

CALORIMETRY OF THE Pd + D CODEPOSITION

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Thermal activities associated with electrochemical compression of deuterium produced on electrodes prepared by Pd+D codeposition are discussed. Three cases are considered: activities during and shortly after commencement of current flow, those observed during runs of several days duration, and surface temperature distribution recorded by infrared scanning. Experimental results show excellent reproducibility, high-power outputs, and the development of thermal instabilities resulting in the formation of local hot spots.

I. INTRODUCTION

An alternate method for the initiation of the Fleischmann-Pons effect is to employ an electrode prepared by Pd + D codeposition. This technique involves the electrodeposition from a Pd²⁺ salt solution at cell currents (potentials) so adjusted as to deposit the Pd film in the presence of evolving deuterium.¹ The effectiveness of this approach with regard to generation of nuclear and thermal events was reported by us in the initial phase of our investigation. One advantage of the codeposition process is rapid saturation with deuterium; atomic ratios D/Pd > 1.0 were measured within minutes.² Thus, the condition for the initiation of the Fleischmann-Pons effect is realized after brief periods of time as demonstrated by X-ray emission³ and tritium production.⁴

Early in the investigation of the codeposition process, we reported that cathodically polarized Pd + D electrodes are hotter by 1.5 to 2°C than the electrolyte solution when measured by a thermocouple.¹ However,

when viewed with an infrared camera, the electrode surface temperature exceeded that of the electrolyte by ~6°C (Ref. 5). In what follows, we present evidence for excess enthalpy production: Sec. IV.A, shortly after completion of the codeposition process; Sec. IV.B, in the course of a long charging time; and Sec. IV.C, the development of instabilities. The appropriate experimental procedures are briefly outlined.

II. FORMULATION OF CALORIMETRIC EQUATION

In the simplest arrangement, an electrochemical cell is a three-phase, multicomponent assembly wherein the charge transfer reactions and associated transport processes occur. Initially, this system is in thermal, mechanical, and chemical equilibrium. On initiation of current flow, significant changes in temperature and concentration take place, i.e., the development of gradients, which in turn initiate transport processes in the electrolyte phase and across the electrolyte-gas interface. The increase in temperature arises from the irreversible processes: the joule heating, the electrodic processes, and the exothermic absorption of deuterium by the palladium electrode as well as due to exchange with the environment.

II.A. Enthalpy Balance

In deriving the calorimetric equation, we balance the change in the enthalpy of the electrolyte phase with the enthalpy gain or loss attributed to the participating processes. In particular, applying the enthalpy balance to an open electrochemical system (not including the cell walls and electrodes), we obtain, with $dn_j < 0$,

$$\frac{\partial H}{\partial T} \cdot dT - \sum \frac{\partial H}{\partial n_j} \cdot dn_j = dH^* - dw + \sum dH^{(1 \rightarrow \nu)} + \sum dH^{(1 \rightarrow e)}, \quad (1)$$

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where

dH^* = energy produced (e.g., heat of absorption, excess enthalpy)

dw = work done on the surroundings

$\Sigma dH^{(1 \rightarrow v)}$ = enthalpy transferred between the electrolyte and the gas phase

$\Sigma dH^{(1 \rightarrow e)}$ = enthalpy transferred to or from the environment.

The direction of transfer determines the sign, i.e., the quantity removed from the system is negative. By dividing each term of Eq. (1) by dt and identifying the participating processes, we obtain the governing differential equation

$$\left[\Sigma m_i c_i \frac{dT}{dt} \right] + m_o c_s \left[1 - \frac{It}{2m_o F} \right] \frac{dT}{dt} = J^* + I(E_c - E_{th}) + \Sigma J^{(1 \rightarrow 2)} + \Sigma J^{(1 \rightarrow e)}, \quad (2)$$

where the first term accounts for the contribution of all cell components except the electrolyte. This term must be carefully evaluated during the course of long-term experiments and, in particular, during the calibration procedure because the relaxation time is strongly affected by the physicochemical properties of walls and enclosures.

