the aluminium cylinders, as defined by the two end rings, was then filled with silicone oil. The regions above and below the support rings contained a thick layer of polyethylene foam insulation. This minimized heat losses in the axial directions and ensured that the majority of the heat transfer from the inner to outer aluminium cylinders occurred radially across the silicone oil layer.

The thermal output of the calorimeter was determined by measuring the temperature of each aluminium cylinder with two calibrated thermistors (type RTC, $20\text{ k}\Omega$ at 25°C). Each thermistor was sealed in a separate thin-walled glass tube which had been filled with a small amount of

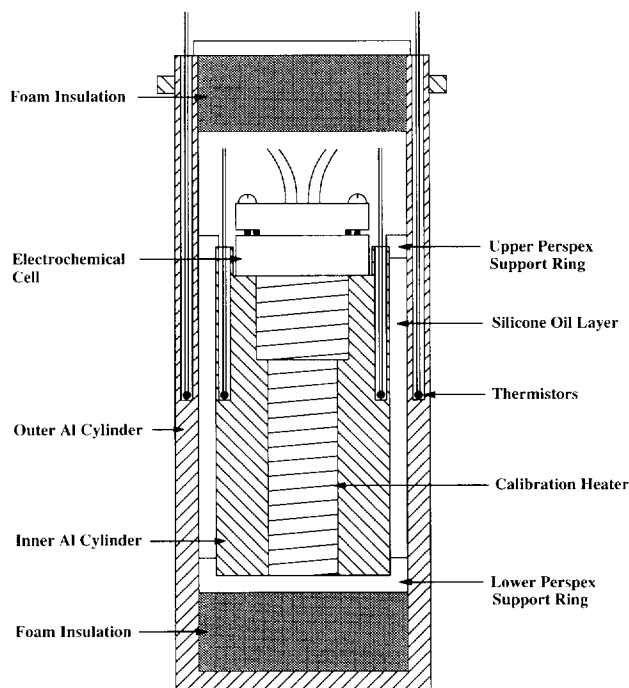


Fig. 1. A schematic diagram of the isoperibolic calorimeter and the electrochemical cell.

silicone oil to increase thermal conduction. To accommodate the thermistor probes, two vertical holes separated by 180° were drilled into the aluminium cylinders. These holes were positioned so that the thermistor probes in the inner and outer cylinders were exactly aligned in both the horizontal and vertical senses. In this manner, the temperature difference between the two aluminium cylinders was sensed at two separate locations. This provided some redundancy in the temperature measurements, and offered protection against errors caused by thermistor malfunction. For each aluminium cylinder, the temperatures measured by the two thermistors always agreed to within $\pm 0.01^\circ\text{C}$, indicating that the temperature distribution within each cylinder was very uniform.

The entire calorimeter assembly was immersed in a well-stirred thermostat bath containing a 1:1 mixture of ethylene glycol and deionized water. This was maintained at a constant temperature of $25.00 \pm 0.01^\circ\text{C}$ using a Tronac PTC-40 precision temperature controller. Measurements at various positions in the water bath indicated temperature uniformity to within $\pm 0.003^\circ\text{C}$. The bath contained two identical calorimeters, one containing a D_2O test cell and the other an H_2O control cell. This concurrent running of control and test experiments enabled thermal artefacts arising from variations in the bath or ambient temperatures to be distinguished from genuine excess heat production. The room in which the calorimetric experiments were performed was maintained at a temperature of $21 \pm 1.5^\circ\text{C}$. The ambient temperature was continuously monitored with a calibrated thermistor (type RTC, 20 k Ω at 25°C) posi-

tioned directly between the two calorimeters and approximately 10 cm above the liquid level in the bath. The water bath temperature was also monitored with a thermistor.

The electrochemical cell used in the present study has been fully described previously [11]. The only substantial modification to the earlier cell design was the cutting of a helical groove into the outer surface of the cell body to accommodate a calibration heater. The heater consisted of a 2 m length of insulated manganin wire (Goodfellow Metals), and had an electrical resistance of 18.2 Ω . All calorimetry experiments were performed in a 'closed-cell' mode where the evolved gases were recombined back to D_2O or H_2O using an internal recombination catalyst. The catalyst used in the majority of the experiments was a 10 cm^2 piece of a fuel cell electrode obtained from Giner Inc. However, the catalyst used in experiments G2 and G4 was a 12 cm^2 piece of a ESN-type fuel cell electrode obtained from E-Tek Inc.

All calorimetric experiments were performed in an electrolyte containing 1.0 M LiOD or LiOH prepared by dissolving lithium metal (Aldrich, 99.9% Li) in D_2O (Cambridge Isotope Laboratories, 99.9%) or high purity H_2O (Millipore Milli-Q water). The D_2O solutions were made up under a protective nitrogen atmosphere to minimize contamination with light water. In addition, the electrolytes used in experiments H1–H4 contained 200 ppm dissolved Al (BDH, > 99% Al), while those used in experiments G1–G4 contained 200 ppm dissolved SiO_2 (Cabot Corporation). The electrolytes used in experiments F1–F4 initially contained no Al, but three 200 ppm additions were made during the experiments.

The electrode pretreatment procedures used in the present study were essentially identical with those employed in the earlier loading study [11]. In summary, all cathodes were constructed from 0.10 cm diameter Pd wire obtained from Goodfellow Metals (99.95% Pd). The wire was manufactured by initially drawing down a Pd rod to a wire and then annealing it. The annealed wire was then redrawn to a final diameter of 0.10 cm. The manufacturer specifies the following major impurity levels for a typical analysis: 50 ppm Ag, 20 ppm Rh, 20 ppm Si, 10 ppm Fe, 10 ppm Cu and 10 ppm Pb. These wires were machined to a length of 32 mm and Pt wire connections were attached by spot welding. The electrodes were then degreased in hexane, annealed at 850°C for 3 h under vacuum ($< 10^{-5}$ Torr) and cooled to room temperature. For experiments H1–H4, the cathodes were then acid etched by sonication in a 1:1 $\text{HNO}_3 + \text{HCl}$ mixture for 5 min. Finally, the cathodes were repeatedly rinsed and sonicated in high purity water, dried in a desiccator and mounted in the electrolysis cells. An identical procedure was adopted for experiments F1–F4 and G1–G4, except that the acid etching step was omitted.

The D(H)/Pd loading ratio of the palladium cathodes was determined in situ using the experimental procedures described previously [11]. Essentially, this involved dc measurements of the electrical resistance of the cathode

using the standard four-probe technique. These resistance data were then converted to a loading ratio using calibration data available in the literature [11]. The estimated uncertainty in the D(H)/Pd loading ratios derived from such resistance measurements was estimated to be ± 0.02 .

All experimental parameters were recorded using a pair of data loggers (Data Electronics DT100) interfaced serially to two microcomputers (IBM PS2 model 30). Control of the data acquisition was implemented using the Labtech Notebook software package, with all cell data being displayed continuously on the computer monitor and also logged to disc. Cell voltages, currents and temperatures were recorded every 2 min, and the cathode resistance was measured at 5 min intervals. As in previous studies, data acquisition was performed in 24 hour cycles to allow the data loggers to undergo daily self-test and internal recalibration procedures. In addition, the calibration of each logger was periodically checked against a calibrated 51/2 digit multimeter (Hewlett Packard, HP 3468B) and a set of standard resistors (type 2782, Yokogawa Electric Works, Tokyo, $\pm 0.01\%$ basic accuracy).

