CALORIMETRY AND ELECTROCHEMISTRY IN THE D/Pd SYSTEM
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ABSTRACT

Experiments have been performed to examine the anomalous effects associated with the D/Pd system, and to discover some of the experimental variables that might be important to the effects. Experiments were concerned with calorimetry of the D/Pd system, but also monitored those experimental variables that might be important in causing the effects: the D/Pd ratio and its rate of change, interfacial phenomena such as the reduction of D₂O, or reduction of contaminant species.

Two types of calorimeters were employed: a differential calorimeter and a flow calorimeter. In both of these instruments the electrochemical cell was pressurized with D₂ gas to 60 atm. The calorimeters were designed to facilitate on-line measurement of the resistance of the Pd cathode, and for high quality measurements of the interfacial impedance. In both calorimeters the electrochemical system has produced evidence of heat output appearing in bursts, apparently in excess of known input power sources. These bursts last for several hours or tens of hours, and produce energies up to several hundred thousand joules.

In electrodes that are heavily loaded with D, the electrical resistance of the Pd cathodes was observed to pass through a maximum with increasing time of cathodic charging, which is consistent with the known behavior of the H/Pd system. The electrochemical interfacial impedance of the cathode gives evidence of one, and at times two relaxation phenomena; it is also sensitive to accumulation of cathodically deposited impurities that may influence the rate and degree of D loading.

RESISTANCE MEASUREMENTS

A further feature of all our experiments was to have comprehensive monitoring of all the experimental parameters, e.g. cell current and voltage, reference voltage, Pd cathode resistance, electrochemical impedance, gas pressure, and of all temperatures pertinent to the experiment.

INTRODUCTION

Following the announcement last year by Fleischmann, Pons and Hawkins [1] of anomalous effects in the D/Pd system, we have performed a series of experiments designed to examine anomalous excess enthalpy associated with this system and to discover some of the experimental variables that might be important to the effects.

We have designed our experiments with two important principles in mind: the need in precise calorimetric measurements for a closed system, and for knowledge at all times of the composition of the reacting system. These principles were based on the understanding that calorimetry in an open system is subject to more error than in a closed one; this is especially important when seeking small excess enthalpies relative to the total power input into the system. The second principle is based on the belief that anomalous phenomena associated with the D/Pd system probably are related in some way to the D/Pd ratio, and that a high ratio, which is equivalent to a high D fugacity in the metal, is an important factor in determining the onset of the phenomena. In order to facilitate high loading we have operated our calorimetric electrochemical charging cells at an elevated pressure of D₂ gas, and at low temperatures. Deuterium solubility in Pd is a function of the applied emf, the D₂ gas pressure, and the temperature. The effect of temperature on solubility is very significant; the solubility at 5°C is 7 fold that at 50°C, so lowering the temperature (thereby increasing the deuterium solubility) is equivalent to increasing the gas pressure. A high pressure of D₂ has the important effect also of depolarizing the anode reaction hence reducing problems associated with O₂ production.
Figure 1 shows the known data for the resistance ratio, $R/R_0$, as a function of hydrogen loading from the data of Baranowski and Wisniewski [3] and deuterium loading from the data of Barton, Lewis and Woodward [4]. The solid line shows an extrapolation of the $D/Pd$ resistance

\[ y = 0.9769 + 3.000x + 44.119x^2 + 17.577x^2 + 1.78x^3 + 0.19x^4 + 8.999 \]

$R^2 = 0.999$

Figure 1. $R/R_0$ versus loading; data from references [4,H] and [5,D].

data, based on the assumption that the resistance behavior of the H and D systems are similar, and that resistance maxima occur at the same degree of loading. The inferences that we make about degrees of loading higher than 0.65 for $D/Pd$ are based on this assumption, and are obtained by fitting the measured resistance ratio data to the fifth order polynomial given in Figure 1. It is clear that the assumption of similar resistance behavior for H and D in Pd, differing only in the magnitude of the effect, and the length of the extrapolation, results in significant quantitative uncertainty at high loading levels. We nevertheless expect the loading levels inferred from resistance measurement to be useful qualitatively.