The solution of Eq. (2) requires specification of the initial conditions and evaluation of all other terms consistent with the mode of operation and the cell design. The initial conditions are the equilibrium conditions, i.e., the temperature of the whole system is that of the environment, and the composition of the gas phase is $D_2:O_2 = 2:1$ with vapor in equilibrium with the electrolyte. The rate of heat transfer out of the cell depends on the cell geometry, construction of the enclosure, and mode of transport. The simplest case is that of an adiabatic wall. If the enclosure is a diathermal wall, then the heat transfer may occur via radiation with some convective contributions or via convection with minor radiative contributions.

II.B. Heat Content of the Electrolyte Phase

As written, the second term on the left side in Eq. (2) represents the rate of change in the heat content of the electrolyte as a function of time, evaluated at the temperature $T(t)$. Assuming a 100% faradic efficiency, the consumption of D_2O , in a cell operating for t s at the current density, I ($A \cdot cm^{-2}$), is $It/2F$, so that the time rate of change in the electrolyte heat content is $m_o c_s (1 - It/2Fm_o)$, where m_o is the initial amount of D_2O .

II.C. Electrical Work dw

A unique feature of an operating electrochemical cell is the occurrence of charge transfer reactions whereby electrons are generated at the negative electrode and are

transferred in an external circuit and consumed at the positive electrode in another charge transfer reaction. In a steady state, the number of electrons leaving and entering the cell is the same, which means that an electrochemical cell can be considered a closed system with regard to the electrical charge (note that potential difference buildup occurs at the phase boundary only). Irrespective of the direction of current flow, the product IE_C must be a positive quantity. By convention, the positive current is flowing out of the cell so that the electrical work term in Eq. (1) is positive. The enthalpy input to the cell is $I(E_c - E_{th})dt$, where E_{th} is the thermoneutral potential.

II.D. Rate of Enthalpy Transfer

The $J^{(1 \rightarrow e)}$ term is, as a rule, of the form of the generalized Ohm's law, $J_q = k[T^{(1)} - T^{(2)}]$, and where k is usually taken to be constant within this temperature range. Its numerical value depends on the composition of the wall, with the applicable computation methodology described in textbooks on heat transfer.

In the system under consideration, the $J^{(1 \rightarrow v)}$ term represents the sum of the enthalpy carried out by the rising bubbles saturated with D_2O vapor at the cell temperature $J_1^{(1 \rightarrow v)}$ and that due to the phase change $J_2^{(1 \rightarrow v)}$. The respective rates are the following:

$$\frac{I}{F} [0.5c_{D_2} + 0.25c_{O_2} + 3pc_s/4(p^* - p)]$$

and

$$0.75IpL^{(1 \rightarrow v)}/F(p^* - p),$$

where

p^* = atmospheric pressure

p = vapor pressure of D_2O

L = latent heat of evaporation.

II.E. Temperature-Dependent Parameters

Excluding the J^* term, all terms on the right side of Eq. (2) are temperature dependent in a simple way except for the $I(E_c - E_{th})$ term. The temperature dependence of the specific heat is usually taken as a linear function of temperature. The term accounting for the enthalpy transport to the vapor phase consists of two parts: $J_1(I, T)^{(1 \rightarrow v)}$ and $J_2(p^*, T)^{(1 \rightarrow v)}$, of which J_1 identifies the small amount of heavy water evaporating into the D_2 and O_2 gas bubbles. This term is a function of the cell current and temperature, and it is negligible except at high solution temperatures and/or cell currents. The second, J_2 , denotes the loss of water due to evaporation. The rate of evaporation is proportional to the solution temperature, and as the temperature approaches the boiling point, the J_2 dominates. The J_2 dependence is calculated using the Clausius-Clapeyron formula and can be evaluated quite

easily, but not the J_1 term because of the number of factors that must be considered, among them the size of the gas bubbles, the degree of their saturation, etc. Less clear is the temperature dependence of the term $I(E_c - E_{th})$. Following Fleischmann et al.,⁶ the correction factor is

$$\psi = \frac{dE_c}{dT} \Delta T + \frac{3}{4F} \cdot \frac{d}{dT} \left[\frac{p}{p^* - p} (c_s \Delta T + L^{(1 \rightarrow v)}) \right] \Delta T .$$

This procedure involves expanding the temperature dependent ($E_c - E_{th}$) term into the Taylor series, retaining the first term only on account of smallness of T , and expressing E_{th} by the change in the enthalpy function of the electrolyte due to the increase by T .