Cell voltages were measured directly by the data loggers, while cell currents were measured as the voltage drop across calibrated ($2.500 \pm 0.002 \Omega$) wire-wound resistors. The estimated uncertainties in these measurements were $\pm 0.1\%$ and $\pm 0.2\%$ respectively. The calorimeter, bath and ambient temperatures were determined by measuring the resistances of the thermistors directly with the data logger. The overall accuracy of the resistance measurements was $\pm 0.02\%$, corresponding to an uncertainty in the temperature measurements of approximately $\pm 0.0025^\circ\text{C}$. The thermistors were initially calibrated against a high

resolution mercury thermometer with an NIST traceable calibration, and showed negligible ($< 0.005^\circ\text{C}$) drift over a period of several months. Linearization of the thermistor response and the conversion from resistance to temperature were implemented in the data logger software.

All electrolysis experiments were performed galvanostatically using a dual dc power supply (Thurlby PL 320). Typically, current densities between 50 and 300 mA cm^{-2} were employed, and this resulted in cell voltages of between 2.4 and 3.5 V, and Joule input powers of 0.12–1.1 W.

2.2. Calibration of the calorimeter

The steady-state power output P_{out} of an isoperibolic calorimeter is given by the equation [18]

$$P_{\text{out}} = k_i \Delta T \quad (1)$$

where k_i is the thermal calibration constant and ΔT is the temperature difference between the inner and outer aluminium cylinders. Calibration of the calorimeter was performed by applying varying amounts of power P_h via the electrical heater and measuring the resulting steady-state value of ΔT . The value of k_i was then determined from the slope of a plot of P_h versus ΔT .

Fig. 2 shows the variation of ΔT with time in a typical calibration experiment in which the heater power was stepped from 0 to 1.50 W in 0.25 W increments. The transient response of the calorimeters to such heater power increments indicated thermal time constants of approximately 23 min. Note also that the temperature responses of the two pairs of thermistors are practically identical, indi-

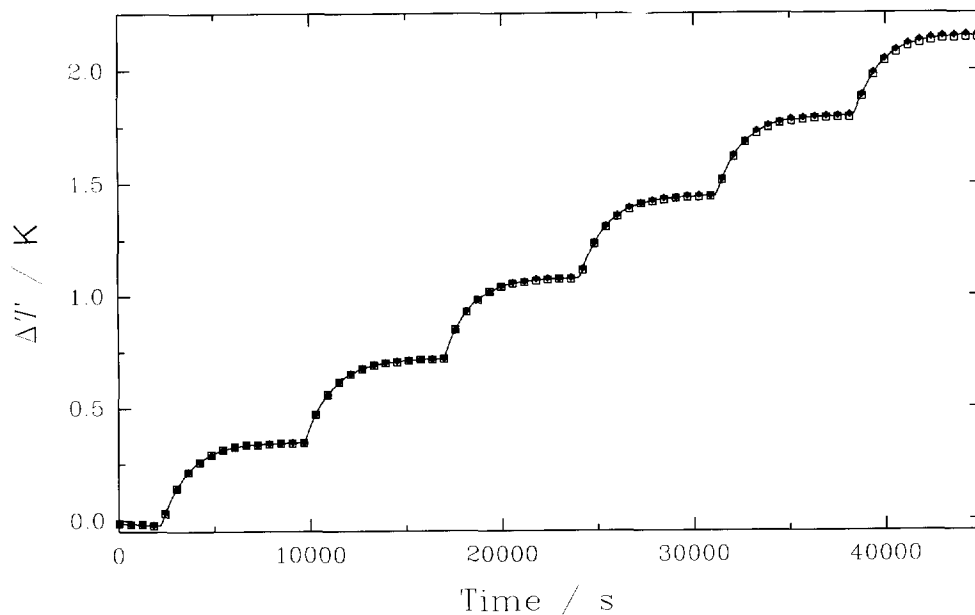


Fig. 2. The variation of ΔT with time during a typical calibration experiment. Symbols \blacklozenge and \square denote the responses of the individual thermistor pairs. The solid line represents the average value of ΔT obtained from these two independent determinations.

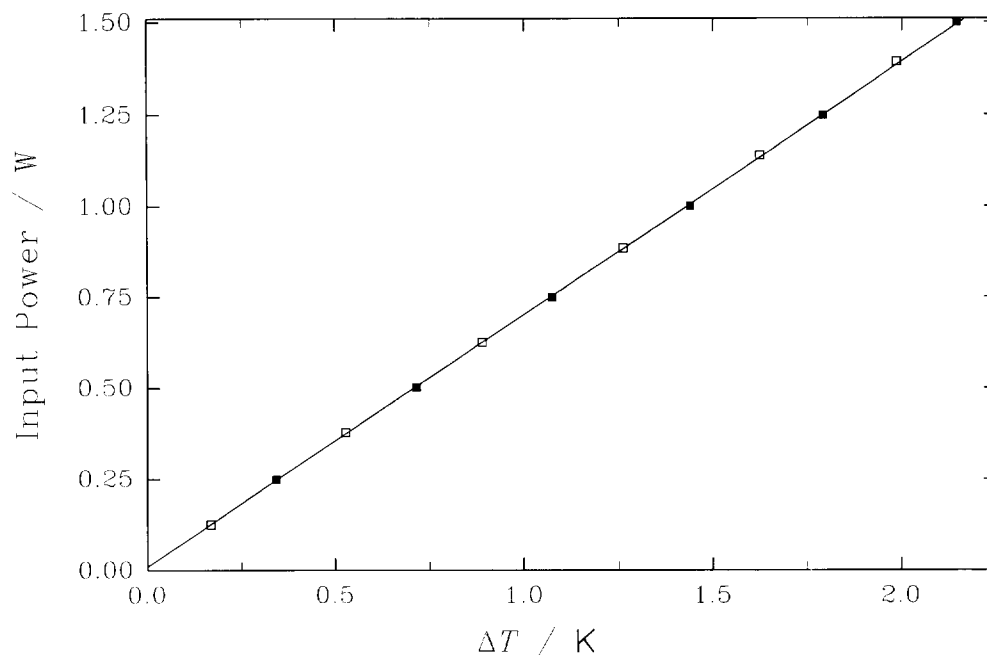


Fig. 3. A typical calibration curve for the isoperibolic calorimeter obtained from heater (■) and electrolytic (□) calibration experiments. The solid line represents a linear least-squares fit to the data obtained from the heater calibration (slope, $k_i = 0.6920 \text{ W } ^\circ\text{C}^{-1}$; correlation coefficient, $r = 0.99997$).

cating very similar values of k_i . The calibration curve obtained from these data is shown in Fig. 3. It is clear from this figure that the relationship between ΔT and P_h is highly linear over the range 0–1.5 W. Also shown in Fig. 3 are the steady-state values of ΔT obtained when power was introduced into the electrochemical cell via electrolysis at a platinum cathode. The values of k_i ob-

tained for the heater and electrolytic calibrations were $0.692 \pm 0.003 \text{ W } ^\circ\text{C}^{-1}$ and $0.694 \pm 0.003 \text{ W } ^\circ\text{C}^{-1}$ respectively. The excellent agreement between these two different modes of calibration indicates that the values of k_i derived from heater calibrations can be used to determine the power output in electrolytic experiments without introducing significant errors.