Several factors may influence the measured resistance. Of these, temperature, the occurrence of cracking, and inhomogeneity of loading in the metal phase produce the most significant effects. As shown in Figure 2, the temperature coefficient of resistance for the H/Pd system varies over a considerable range from the pure metal to H/Pd = 0.7; however, we have no data on the behavior in this regard of $D/Pd$ up to 0.7, or of any hydrogen isotope at higher loadings. Our own results suggest that the behavior shown in Figure 2 is closely obeyed in the deuterium system, but that the temperature coefficient remains more or less constant at $\sim 2 \times 10^{-3}$ K$^{-1}$, at higher loadings. This functional form is assumed in correcting our resistance data for temperature effects.

When the profile of composition in the metal phase is significantly nonuniform, due to high absorptions or desorption fluxes, the average resistance may not reflect the average loading. This problem arises particular during anodic deloading, when the surface achieves the low resistance of the $\alpha$-phase. At low absorption fluxes the concentration profiles are sufficiently flat that this seldom complicates the interpretation of resistance data.

Resistance inhomogeneities due to cracking or phase nucleation also may yield measured resistances that do not reflect the average composition of the D/Pd system. The extent of cracking can be minimized by loading the electrode unidirectionally, or by pre-loading at temperatures higher than $\sim 350^\circ$C, to avoid the $\alpha$ to $\beta$ phase transformation.

DIFFERENTIAL CALORIMETRY

Concept

Because of the applied current, electrochemical "cold fusion" cells produce Joule heat, and any extraneous heat producing reactions must be detected in addition to this heat. A convenient way of detecting chemical or nuclear reaction enthalpy is by comparing the temperature or heat flux from identical cells, where one cell is restricted to producing Joule heat only.

Heat is produced in an electrochemical cell with $D_2O$ electrolyte and Pd cathode as a result of several phenomena: absorption of D in Pd, overvoltages on the
cathode and anode, and \( I^2R \) heating in the electrolyte. The first of these factors becomes less significant once the \( D/Pd \) ratio has reached a steady state. Ideally, the other two factors should be the same in the experimental cell and the reference cell, the latter being the cell where the heat production is limited to \( J_0 \) heating only. \( J_0 \) heating differences in the two cells were minimized by using electrode surfaces and cells of identical size and shape, as well as identical electrolytes. Any bulk phase reactions arising from the palladium were minimized in the reference cell by using a palladized Cu electrode. This approach to the construction of the reference cell is based upon the tenet that fusion reactions occur, if at all, in the bulk phase and not on the surface of the electrode. If surface reactions are heat producing, then they are likely to occur in the Cu/Pd cathode before comparable reactions occur in the bulk Pd rod, since the thin Pd layer on the Cu rod would become saturated with deuterium before the Pd rod.

An alternative approach is to use \( H_2O \) in the reference cell. However, because \( H_2O \) electrolytes have different overpotentials and different electrical and thermal conductivities than their \( D_2O \) equivalents, the \( J_0 \) heating will be different. In addition, the heat of adsorption of D in Pd is significantly different from that of H in Pd. For these reasons, light water provides a poor blank for the experiments described below.

The electrolysis of water in our cells was minimized by keeping the applied cell voltage below that required for oxygen evolution. From the known thermodynamic and kinetic values, we calculated the minimum cell voltage required for the evolution of oxygen from light water, as 1.27 V, and even at 1.8 V the electrolysis current would not be above 1 mA.

**Experimental Approach**

Figure 3 illustrates a cell design that incorporates the features referred to above, which, except for the Pd electrode, represents identically both the experimental and reference cells.

The body of the cell was constructed from copper, which was chosen for its high thermal conductivity and low solubility and diffusivity of hydrogen isotopes, and its ability to accommodate a pressure of at least 50 atm. All interior surfaces were platinum coated on nickel. Both these metals are resistant to corrosion in LiIOD under the conditions applicable to this experiment. Temperature was measured with a four terminal resistance temperature device (RTD) embedded in each cathode.