III. REMARKS CONCERNING THE OPEN CELL CALORIMETRY

A calorimeter is an apparatus designed to measure quantities of heat associated with the occurrence of specific processes (e.g., heat of reaction, heat of absorption, etc.) or the property of matter (e.g., specific heat). The basis for such measurements is the conservation of energy and requires knowledge of the processes under consideration, the sequence of events, the construction of the apparatus, and the experimental procedure employed, i.e., the development of the calorimetric equation for an operating electrochemical cell employs conservation of energy and adjusts the applicable walls and constraints in a manner consistent with the cell design and relevant experimental procedures. Procedures for the isoperibolic designs, employed for long charging times, have been described in a number of publications (Ref. 7 and references therein) and will not be discussed here. For the examination of short duration runs, an adiabatic enclosure might be appropriate. A comprehensive description is given in the following discussion.

III.A. Calorimetric Equations in Condensed Form

Consider a system consisting of an electrochemical cell containing a known amount of electrolyte and totally immersed in a water bath. Initially this system is in equilibrium and, for the duration of an experiment, the bath is in contact with an infinite heat sink (i.e., $T^{(e)} = \text{const}$). Applying the conservation of energy, in the form of condensed Eqs. (1) and (2), the time rate of the temperature change in the cell after its activation is

$$C_1 \frac{dT^{(1)}}{dt} = Q_1 - J_q^{1 \rightarrow 2} - J_q^{1 \rightarrow e} \quad (3)$$

and in the water bath

$$C_2 \frac{dT^{(2)}}{dt} = Q_2 + J_q^{1 \rightarrow 2} - J_q^{1 \rightarrow e} , \quad (4)$$

where

$C_1 = m_i c_i =$ heat capacity of the electrolyte and includes all cell components

$C_2 =$ heat capacity of the fluid bath

$Q_1 =$ rate of heat production in the electrolyte phase

$Q_2 =$ heat supplied to the bath to maintain $T^{(1)} = T^{(2)}$

J_q 's = heat fluxes exchanged between the system elements.

III.B. Construction of an Adiabatic Wall

Equation (3) is the energy balance in terms of the rate of heat generation due to irreversibilities of the charge transfer processes, the rate of heat exchange between the cell and the water bath, and the rate of heat loss to the environment. Since the term Q_1 is always positive, it follows that $T^{(1)} > T^{(2)}$ results in an outflow of heat generated within the cell. The construction of an adiabatic wall requires that $J_q^{(1 \rightarrow 2)} = J_q^{(2 \rightarrow 1)}$ at all times. This requirement is fulfilled as long as $\Delta T = 0$, i.e., as long as $J_q^{(2 \rightarrow e)} = Q_2 - C_2 [Q_1 - J_q^{(1 \rightarrow e)}] / C_1$, which for $Q_1 \gg J_q^{(1 \rightarrow e)}$ is further simplified to $J_q^{(2 \rightarrow e)} = Q_2 - C_2 Q_1 / C_2$ and provides a rough guide for the design and operation of an adiabatic wall separating the cell from the bath. Since, in practice, $\Delta T \neq 0$, the maintenance of an adiabatic wall requires that $\int J_q^{(1 \rightarrow 2)} dt = \int J_q^{(2 \rightarrow 1)} dt$, i.e., that ΔT oscillates about its zero value. Employing for the thermal flux an expression of the form $J_q = k \Delta T$ and introducing a new set of variables, i.e., $\Delta T = T^{(1)} - T^{(2)}$, $\theta = T^{(1)} - T^{(e)}$ with $\theta = \text{const}$, Eq. (3) becomes Eq. (5):

$$\frac{d\theta}{dt} = q_1 - \kappa_{12} \Delta T - \kappa_{1e} \theta . \quad (5)$$

Using the same variables, by subtracting Eq. (4) from Eq. (3), we obtain an expression for the change in T .