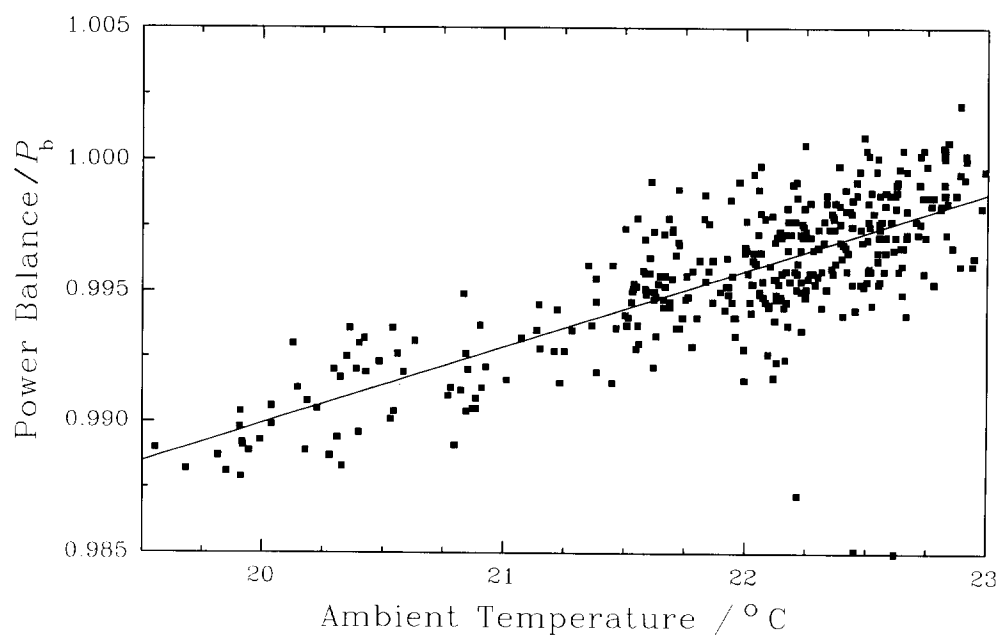


Fig. 4. The influence of ambient temperature fluctuations on the instantaneous power balance (■) in a typical control experiment. The average Joule input power during these measurements was 0.990 W. The solid curve represents a linear least-squares fit to the data (slope, $3.0 \text{ mW } ^\circ\text{C}^{-1}$; correlation coefficient, $r = 0.76$). In this particular experiment the ambient temperature was allowed to vary over a wider range than normal so that the the temperature dependence of P_b could be better established.

The values of k_i obtained in these initial calibration experiments were periodically redetermined by measuring ΔT at a single input power level. These single-point calibrations were performed by reducing the cell current density to 50 mA cm^{-2} and adding power via the electrical heater so that the total input power was approx. 1 W. Calibration constants obtained in this manner were in good agreement with earlier determinations, and the variation in k_i between calibration cycles was typically less than $\pm 0.3\%$. For the experiments reported here, the thermal calibration constants for the H_2O control and D_2O test calorimeters were approximately $0.69 \text{ W } ^\circ\text{C}^{-1}$ and $0.71 \text{ W } ^\circ\text{C}^{-1}$ respectively.

For the isoperibolic calorimeter used in the present study, the total error in the overall power balance arose principally from uncertainties in the measurement of ΔT , k_i and the Joule input power P_j . The estimated uncertainty in ΔT was $\pm 0.005^\circ\text{C}$, corresponding to a relative error of $\pm 0.4\%$ at a (typical) input power level of 1 W. The error in P_j was of the order of $\pm 0.3\%$ and arose from the uncertainties in the measurement of the cell voltage ($\pm 0.1\%$) and current ($\pm 0.2\%$). Finally, based upon the results of a number of calibration experiments, the uncertainty in k_i was estimated to be $\pm 0.3\%$. These individual errors indicated an overall uncertainty in the calorimeter power balance of $\pm 1\%$ (i.e. of $\pm 10 \text{ mW}$ at an input power of 1 W).

However, the results of a number of control experiments indicated an actual experimental error that was small but significantly higher than the above estimate. The origin of this additional source of error was eventually traced to the influence of ambient temperature variations on the amount of heat conducted out through the top of the calorimeter. Although this region of the calorimeter was well insulated, the large number of leads required for various electrical measurements meant that some conductive losses to the surroundings occurred. This effect is clearly delineated in Fig. 4 which shows the output power measured by the calorimeter as a function of the ambient temperature in a typical control experiment. Despite the large amount of scatter, the output power and ambient temperature appear to be linearly related, with a slope of around $3 \text{ mW } ^\circ\text{C}^{-1}$. Assuming an input power level of 1 W and a room temperature variation of $\pm 1.5 \text{ } ^\circ\text{C}^{-1}$, this effect constituted an additional error of $\pm 0.5\%$. Therefore the overall experimental error was estimated to be $\pm 1.5\%$. As will be seen later, this revised error limit was in good agreement with the uncertainties observed in a large number of control (and test) experiments.

2.3. Overview of experimental procedures

The present study involved loading and calorimetric measurements on a total of 12 electrolysis cells. These 12 experiments were grouped into three experimental series (designated F, G and H), with each series consisting of two

pairs of control cells and test cells. Each cell within a series had an identical electrolyte composition and electrode pretreatment, and was operated under the same electrolysis conditions. Typically, the duration of an experiment was around 30 days, and calorimetric and loading data were recorded continuously over this period.

The initial stage of each experiment involved charging the palladium cathode with deuterium (or hydrogen) at a current density of 50 mA cm^{-2} . The duration of this initial electrolysis period was about 300 h, which corresponds to the average initiation time specified by McKubre [19] for excess heat production. Subsequently, the current density was increased to 300 mA cm^{-2} and maintained at this value for 48 or 72 h. This value was in excess of the threshold current density mentioned above and, assuming that the loading and initiation time requirements had also been met, excess heat was anticipated during these periods of high current operation. A total of four such periods of high current operation were performed during each experiment, with each high current period being separated by a 24 or 48 h period when the electrolysis current was reduced to 50 mA cm^{-2} .

Most periods of high current were deliberately preceded by a brief period where the cathode was partially unloaded and then reloaded with deuterium or hydrogen, as this procedure has previously been shown [14,15] to lead to enhanced $\text{D(H)}/\text{Pd}$ loading ratios. The unloading was achieved by reversing the direction of the cell current so that deuterium (or hydrogen) was anodically stripped from the cathode. Anodic unloading was performed at low current densities (approx. $3\text{--}5 \text{ mA cm}^{-2}$) and with the cell voltage clamped at approx. 0.6 V in order to prevent the formation of palladium oxide or the evolution of O_2 [15]. Typically, this unloading procedure was carried out for a period of 2 h, during which the loading ratio $\text{D(H)}/\text{Pd}$ decreased from more than 0.9 to about 0.8. The cathode was subsequently reloaded with deuterium or hydrogen during the following high current period.