For the experimental cell, the cathode was made from twice vacuum melted Pd, which was machined, then annealed in a vacuum at 800°C for three hours, then backfilled at temperature with \( D_2 \). Palladized copper was used for the reference cell cathode. The electrolyte was prepared by the addition of 99.9% Li metal (Ventron Alfa Products) to 99.9% \( D_2O \) (Aldrich Chemicals).

The cells were placed, as shown in Figure 4, in an insulated bath cooled to ~ 7°C. Pressure was applied to the cells from a \( D_2 \) gas cylinder. Each cell could be pressurized independently or removed from the gas system; a relief valve was also included to prevent overpressurization of the system in the event of a large exothermic reaction.

An Apple Macintosh microcomputer with a Keithley data acquisition system was used to monitor every minute the temperature of the Pd and Cu cathodes, the bath temperature, both cell voltages and the current. The interfacial impedances were measured every ten minutes during the latter part of the experiment.

The cells were filled with electrolyte, and the cathodes charged galvanostatically in series at 10 mA cm\(^{-2}\) for five days. On the establishment of steady-state temperatures and voltages, the Pd electrode resistance was measured, and the current increased by an amount just sufficient to keep the applied cell voltage below 1.5 V, to prevent oxygen evolution. The above sequence was repeated periodically.
At intervals during the charging process, the resistance of the bulk palladium electrode was measured using a four terminal ac measurement of the longitudinal impedance to determine the deuterium loading level. Measurements also were made of the two-terminal cell impedance, to determine what fraction of the dc cell voltage was associated with IR drop in the electrolyte and what was due to the deuterium redox overpotential.

Calorimetry

If \( I \) is the current and \( V \) the cell voltage then, in the steady state, the input power is the sum of the product \( IV \) and any extraneous sources of heat, \( Q_u \). If the calorimeter heat capacity and cooling constant are \( C_p \) and \( K \) respectively, then, for an elapsed time \( t \)

\[
IV + \frac{Q_u}{t} = (C_p + K) \Delta T \tag{1}
\]

where

\[
\Delta T = T_{cell} - T_{bath}
\]

this relationship can be further expressed as:

\[
IV = C_p'\Delta T - \frac{Q_u}{t} \tag{2}
\]

The calorimeter was calibrated by varying the input electrochemical power to the two cells in series. With \( Q_u = 0 \) we expect a linear relationship between the input Joule power to each cell, \( IV \), and the observed temperature difference between cell and bath:

\[
IV = a\Delta T + b
\]

The cells were calibrated according to equation [3], using both stepped and ramped currents, to establish a steady state slope and intercept: \( a \) and \( b \) for the working cell and \( a' \) and \( b' \) for the reference cell. We do not make any attempt to calculate or calibrate the temporal response of these cells to a change in input Joule heat or thermal conditions. Instead, in the differential mode, we assume that the only differences between the response of the working and reference cells are those due to the difference in the steady-state calibration coefficients \( (a \) and \( a', b \) and \( b') \), and the possible existence of extraneous heat, \( Q_u \), in the working cell. That is,

Working cell: \( a\Delta T + b = IV + Q_u \)

Reference cell: \( a'\Delta T' + b' = IV' \)

\[
Q_u = a\Delta T + b - (a'\Delta T' + b') \frac{V}{V'} \tag{4}
\]

Equation [4] reflects the extraneous heat if all influences on the two cells are the same except for the quantified and calibrated differences between the primed and unprimed variables. This procedure yields a positive excess if the extraneous heat occurs in the working (solid Pd) cell, a "negative excess" if this heat occurs in the reference (Pd coating) cell, and zero if there are no extraneous, uncorrelated influences.

Results

Table 1 displays a chronology of observations. Except for the times noted in Table 1, the differential calorimeter operated with \( Q_u \) close to zero, with a statistical fluctuation of \( \pm 200 \) mW. We observed anomalous enthalpic effects from the experimental cell, and possibly also from the reference cell. The enthalpic events referred to occurred when the output power, observed as heat, was in excess of the input power.