$$\begin{aligned} \frac{d\Delta T}{dt} &= (q_1 - q_2) - (\kappa_{12} + \kappa_{12}^* + \kappa_{2e}) \Delta T \\ &\quad + (\kappa_{2e} - \kappa_{1e}) \theta , \end{aligned} \quad (6)$$

where $q_i = Q_i / C_i$; $\kappa_i = k_i / C_i$; and $\kappa^* = k_{12} / C_2 = \kappa_{12} C_1 / C_2$. Conditions forcing ΔT to oscillate about zero can be determined by solving the set of coupled differential equations.⁸

To maintain an adiabatic wall, the positive ΔT due to $q_1 > 0$ must be countered by q_2 to reverse the direction of the heat flow. One way to construct and maintain an adiabatic wall is as follows: At $t < t_0$, the system is in equilibrium. At t_0 the flow of cell current is initiated causing the system's temperature to rise as shown schematically in Fig. 1 by solid $T^{(1)}$ and dashed $T^{(2)}$ lines. At t_1

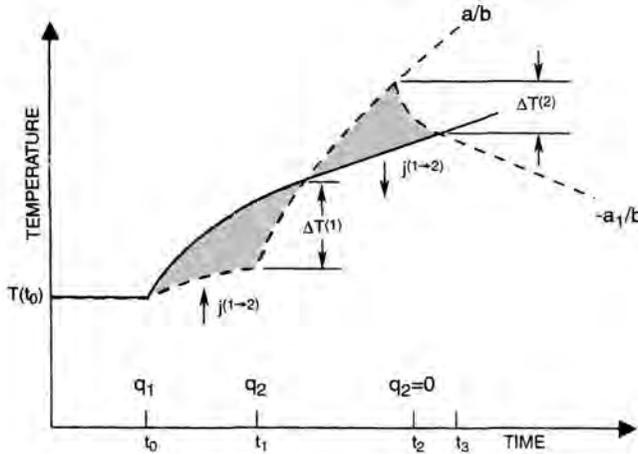


Fig. 1. Temperature tracking to maintain an adiabatic wall. The values $T^{(1)}$ and $T^{(2)}$ are the temperature differences that trigger (on/off) the heat source in the bath.

the difference T reaches an a priori specified value, and the heat source q_2 in the bath is activated. If $q_2 > q_1$, then the temperature $T^{(2)}$ rises faster than $T^{(1)}$, in time—at t_2 —reducing T to zero. To maintain the adiabatic wall, it is necessary to transfer the same amount of heat in both directions [$H^{(1 \rightarrow 2)} = H^{(2 \rightarrow 1)}$]. These periods are determined by numerically solving Eqs. (5) and (6).

Some rough and yet useful information concerning the form of the $T(t)$ function can be derived if θ is considered a constant. Rewriting Eq. (6) in an equivalent form, yields

$$\frac{d\Delta T}{a - b\Delta T} = dt, \tag{7}$$

where

$$a = (q_1 - q_2) + (\kappa_{2e} - \kappa_{1e})\theta$$

$$b = (\kappa_{12} + \kappa^* + \kappa_{2e}).$$

Upon integration, we get for $q_2 = 0$ and for $q_2 > q_1 + (\kappa_{2e} - \kappa_{1e})\theta$, respectively,

$$\Delta T = \frac{a}{b} + \left[\frac{a}{b} - \Delta T(0) \right] e^{-b(t-t(0))}. \tag{8}$$

and

$$\Delta T = -\frac{a}{b} + \left[\frac{a}{b} - \Delta T(0) \right] e^{-b(t-t(0))}. \tag{9}$$

Evidently, the system relaxes with the characteristic time constant, $\tau = 1/(\kappa_{12} + \kappa^* + \kappa_{2e})$, i.e., the relaxation time is governed by the C_1/C_2 ratio, the cell temperature, materials of construction, and the system's contact with the environment. For any selected $\Delta T^{(1)}$, there is a corresponding $\Delta T^{(2)}$ that ensures $H^{(1 \rightarrow 2)} = H^{(2 \rightarrow 1)}$. For

practical purposes, this condition is satisfied by the requirement that $T(t)$ oscillates about zero.