The overall electrolysis conditions used in each of the experimental series are conveniently summarized in Fig. 5. This figure shows the current density program employed in each study, and clearly indicates alternate periods of low and high current operation and also intervals where the cathode was anodically unloaded. For the series F experiments, three additions of Al were made to the cell electrolyte during the course of the experiments and these are also indicated in Fig. 5.

2.4. Analysis of calorimetric data

Although calorimetric data were recorded over the entire duration of each experiment, the instantaneous power balance P_b and the excess heat ratio R were determined only for periods where the current density was deemed high enough for excess heat to occur (i.e. at a current of 300 mA cm^{-2}). For these periods of high current opera-

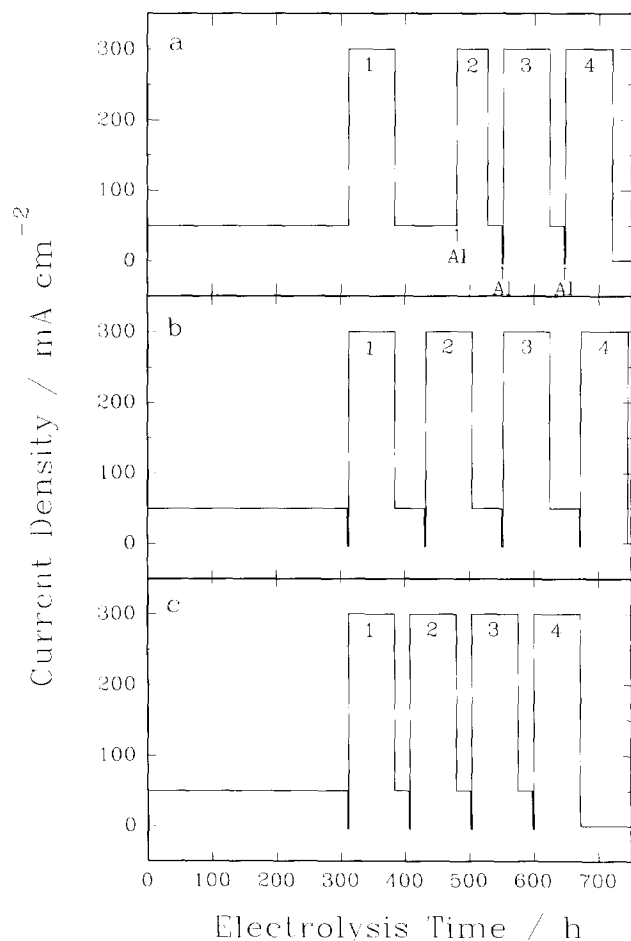


Fig. 5. Summary of the electrolysis conditions employed in (a) experiments F1–F4, (b) experiments G1–G4 and (c) experiments H1–H4. The four periods of high current operation are labelled 1, 2, 3 and 4. Also indicated are periods when 200 ppm Al was added to the electrolyte.

tion, the power balance P_b was determined as the ratio of the thermal output power P_{out} measured by the calorimeter to the total Joule input power P_j . For closed-cell electrolysis, the Joule input power is simply the product of the cell voltage E_{cell} and the cell current I , so that

$$P_b = k_i \Delta T / E_{\text{cell}} I \quad (2)$$

Similarly, the excess heat ratio R was determined as the ratio of the integrated thermal output power to the integrated Joule input power:

$$R = k_i \int_{t_1}^{t_2} \Delta T dt / I \int_{t_1}^{t_2} E_{\text{cell}} dt \quad (3)$$

where t is time and t_1 and t_2 define the beginning and end of each 48 or 72 h period of high current operation. However, it should be noted, that the calorimetric data obtained during the first 2 h, immediately following the stepped increase to 300 mA cm⁻², were not included in the calculation of R . During this interval, the thermal output power of the calorimeter was distorted by the

calorimeter time constant, resulting in substantial errors in the measured power balance. However, after this period (corresponding to about five thermal time constants) the calorimeter output had settled to within 0.5% of its steady-state value, and a reliable determination of the power balance could be made.

In practice, two separate measurements of the calorimeter's thermal output were made, using the values of k_i and ΔT obtained for each pair of thermistors. These independently determined values of P_{out} were then used to calculate the corresponding values of P_b and R . In all experiments, the values of P_{out} , P_b and R obtained for each thermistor pair agreed within $\pm 0.5\%$, and the calorimetric results presented in this section of the article always represent the mean value of these two independent determinations.

3. Results

Fig. 6 shows the instantaneous power balance P_b and the D/Pd loading ratio as a function of time for test experiment H1 during a 72 h period of high current operation. The upper and lower solid curves in this figure represent the D/Pd loading ratio and power balance P_b respectively. The two dashed lines represents the $\pm 1.5\%$ error limits for the cell's power balance. Although the power balance does vary slightly over time, it is clear that, within experimental error, there is no evidence for any excess heat production in this particular run. Fig. 7 shows similar data for control experiment H2 which was run simultaneously with experiment H1. Once again, a power balance close to unity was obtained, and the calorimetric data are consistent with the absence of any excess heat production. On average, the power balance in the test cell was about 0.4% higher than in the control cell, but this difference is considerably smaller than the estimated experimental error.

It is interesting to note that many of the small fluctuations in the calorimeter power balance occur synchronously in the test and control cells. These fluctuations reflect variations in the ambient temperature which, ideally, should influence both calorimeters equally. Occasionally, however, a small variation in the power balance of one calorimeter is not mirrored in the other. Such asynchronous thermal events probably reflect changes in the efficiency of the recombination catalyst or sudden changes in the input power level [12]. While it is possible that some of these fluctuations arise from small excess heat events, the fact that they occur in both control and test cells strongly suggests that they are artefactual in nature.

In order to examine further the variability in the calorimeter's power balance, the data in Figs. 6 and 7 were plotted as frequency histograms. These are shown in Figs. 8 and 9 respectively. Examination of these plots reveals that the data are normally distributed, and standard devia-