The events described as \( \delta V \), refer to occasions when the cell voltage underwent spontaneous changes at constant current, temperature and pressure. These events occurred without accompanying bursts of power in excess of that provided by the input electrical power, and were observed for the experimental cell only.
Table 1

Chronology of Anomalous Events in the Differential Calorimeter

<table>
<thead>
<tr>
<th>#</th>
<th>DATE</th>
<th>TIME</th>
<th>TYPE</th>
<th>H/J</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5/15</td>
<td>2300</td>
<td>(\partial H) XSCu</td>
<td>&lt;3</td>
</tr>
<tr>
<td>2</td>
<td>5/17</td>
<td>1800</td>
<td>(\partial H) XSCu</td>
<td>~10</td>
</tr>
<tr>
<td>3</td>
<td>5/18</td>
<td>0530</td>
<td>(\partial Vp_d)</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>5/18</td>
<td>2100</td>
<td>(\partial H) XSpd</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>5/19</td>
<td>0800</td>
<td>(\partial H) XSpd</td>
<td>32</td>
</tr>
<tr>
<td>6</td>
<td>5/20</td>
<td>0100</td>
<td>(\partial Vp_d)</td>
<td>0</td>
</tr>
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<td>(\partial Vp_d)</td>
<td>0</td>
</tr>
<tr>
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<td>5/24</td>
<td>1800</td>
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<td>&lt;3</td>
</tr>
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<td>1700</td>
<td>(\partial Vp_d)</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
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</tr>
<tr>
<td>12</td>
<td>6/01</td>
<td>0700</td>
<td>(\partial H) XSpd</td>
<td>6</td>
</tr>
</tbody>
</table>

where \(H=\)enthalpy, \(V=\)voltage, \(XS=\)excess.

Figures 5 and 6 show data for \(Q_u\) calculated using equation [4]. Also displayed is the excess energy for the two periods of essentially twelve hours, although the features in Figure 6 presumably are continuations of the event in Figure 5. The event in Figure 5 appears to have been initiated by a transient decrease in the cell temperature, both of which occurred in the interval between 16 and 17 hours in that figure. During this time a slow increasing current ramp was begun, although this was initiated some 20 minutes after the leading edge of the apparent positive power excess.

Figure 5. Differential calorimeter excess power and energy: May 31, 1989.
FLOW CALORIMETRY

Concept

A second series of experiments was performed in a flow calorimeter operated isothermally. Figure 7 depicts the calorimeter schematically. In the experiment described here only one calorimeter cell was used. During operation the electrochemical cell was contained inside the calorimeter Dewar flask, and the heat transfer fluid (silicone oil) was pumped through it. Temperature control was maintained by mounting the calorimeter in a well regulated bath (± 0.01°C) and by equilibrating the temperature of the oil with that of the bath before it was pumped into the Dewar flask. The flow rate was maintained constant to within ± 1% by means of an FMI metering pump; this was monitored continuously with a rotameter-type flow meter, and periodically by weighing timed samples removed from the flow. Two RTD temperature sensors were placed in the inlet to, and outlet from the calorimeter; turbulence promoters were employed to ensure that the fluid was well mixed before it passed over the outlet sensors.

The electrochemical cell was a nickel pressure vessel whose interior and all other fittings were coated with Pt. Provision was made for four-terminal resistance measurements, and a reference electrode. A helical electrical heater was mounted in grooves on the outside of the pressure vessel.
Calorimetry

To assist in rapid transfer of heat to the heat transfer fluid a "finned jacket" was placed around the outside of the vessel. In operation, the total input power to the calorimeter was maintained at a preset constant value by using the data acquisition computer to calculate the input electrochemical power and adjust the heater power. In this way, at constant mass flow of calorimetric fluid, the presence of excess power could be inferred from an increase in the temperature difference measured between the inflow and outflow. In the absence of excess power any second order effects of heat loss should remain constant since the temperature profile inside the Dewar flask is essentially constant.

The calorimeter was calibrated by several methods: by adjusting the heater power, and the electrochemical power in a stepwise manner allowing the system to come to a steady state, and by dynamic methods where a sinusoidal or sawtooth waveform was applied to the heater.