III.C. Temperature Tracking

In any implementation of calorimetric measurements based on Eqs. (3) and (4), a means of controlling the heat input to the bath surrounding the reaction cell must be provided to maintain the temperature difference, $T = 0$, or at least, so that it averages to zero over an experimental run. Because of the large amount of temperature data required for an experiment, digital acquisition of the data is necessary. Consequently, digital control of the experiment is a natural choice. In a digital system, the relevant temperature measurements are made in sequence in a repetitive cycle, with some dead time for writing data to a disk, and the analog values are truncated to the precision of the analog to converter being used. These two procedures should not be considered independently because often the truncation error exceeds the allowable temperature error, and appropriate averaging is required. For averaging to improve a measurement, the analog signal must be dithered, either deliberately or by noise over a range corresponding to the least significant bit of the digitized signal. For example, with a 12 bit analog to digital converter having an input of -20 to $+20$ mV, the least significant bit corresponds to a 10μ input signal change or a change of 0.25 C for a T type thermocouple where the sensitivity is about millicoulomb per microvolt. Typically, there might be present 10μ V root mean square noise referred to the input, so that averaging 100 samples would be expected to reduce the error to ~ 0.03 C without having to dither the input. Averaging 100 samples has other implications, however, since the averaging takes place over a range of temperature difference T that depends on both the cooling rate of the cell and the heating rate of the bath as given in Eqs. (5) and (6). On average, a temperature offset occurs that depends on whether T takes longer to recover from a positive value than from a negative value, which would increase the likelihood that the bath heater will be incorrectly turned on rather than incorrectly turned off.

IV. THERMAL EFFECTS DURING CODEPOSITION

To reiterate, the codeposition process is a process where the electroreduction of Pd^{2+} ions occurs simultaneously with the evolution of deuterium. The principal advantage of this technique is the elimination of the prolonged charging time required for, and a better reproducibility of, the initiation of the Fleischmann Pons effect. Three cases of thermal activities seen on Pd electrodes prepared by codeposition will be presented: Sec. IV.A, excess of enthalpy production during and shortly after completion of codeposition; Sec. IV.B, excess enthalpy production monitored over a period of several days; and

Sec. IV.C, the development of thermal instabilities recorded by an infrared scanning.

IV.A. Short Duration Experiment

An example of thermal behavior during the codeposition process is illustrated in Fig. 2 where excess enthalpy $0.239C^{(1)}\Delta T^{(1)} - \int I(E_c - E_{th}) dt$ (y axis) is plotted against the energy supplied to the cell from an external source, $\int IE_c dt$ (x axis). During data collection, the cell was isolated from the environment by an adiabatic wall in the manner described earlier. The electrolytic cell was a thin walled glass vessel with the cathode/anode assembly located at the bottom. (Details of the electrode assembly are given in Ref. 4, Fig. 1). The electrode charging was under potentiostatic control and relevant data, e.g., cell voltage, cell current, electrolyte temperature, and the maintenance of the adiabatic enclosure were recorded, and the excess enthalpy production was plotted. A program taking into account corrections indicated in Sees. II.A through II.E was devised and employed.

Inspection of Fig. 2 reveals two time periods—the first showing a negative while the second a positive gain in enthalpy production. The negative gain indicates that endothermic processes occur shortly after the commencement of codeposition. These reactions cannot be identified at this time except to suggest that they might indicate some form of entropic cooling or, perhaps, the formation

of the gamma phase as indicated by Fleischmann et al.,⁹ where by extrapolation of experimental data a reversal from exothermic to endothermic hydrogen absorption occurs at D/Pd equals -0.85 , becoming substantial at D/Pd = 1.0 (for comparison see Ref. 9, Fig. 4). Such high concentrations are obtained in seconds during codeposition² and might form the gamma phase, thus explaining the rise in the electrode temperature observed on termination of the cell current flow (for comparison see Ref. 1, Fig. 3 insert).

In contrast to the burst like production of tritium⁴ or emanation of soft X rays,³ excess enthalpy generation proceeds at a steady rate with occasional bursts, see points A, B, C, and D in Fig. 2. The rate of excess enthalpy production is only slightly dependent on the electrolyte temperature, at least within the range 20 to 70 C, being higher at higher temperatures.