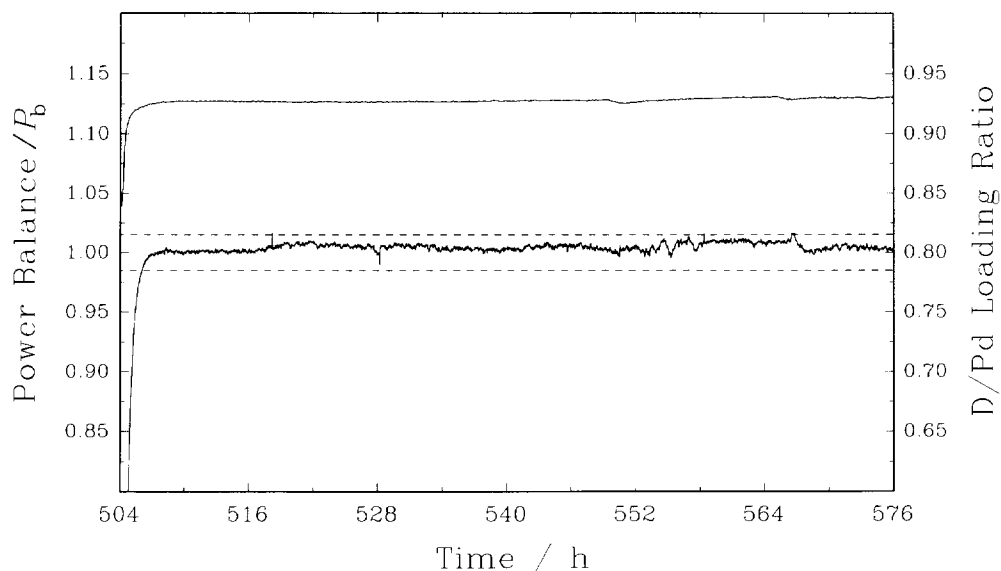


Fig. 6. Calorimetric and loading results obtained in test experiment H1 during the third period of high current operation. The upper line represents the D/Pd loading ratio (right-hand ordinate) while the lower line represents the cell power balance P_b (left-hand ordinate). The dashed lines represent the estimated $\pm 1.5\%$ error limits for P_b .

tions of 0.0034 and 0.0038 were obtained for experiments H1 and H2 respectively. Although the variability in the H2 data are slightly higher than for the H1 data, an F test at the 5% level revealed that this difference was not statistically significant.

Although the results in Figs. 6 and 7 only represent data taken from two experiments, they are typical of the thermal and loading behaviour observed in the other experiments, i.e. none of the D_2O test or H_2O control cells

showed any signs of excess heat production within the estimated experimental error of $\pm 1.5\%$. The overall calorimetric and loading results from each experiment are summarized in Tables 1–3. These tables give the excess heat ratio R and the mean and maximum D(H)/Pd loading ratios for each period of high current operation. Once again there is little indication of any excess heat production in any of the control or test experiments, with R deviating from unity by less than 1% in all cases. Further-

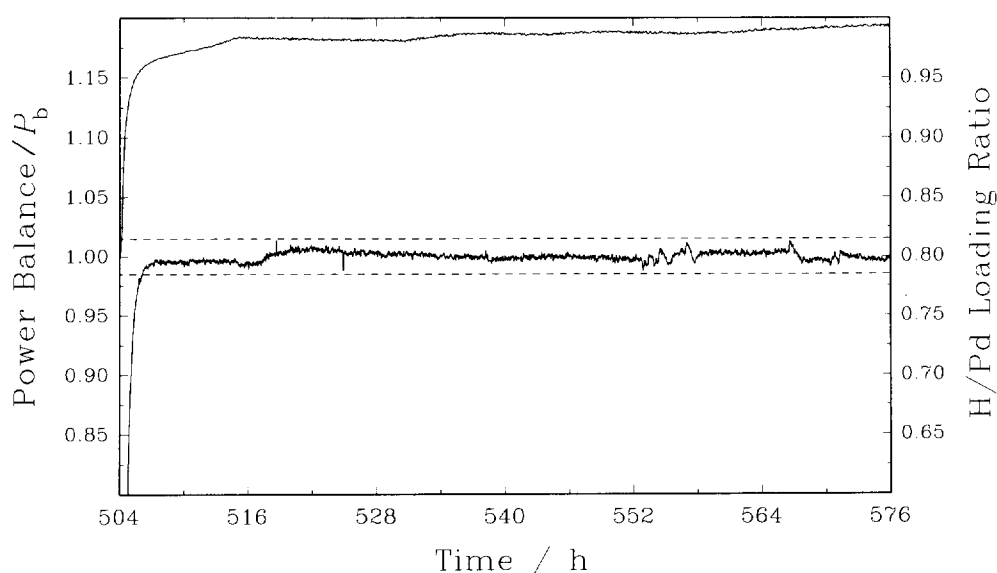


Fig. 7. Calorimetric and loading results obtained in control experiment H2 during the third period of high current operation. The upper curve represents the H/Pd loading ratio (right-hand ordinate) while the lower curve represents the cell power balance P_b (left-hand ordinate). The dashed lines represent the estimated $\pm 1.5\%$ error limits for P_b .

Table 1

Summary of the calorimetric and loading results obtained for experiments F1, F2, F3 and F4

Experiment	High current period (see Fig. 5(a))	Duration/h	Mean input power/W	Excess heat ratio R	Mean loading ratio	Maximum loading ratio
F1 (test)	1	72	1.037	0.998	0.87	0.91
	2	48	0.971	1.000	0.82	0.83
	3	72	0.921	0.998	0.90	0.92
	4	72	0.918	0.998	0.91	0.92
F2 (control)	1	72	0.999	1.000	0.95	0.96
	2	48	0.916	1.001	0.93	0.95
	3	72	0.892	0.998	0.94	0.96
	4	72	0.918	1.000	0.94	0.95
F3 (test)	1	72	1.048	0.996	0.88	0.91
	2	48	1.094	0.993	0.82	0.83
	3	72	1.076	0.997	0.86	0.88
	4	72	0.998	0.998	0.87	0.88
F4 (control)	1	72	0.952	0.992	0.87	0.96
	2	48	0.887	0.995	0.92	0.94
	3	72	0.887	1.001	0.92	0.95
	4	72	0.883	0.996	0.92	0.94

more, the mean values of R for the D_2O and H_2O experiments were 0.997 and 0.998 respectively, indicating very little difference in the overall thermal behaviour of the test and control cells.

4. Discussion

4.1. Calorimetric results

The results of the present calorimetric study (Tables 1–3) clearly provide no evidence for the production of

excess heat during the electrolysis of D_2O or H_2O at palladium electrodes. In particular, these results do not agree with the earlier findings of excess heat by McKubre and coworkers [12–14] and Hasegawa and coworkers [16,17]. However, these workers observed excess heat production only when certain experimental criteria had been met, and it is important to re-examine the extent to which these (and other) experimental conditions were satisfied in the present investigation. It is clear that if one or more of these criteria were only partially met, then the null results obtained in the present experiments might be explained.