The thermal output of the calorimeter is observed to have the following dependence on input power:

\[ P_{\text{heater}} + P_{\text{electrochem}} = (C_p \frac{dm}{dt} + k') \Delta T \]  

where \( C_p \) is the heat capacity of the calorimetric fluid, \( \frac{dm}{dt} \) the rate of mass flow through the calorimeter, and \( k' \) is a small loss term due primarily to heat loss through the electrical and pressure interconnects that penetrate the top of the calorimeter vessel.

The values of the constants \( C_p \) and \( k' \) were determined by a series of calibrations, varying the input heater power at constant flow rate, and the flow rate at constant input power. The value of \( C_p \) obtained was in precise accord with that obtained by independent heat capacity measurements, and with the value supplied by the manufacturer. At the flow rates normally employed in the calorimeter (2-3 g/s), \( k' \) represents less than 5% loss due to conduction.

Experimental

LiOD of 0.1 M concentration was prepared by reacting pure Li metal with D\textsubscript{2}O under nitrogen in a glove box.

The Pd electrode was prepared by etching in aqua regia, annealing the sample in a vacuum for 4 hours at 800°C, and then cooling under D\textsubscript{2}. Upon cooling to room temperature the electrode was placed in the electrochemical cell.

Parameters monitored were the cell current and voltage, reference voltage, Pd resistance, two inlet and two outlet temperatures, two cell temperatures, cell pressure, and calorimetric fluid flow rate. Electrochemical impedance measurements were made at regular intervals to monitor the kinetic processes at the Pd/LiOD interface.

The cell was operated with 60 atm of D\textsubscript{2} pressure, and with varying cathodic current densities up to 600 mA cm\textsuperscript{-2}. Experiments were performed at 25 and 4°C.

Table 2 displays a chronology of excess heat observations, where \( \Delta T \) increased spontaneously in the apparent absence of any spurious effects. Figure 8 shows the raw data for event #2, calculated from the difference between the calorimeter output power from equation [5], and the known input power \( P_{\text{electrochem}} + P_{\text{heater}} \). This figure provides a good indication of the level of baseline variation of the "excess" power; for some period prior to and subsequent to the positive excursion shown in Figure 8, the "excess" power registers zero with a random variation of roughly 0.2 W. The structured variation of the "excess" power apart from the burst is due to the enthalpy of partial recombination of D\textsubscript{2} and O\textsubscript{2}. At high current densities, the anodic reaction is not completely depolarized by the D\textsubscript{2} pressure, and electrolysis occurs. The products of this reaction (and all the associated enthalpic effects) are contained within the calorimeter. Recombination occurs on the inner exposed surfaces of the Pt coated pressure vessel, and its progress can be monitored by the pressure. We observe oscillations in the pressure of period approximately 30 minutes, consistent with small positive and negative fluctuations of the "excess" heat. No significant change was observed in the cell pressure associated with the heat burst in Figure 8, and the recombination fluctuations occurred throughout this positive heat excursion.

Also shown in Figure 8 is the electrochemical input power. At this time the heater was employed for power calibration only at the times marked "P". The average of the positive excursion is approximately 1.25 W; nearly 33% of the total input power to calorimeter at that time. The excess energy was calculated from the area of the envelope of the event in Figure 8 to be 49 kJ, excluding the effects of heater calibration pulse which are incompletely removed from the steady state calculation. At no times were negative excursions observed in the data record of similar form or comparable magnitude. The energy total of the four events of apparent excess heat in this experiment was 298 kJ, this is 7.45 MJ/mol for an electrode which comprised 0.04 mol of Pd.
Table 2

Cell P2 Excess Enthalpy

<table>
<thead>
<tr>
<th>#</th>
<th>DATE</th>
<th>TIME</th>
<th>DURATION/h</th>
<th>H/kJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10/11</td>
<td>21:40</td>
<td>Cell Start Up</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>11/1</td>
<td>22:00</td>
<td>13</td>
<td>49</td>
</tr>
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<td>4</td>
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<td>23:00</td>
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<td>5</td>
<td>12/10</td>
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<td>46</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>TOTAL</td>
<td></td>
<td></td>
<td>298</td>
</tr>
</tbody>
</table>

Figure 8. Isothermal flow calorimeter excess heat event #2.
Impedance Measurement

At low loading levels the electrochemical impedance of the Pd/LiOD interface exhibits a single semicircle in the complex plane suggesting that the response is due to the double layer capacitance and charge transfer resistance. At high rates of loading (high surface loading) or high equilibrium loading levels (high bulk loading) the interfacial impedance response exhibits a more complex behavior.