Table 2

Summary of the calorimetric and loading results obtained for experiments G1, G2, G3 and G4

Experiment	High current period (see Fig. 5(b))	Duration/h	Mean input power/W	Excess heat ratio R	Mean loading ratio	Maximum loading ratio
G1 (test)	1	72	1.057	0.996	0.89	0.92
	2	72	1.046	0.997	0.91	0.93
	3	72	1.071	0.998	0.90	0.92
	4	72	1.086	0.999	0.89	0.92
G2 (control)	1	72	0.997	0.999	0.89	0.97
	2	72	0.972	0.993	0.93	1.00
	3	72	0.966	0.993	0.93	1.01
	4	72	0.954	0.994	0.92	0.99
G3 (test)	1	72	1.042	0.994	0.89	0.90
	2	72	1.035	0.995	0.89	0.90
	3	72	1.052	0.996	0.90	0.92
	4	72	1.128	0.995	0.88	0.89
G4 (control)	1	72	0.998	0.997	0.88	0.96
	2	72	0.982	0.997	0.88	0.95
	3	72	0.984	1.000	0.88	0.91
	4	72	1.044	1.000	0.88	0.91

Table 3

Summary of the calorimetric and loading results obtained for experiments H1, H2, H3 and H4

Experiment	High current period (see Fig. 5(c))	Duration/h	Mean input power/W	Excess heat ratio R	Mean loading ratio	Maximum loading ratio
H1 (test)	1	72	1.079	0.997	0.92	0.93
	2	72	1.098	0.995	0.92	0.93
	3	72	1.045	1.004	0.93	0.93
	4	72	1.079	0.997	0.92	0.93
H2 (control)	1	72	0.983	0.993	0.98	1.00
	2	72	0.959	0.993	0.99	1.01
	3	72	0.941	1.000	0.98	1.00
	4	72	0.926	0.999	0.97	0.98
H3 (test)	1	72	1.010	0.999	0.87	0.88
	2	72	0.989	0.994	0.89	0.89
	3	72	1.014	0.997	0.90	0.90
	4	72	1.068	0.998	0.90	0.91
H4 (control)	1	72	0.971	0.995	1.00	1.00
	2	72	0.990	1.008	0.99	1.00
	3	72	1.006	1.006	0.98	0.99
	4	72	1.004	1.006	0.98	0.99

Table 4

Excess power levels reported by McKubre and coworkers [12,13] and Hasegawa et al. [16] related to the surface area and volume of the cathode used

	Ref. [16]	Experiment P12 in Ref. [12]	Experiment C1 in Ref. [13]
Average excess power observed/W	0.35	0.70	0.45
Current density/ mA cm^{-2}	300	300	300
D/Pd loading ratio	ca.0.85	0.91	0.89
Excess power scaled with respect to cathode surface area/ W cm^{-2}	0.15	0.15	0.04
Excess power scaled with respect to cathode volume/ W cm^{-3}	1.5	2.0	1.6

Of initial concern is whether or not the isoperibolic calorimeter employed in this investigation possesses sufficient accuracy to detect reliably the levels of excess heat

production reported by McKubre and coworkers [12–14] and Hasegawa and coworkers [16,17]. However, before such an assessment can be made, it is necessary to make

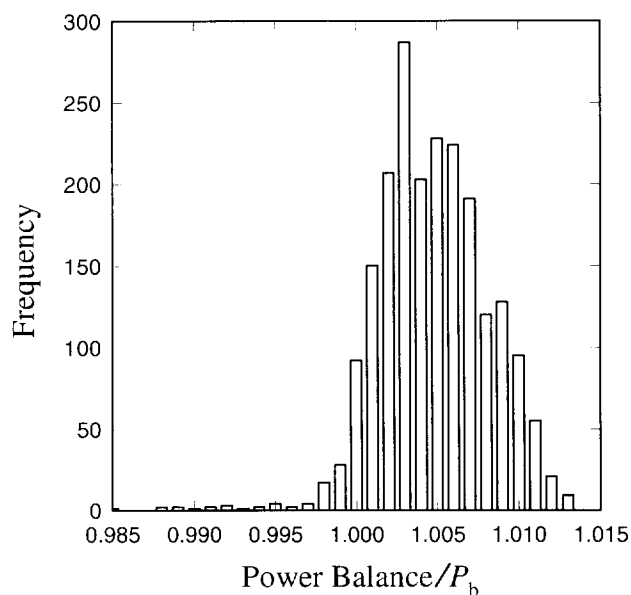


Fig. 8. A frequency histogram of the power balance in test experiment H1. The data are taken from Figure 6.

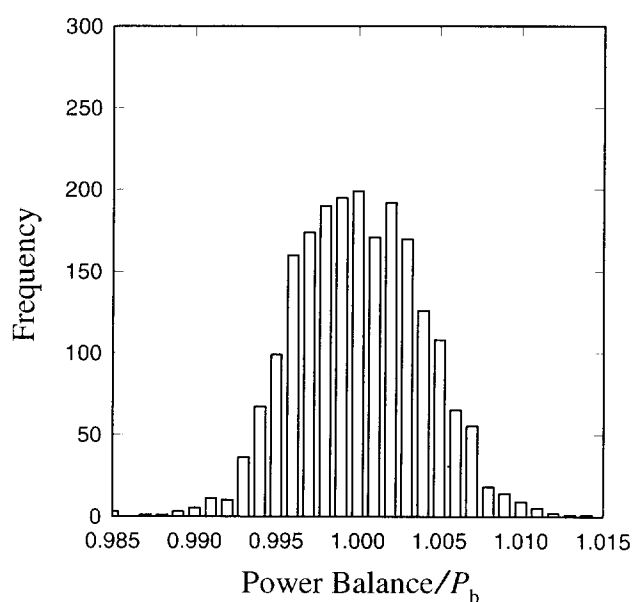


Fig. 9. A frequency histogram of the power balance in control experiment H2. The data are taken from Fig. 7.

some allowance for the fact that the cathodes used in the present study were considerably smaller than those used by the above workers. For example, if the excess heat phenomenon is a bulk effect [1], then it may be appropriate to normalize the data with respect to the electrode volume. Similarly, if the excess heat phenomenon is predominantly a surface effect [20–22], normalizing the excess power levels with respect to the electrode area might be warranted. Gerischer [23] has noted that the evidence for a surface effect is in fact more compelling than that for a bulk effect, so that the latter approach may be more appropriate.

Table 4 shows the excess power levels observed by McKubre and coworkers [12,13] and Hasegawa et al. [16] under conditions where the applied current density and D/Pd loading ratio were comparable to those employed in the present study. Also shown in Table 4 are the levels of excess power observed in relation to the area and volume of the cathode employed in each study. In comparison, the isoperibolic calorimeter employed in this study had a basic accuracy of ± 0.015 W. When this is related to the area and volume of the 1 mm diameter cathode used, this accuracy corresponds to detection limits of 0.015 W cm^{-2} and 0.6 W cm^{-3} respectively. Comparing these values with the data in Table 4, it is clear that the excess power levels reported by McKubre and coworkers and by Hasegawa and coworkers would have been detectable in the present isoperibolic calorimeter regardless of the manner in which the excess power scales with cathode size. Thus it would appear that the null results obtained in the present experiments cannot be rationalized on the grounds that the calorimeter used did not possess adequate sensitivity or accuracy.

Experimental requirements relating to the duration of electrolysis [12,13] and the applied current density [12,13,16,17] appear to have been met satisfactorily in the present study. Typically, calorimetric measurements were commenced after 300 h, and the total duration of each experiment exceeded 700 h. These experimental time-scales are comparable with those employed by McKubre [19] who has observed initiation times of between 200 and 600 h for 3 mm diameter palladium cathodes. Thus the duration of the present experiments would appear to be quite sufficient for excess heat to be observed. It should also be noted that Hasegawa et al. [16] have reported excess heat production within a few days of commencing electrolysis, so that the electrolysis time requirement would appear to be relaxable under certain experimental conditions. Similarly, the current density employed during the high current runs (300 mA cm^{-2}) was considerably above the threshold value of about $100\text{--}200 \text{ mA cm}^{-2}$ specified by McKubre and coworkers [12,13] and Hasegawa and coworkers [16,17].

The loading requirement for excess heat production also offers a possible means by which the null results of the present study could be rationalized. For example,

McKubre et al. [14] have observed that excess heat was not produced in any of their experiments when the maximum D/Pd loading ratio attained was less than 0.90. However, for loadings in excess of 0.95 excess heat was observed on every occasion. In the region $0.90 < \text{D/Pd} < 0.95$, approximately half of the experiments performed by McKubre's group produced excess heat [14]. In the present study, a maximum D/Pd loading ratio of less than 0.90 was observed in seven out of 24 high current runs, and therefore if the threshold were 0.90, excess heat might not be anticipated in such cases. However, in the remaining 17 runs, maximum D/Pd loading ratios of between 0.90 and 0.95 were observed and thus some instances of excess heat production should have occurred. It should also be noted that the lower loading threshold of ca. 0.85 proposed by Hasegawa et al. [16,17] was exceeded in all but two of the high current runs. Thus it would appear that the loading requirement specified by these workers has been satisfied in the majority of experiments performed in this study.

A final possibility is that, in addition to the above three criteria, there are other unknown experimental requirements that must be satisfied before excess heat is observed. These requirements may have been met adventitiously in the experiments of McKubre and coworkers [12–14] and Hasegawa and coworkers [16,17], but not in the present investigation. For example, it has been suggested that excess heat production is sensitive to the bulk and surface properties of the cathode material (e.g. to impurity content or metallurgical structure) [24–26] and to experimental conditions such as the electrolyte composition and temperature [5,20,24]. In order to cover this possibility, the electrode pretreatments, electrolyte compositions, electrolysis conditions and temperatures adopted in the present study were as described by McKubre and coworkers, and, to a lesser extent, those of Hasegawa and coworkers. However, there were slight differences in the experimental protocols employed in the present work and those mentioned above, and the possibility remains that some of these differences were critical.

The above suggestion is difficult to rule out completely but, superficially at least, the experimental results of McKubre and coworkers [9,12–14] and Hasegawa and coworkers [16,17] do not appear to indicate that excess heat production is particularly sensitive to slight changes in experimental conditions. For example, both these groups have observed excess heat production from palladium cathodes obtained from a number of different sources. These included wire, rod and foil specimens of varying size, purity and metallurgical history. In addition, these cathode materials were subjected to a number of pretreatment procedures including vacuum annealing [13,16,17], ion implantation [12], acid etching [12,16] and preloading with D_2 gas at elevated temperatures [9]. Similarly, excess heat has been observed in a number of different electrolyte systems and for temperatures between 10°C and 30°C [9,12,13,16,17]. Thus a case could be made from these two

studies that reproducible excess heat production can be observed under a fairly broad range of experimental conditions, provided that the experimental duration, current density and loading requirements mentioned above are satisfied.

4.2. Loading results

The loading results obtained in the present study are summarized in Tables 1–3, which show the mean and maximum D(H)/Pd loading ratios obtained in each of the 48 high current runs. For the D₂O experiments, D/Pd loading ratios of between 0.88 and 0.91 were fairly typical, although values as high as 0.93 were occasionally obtained. The H/Pd loading ratios observed in the H₂O experiments were correspondingly higher, and typically ranged from 0.95 to 0.98. This isotopic effect on loading was also observed in an earlier loading study [11] and has been reported by other workers [27–29]. In a number of experiments (e.g. G2, H2 and H4) H/Pd loading ratios of unity were achieved. This corresponds to a situation where all the octahedral sites in the palladium lattice are occupied [4,30]. However, within experimental error, there was no evidence of loading ratios in excess of unity, and it is unlikely that any significant occupancy of tetrahedral sites occurred.

The variation of the loading ratio with experimental conditions such as current density and electrolysis time (e.g. Figs. 6 and 7) was in good agreement with the findings of the earlier loading study [11]. For example, in most instances an increase in current density resulted in an improvement in the D/Pd and H/Pd loading ratios, al-

though there was a tendency for the loading ratios to deteriorate with time. As mentioned earlier, McKubre and coworkers [12,13] have advocated adding Al and SiO₂ to the electrolyte to minimize this effect, and this approach was adopted in the present study. The addition of 200 ppm SiO₂ to the electrolyte did not appear to lower the rate of unloading substantially, although Al was more effective in this regard. In many cases (e.g. Fig. 6) unloading of the cathodes was completely prevented. However, the data in Tables 1–3 indicate that the steady-state D/Pd loading ratios obtained in the presence of Al or SiO₂ were not significantly higher than the values obtained in the absence of these species. Therefore it would appear that Al does not contribute to the achievement of high loading but it does help maintain it.

As mentioned previously, the cathodes used in the present experiments were periodically unloaded and then reloaded with deuterium, as this procedure has previously been shown [14,15] to lead to improvements in the D/Pd loading ratio. However, the results in Tables 1–3 indicate that there is little evidence that repeated unloading and reloading cycles result in significant improvements to the steady-state D/Pd loading ratio.

4.3. The relationship between excess heat and loading

Despite the lack of any obvious excess heat production, it was decided to investigate further any possible relationship between the excess heat ratio R and the maximum D/Pd loading ratio. For example, it is possible that excess heat was being produced at levels just below the detection limit of the calorimeter, and these small thermal effects

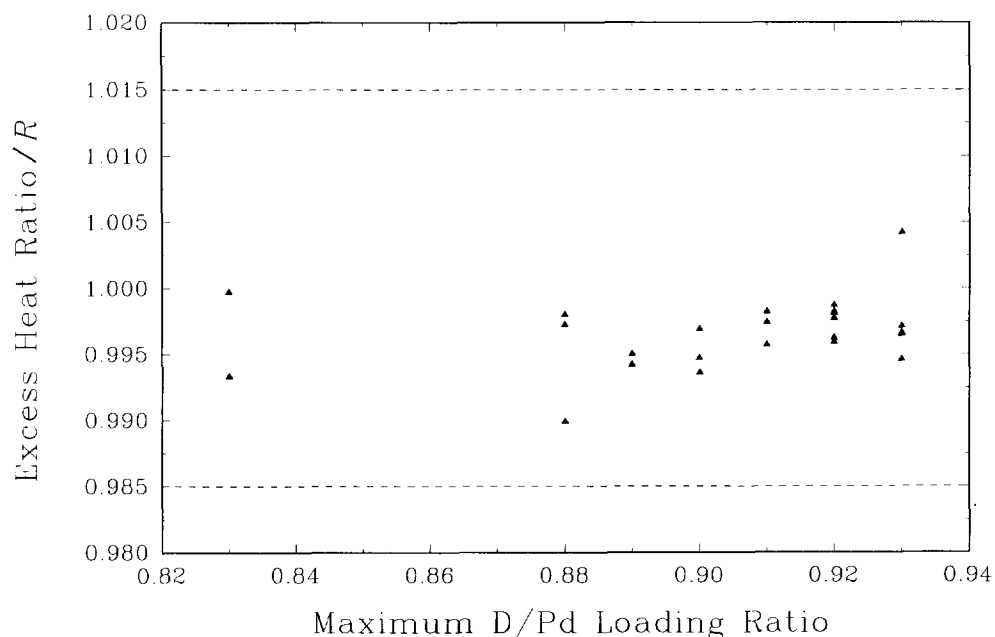


Fig. 10. The relationship between the excess heat ratio R and the D/Pd loading ratio for each high current run (data taken from Tables 1–3). The dashed lines represent the estimated error limits for the excess heat ratio.

might be revealed in such an analysis. However, Fig. 10 indicates that there is no obvious relationship between these two experimental parameters. In particular, there is little evidence that R increases as the D/Pd ratio becomes larger or that any loading threshold exists.