Figure 9 shows the impedance response of the electrode in the pressurized isothermal flow calorimeter, at 25°C, as a function of applied cathodic current (for an electrode with area = 4 cm²). Based on the measured resistance ratio and the extrapolation of known data suggested by Figure 1, the electrode in this experiment had a bulk D/Pd loading of approximately 1.

Post Test Analysis

One week after the electrode was removed from the pressurized isothermal flow calorimeter it was placed between two layers of Polaroid ASA 3000 film for 12 days. Details of the resulting films are shown in Figure 10. Clear evidence of some type of ionizing radiation is observed. The points of light with diffuse halo exposure suggest that some of the radiation may be coming from point sources within the metal, being scattered by the lattice structure.

The surface and near surface of the sample were subjected to surface analysis by laser ionization (SALT) and compared to an identically treated blank electrode. No changes in isotopic composition were observed, and no unexpected elements were observed that might be consistent with fission products.
Approximately 10% of the total mass of the electrode, comprising one sample from the surface and one from the bulk, were analyzed by Rockwell International for $^3\text{He}$ and $^4\text{He}$ by mass spectrometry of a molten sample. This technique is capable of detecting $10^{11}$ atoms; no He was observed at that detection level.

Mass spectrometry was used to analyze the residual $\text{D}_2$ gas in the pressure vessel for $^3\text{H}$, $^3\text{He}$ and $^4\text{He}$. At a detection level of 1 ppm, none of these isotopes were found.

The electrolyte was sampled for tritium before emplacement in the cell and after removal; no increase in tritium was observed above the background level.

**DISCUSSION**

Experiments were performed in two electrochemical cells comprising a Pt anode, LiOD electrolyte, Pd cathode and $\text{D}_2$ gas. Both experiments appear to give bursts of heat output in excess of the known sources of Joule input heat. In one experiment differential calorimetry was employed; in a subsequent experiment a more sophisticated isothermal flow calorimeter was used. The results nevertheless were qualitatively similar - considerable periods in which the calorimeters were poised in thermal balance, with occasional positive excursions of output power, lasting hours or tens of hours, and in magnitude several tens of kilojoules.

It is difficult to discuss the initiation of these events given the apparent stochastic nature of the excess heat bursts. Nevertheless, we have observed no heat excess from electrodes that were loaded to $\text{D/Pd} \approx 1$ (based on an extrapolation of known resistance ratio data). It may be that such loading is necessary. However, it is clearly not sufficient to produce the anomalous heat effects. In both cases the Pd had achieved its minimum resistance (from which we infer maximum loading) condition, several weeks prior to the observation of anomalous heat.

The interfacial impedance data may give a clue to other conditions that are necessary for anomalous heat effects to be observed. The impedance feature evidenced at low frequencies and appearing in the fourth quadrant of Figure 9 is not present at all times, even for a highly loaded electrode. In a subsequent paper we will demonstrate that the impedance spectra can be accounted for quantitatively by the double layer capacitance in combination with the charge transfer resistance for $\text{D}$ adsorption coupled with recombination and absorption at a fractional monolayer coverage of D. The fourth quadrant feature derives from the coupling of the potential dependent adsorption coverage, and the concentration dependent adsorption flux. In qualitative terms, this "inductive" feature appears only when there is a significant absorption flux: it can be used as an
indicator that the electrode surface is in a state such that the electrode is capable of further absorbing D.

Extended cathodization provides an opportunity for electro-reducible minority components to deposit on the cathode surface. While we did not observe macroscopic fouling of the electrodes in this study, one might expect that the presence of a film of cathodically deposited contaminant species on the surface would block D absorption. In our experience, however, the presence of certain deliberately added impurities appears to create the inductive effect and facilitate loading, whereas anodic stripping of the Pd appears to eliminate the fourth quadrant term. It is therefore likely that the inductive effect is a feature of a specifically modified Pd surface, of unknown origin, but which may be beneficial to loading.

The presence or absence of the inductive term, the existence of which effectively reduces the dc interfacial resistance, can be used also to account for the anomalous changes observed in the cathodic overvoltage of highly loaded electrodes. For both calorimeter cells we have observed cases where the voltage measured between the surface of the cathode and an adjacent Pt pseudo-reference electrode have spontaneously, and over a period of several hours, increased at constant current, decreased at constant current, and, in one case, the overvoltage was observed to decrease with increasing current.

It is possible that both high loading and high interfacial flux are necessary for the anomalous effects to be manifest. In our experience, certain conditions facilitate high loading: high temperature gas loading prior to cathodization, electrode activation in strong acid, low temperature electrochemistry, high current densities, and high pressures of D2. In a number of instances the occurrence of "excess heat bursts" appears to correlate with a change in condition that might well stimulate high D fluxes at the interface of a highly loaded electrode: transient or stepped increases or decreases in the cathodic current and decreases in the temperature. The event shown in Figure 5 occurred 20-30 minutes after a transient decrease in the cell temperature. A decrease in the temperature might be expected to result in an increased absorption flux since the solubility and thus the equilibrium loading level of D in Pd is increased. Additionally, lower temperature is likely to result in an increased electrochemical impedance for the recombination step which, at constant current, may result in a higher adsorption coverage, a larger dynamic overvoltage and facilitate the adsorbed to absorbed reaction step.

The last excess heat event observed in the isothermal flow calorimeter (event #4 in Table 2) was associated with a decrease in cell current, and persisted for some hours following the reversal of cell potential for anodic deloading. If a flux of D is necessary, then it may be that the direction is not important. If both high flux and high loadings are necessary, then it is difficult to maintain high loading at a high steady-state outward D flux, while it is difficult to achieve a high steady-state inward flux at a high loading level. It might be possible to resolve this apparent impass by periodically reversing the direction of the flux.

In both experiments the excess energy in any burst represents at most 1% of the total energy input to the calorimeter before the excess heat event. The precision with which we establish our calorimetric baseline is not sufficient to eliminate the possibility that energy is being stored in the system during the long periods of time that calorimeters are in apparent thermal balance, and released in bursts. While the thermodynamic properties of the D/Pd system are not known for mole fractions of D near 1, we consider it nevertheless unlikely that the excess energies represented by the events chronicled in Tables 1 and 2 can be accounted for by chemical processes. In particular it is unlikely that spontaneous transformation is occurring to a more stable (and hitherto unobserved) phase. If this were so, we would expect to see some evidence in the mechanical character and some evidence in the resistance. No such evidence is observed.

We do not claim to have examined all possible sources of systematic error in our calorimetry. However, highly instrumented and monitored experiments, using calorimeters of considerably different design and principle, have resulted in qualitatively and quantitatively similar results of apparent excess heat bursts outside the standard deviation of the random errors by factors up to 50.

It has been suggested [1] that excess heat is produced in the D/Pd system by nuclear processes. The evidence that we have from the isothermal flow calorimeter cell that produced 300 kJ of excess heat is that sources of ionizing radiation are contained within the Pd cathode, that are not present in a blank electrode prepared identically from the same stock. Experience from autoradiographs of other electrodes heavily electrolyzed in LiOD and LiOH suggests strongly that the exposure evidenced in Figure 10 is not due to contact printing or to chemical exposure by reducing species such as lithium or hydrogen. Autoradiography while sensitive is not specific, and we were unable to identify the species that produced the film exposure, or any other species that might be a product of nuclear reaction. We were unable to identify any isotopic changes or the presence of 3He or 4He in the metal, the presence of 3H in the electrolyte or the presence of 3He, 3He or 4He in the gas. Within the respective detection limits of the various techniques employed, it is not clear that we would expect to see the ~ 3 x 1015 atoms of product that would be associated with 300 kJ of heat from a nuclear process.
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REFERENCES