5. Conclusions

This study involved a search for excess heat production from palladium cathodes that had been highly loaded with deuterium. The major aim of this study was to attempt to verify the earlier findings of McKubre and coworkers [12–14] and Hasegawa and coworkers [16,17], who have reported reproducible excess heat production when (amongst other conditions) the D/Pd loading ratio exceeds a threshold value of about 0.85–0.90. However, despite the achievement of D/Pd loading ratios in excess of 0.90 and the satisfaction of other requirements relating to the experimental duration and current density, no evidence for any excess heat production was found in any of the experiments within the estimated experimental error of $\pm 1.5\%$. Therefore it would appear that additional experimental requirements (not presently understood) may have to be satisfied before excess heat can be observed in the Pd + D system.

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References

- [1] M. Fleischmann, S. Pons and M. Hawkins, *J. Electroanal. Chem.*, 261 (1989) 301; errata 263 (1989) 187.
- [2] E. Storms, *Fusion Technol.*, 20 (1991) 433.
- [3] M. Srinivasan, *Curr. Sci.*, 60 (1991) 417.
- [4] Report of the Cold Fusion Panel: A Report of the Energy Research Advisory Board to the Department of Energy, US Government Printing Office Washington, DC, 1989.
- [5] H. Ikegami, *Oyou Butsuri*, 62 (1993) 717.
- [6] E.K. Storms and C. Talcott, Abstracts from the Workshop on Cold Fusion Phenomena, Santa Fe, 23–25 May 1989.
- [7] G. Preparata, *Fusion Technol.*, 20 (1991) 82.
- [8] A. Takahashi, T. Iida, T. Takeuchi and A. Mega, *Int. J. Appl. Electromagn. Mater.*, 3 (1992) 221.
- [9] M.C.H. McKubre, R.C. Rocha-Filho, S. Smedley, F. Tanzella, J. Chao, B. Chexal, T. Passell and J. Santucci, First Annual Conference on Cold Fusion: Conf. Proc., National Cold Fusion Institute, Salt Lake City, UT, 1990.
- [10] T.I. Quickenden and T.A. Green, *J. Electroanal. Chem.* 344 (1993) 167.
- [11] T.A. Green and T.I. Quickenden, *J. Electroanal. Chem.*, 368 (1994) 121.
- [12] M.C.H. McKubre, S. Crouch-Baker, R.C. Rocha-Filho, S.I. Smedley, F.L. Tanzella, T.O. Passell and J. Santucci, *J. Electroanal. Chem.*, 368 (1994) 55.
- [13] M.C.H. McKubre, S. Crouch-Baker, A.M. Riley, S.I. Smedley and F.L. Tanzella in H. Ikegami (Ed.), *Frontiers of Cold Fusion: Proc. 3rd Int. Conf. on Cold Fusion*, Universal Academy Press, Tokyo, 1993.
- [14] M. McKubre, B. Bush, S. Crouch-Baker, A. Hauser, N. Jevtic, T. Passell, S. Smedley, F. Tanzella, M. Williams and S. Wing, Proc. 4th Int. Conf. on Cold Fusion, Vol. 2, Electric Power Research Institute, Palo Alto, CA, 1994.
- [15] F.G. Will, K. Cedzynska and D.C. Linton, *J. Electroanal. Chem.*, 360 (1993) 161.
- [16] N. Hasegawa, K. Kunimatsu, T. Ohi and T. Terasawa in H. Ikegami (Ed.), *Frontiers of Cold Fusion: Proc. 3rd Int. Conf. on Cold Fusion*, Universal Academy Press, Tokyo, 1993.
- [17] N. Hasegawa, N. Hayakawa, Y. Tsuchida, Y. Yamamoto and K. Kunimatsu, Proc. 4th Int. Conf. on Cold Fusion, Vol. 2, Electric Power Research Institute, Palo Alto, CA, 1994.
- [18] T.M. Gür, M. Schreiber, G. Lucier, J.A. Ferrante, J. Chao and R.A. Huggins, *Fusion Technol.*, 25 (1994) 487.
- [19] M.C.H. McKubre, personal communication, March 1993.
- [20] A.J. Appleby, Y.J. Kim, O.J. Murphy and S. Srinivasan, First Annual Conference on Cold Fusion: Conf. Proc., National Cold Fusion Institute, Salt Lake City, UT, 1990.
- [21] M.H. Miles, R.A. Hollins, B.F. Bush, J.J. Lagowski and R.E. Miles, *J. Electroanal. Chem.*, 346 (1993) 99.
- [22] A. Takahashi, A. Mega, T. Takeuchi, H. Miyamaru and T. Iida, in H. Ikegami (Ed.), *Frontiers of Cold Fusion: Proc. 3rd Int. Conf. on Cold Fusion*, Universal Academy Press, Tokyo, 1993.
- [23] H. Gerischer in T. Bressani, E. Del Giudice and G. Preparata (Eds.), *The Science of Cold Fusion: Proc. 2nd Annu. Conf. on Cold Fusion*, Conference Proceedings, Vol. 33, Italian Physical Society, Bologna, 1992.
- [24] M. Fleischmann and S. Pons, *Fusion Technol.*, 17 (1990) 669.
- [25] E. Storms, *Fusion Technol.*, 23 (1993) 230.
- [26] R.A. Huggins, *Mater. Res. Soc. Symp. Proc.*, 210 (1991) 317.
- [27] A. Kubota, H. Akita, Y. Tsuchida, T. Saito, A. Kubota, N. Hasegawa, N. Imai, N. Hayakawa and K. Kunimatsu in H. Ikegami (Ed.), *Frontiers of Cold Fusion: Proc. 3rd Int. Conf. on Cold Fusion*, Universal Academy Press, Tokyo, 1993.
- [28] D.R. Lawson, M.J. Tierney, I.F. Cheng, L.S. Van Dyke, M.W. Espenscheid and C.R. Martin, *Electrochim. Acta*, 36 (1991) 1515.
- [29] D.E. Williams, D.J.S. Findlay, D.H. Craston, M.R. Sené, M. Bailey, S. Croft, B.W. Hooton, C.P. Jones, A.R.J. Kucernak, J.A. Mason and R.I. Taylor, *Nature*, London, 342 (1989) 375.
- [30] T.B. Flanagan and W.A. Oates, *Annu. Rev. Mater. Sci.*, 21 (1991) 269.