IV.B. Long Term Experiments

The long term experiments were carried out in three Fleischmann Pons type cells. These Dewar type electrochemical cells are silvered in their top portions so that the heat transfer is confined almost exclusively to radiation across the lower part, which is not silvered.^{6,7} In each cell, the copper rod 2.5 cm in length and 0.4 cm in diameter served as the cathode. A platinum wire spirally wound to ensure uniform current density was employed. Initial composition of the electrolyte was as follows:

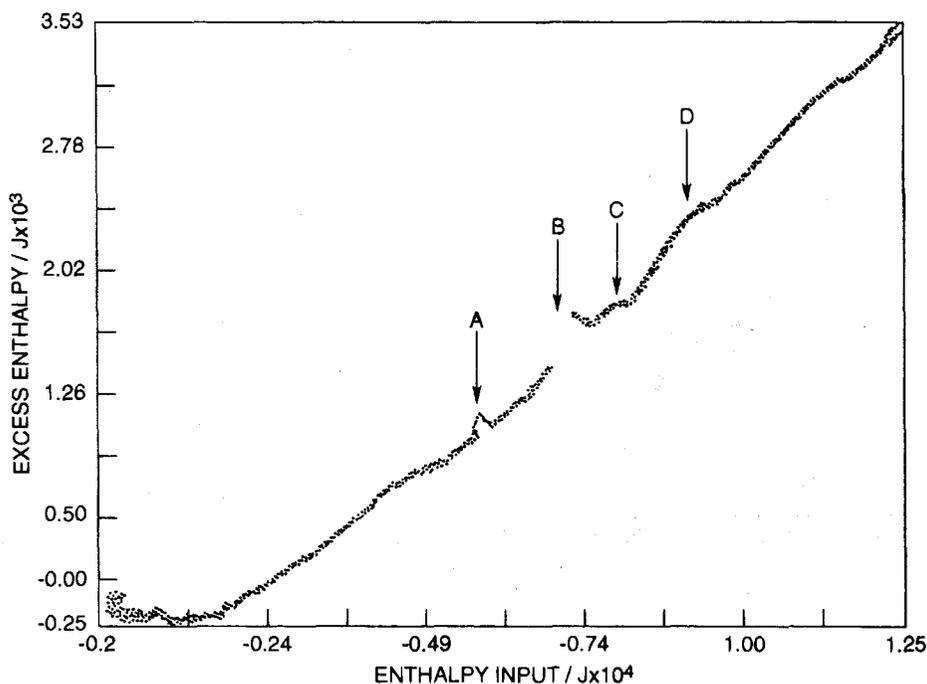


Fig. 2. Excess enthalpy generated in the course of Pd + D codeposition and shortly thereafter. Electrolyte composition: 0.03 PdCl₂ + 0.3 LiCl in D₂O. Points A, B, C, and D indicate accelerated excess enthalpy production.

0.025 PdCl₂ + 0.15 ND₄C1 + 0.15 ND₄OD in D₂O (Isotec, Inc., 99.9 at.% D).

Three cells, each containing 91 cm³ of electrolyte, were operating simultaneously under galvanostatic control. The applied current profile and excess power generated are shown in Fig. 3. It is noted that the codeposition process was completed after 1 day of operation with a marginal excess power commencing immediately and its substantial increase upon an increase in the cell current (see point A, Fig. 3).

While examining Fig. 3, several additional points can be made:

1. Data points in Fig. 3 refer to the excess power generated at the time of measurements.

2. Production of the excess power depends on the cell current; in particular, it increases with the increase in the cell current.

3. The most striking feature is the excellent reproducibility.

4. The excess power output exceeds by far the average reported for solid Pd rods.

IV.C. Development of Thermal Instabilities

Thermal events occurring during the electrochemical compression of the Pd + D system were and are discussed in terms of excess enthalpy produced over a period of time, often several days. Thus, they represent an average value and provide no information on the distribution and nature of heat sources. However, if the surface of a polarized Pd electrode is viewed with an infrared camera, it reveals the presence of randomly distributed, in both time and space, heat sources of short duration. Figures 4a and 4b show snapshots of hot spots (white dots) and temperature gradients associated with their presence, i.e., Fig. 4a is the view perpendicular to the electrode surface, and Fig. 4b presents the three dimensional temperature distribution. Restating, Fig. 4a provides information on the location of hot spots and Fig. 4b on the temperature gradients, the latter suggesting that the hot spots are located just beneath the contact surface.

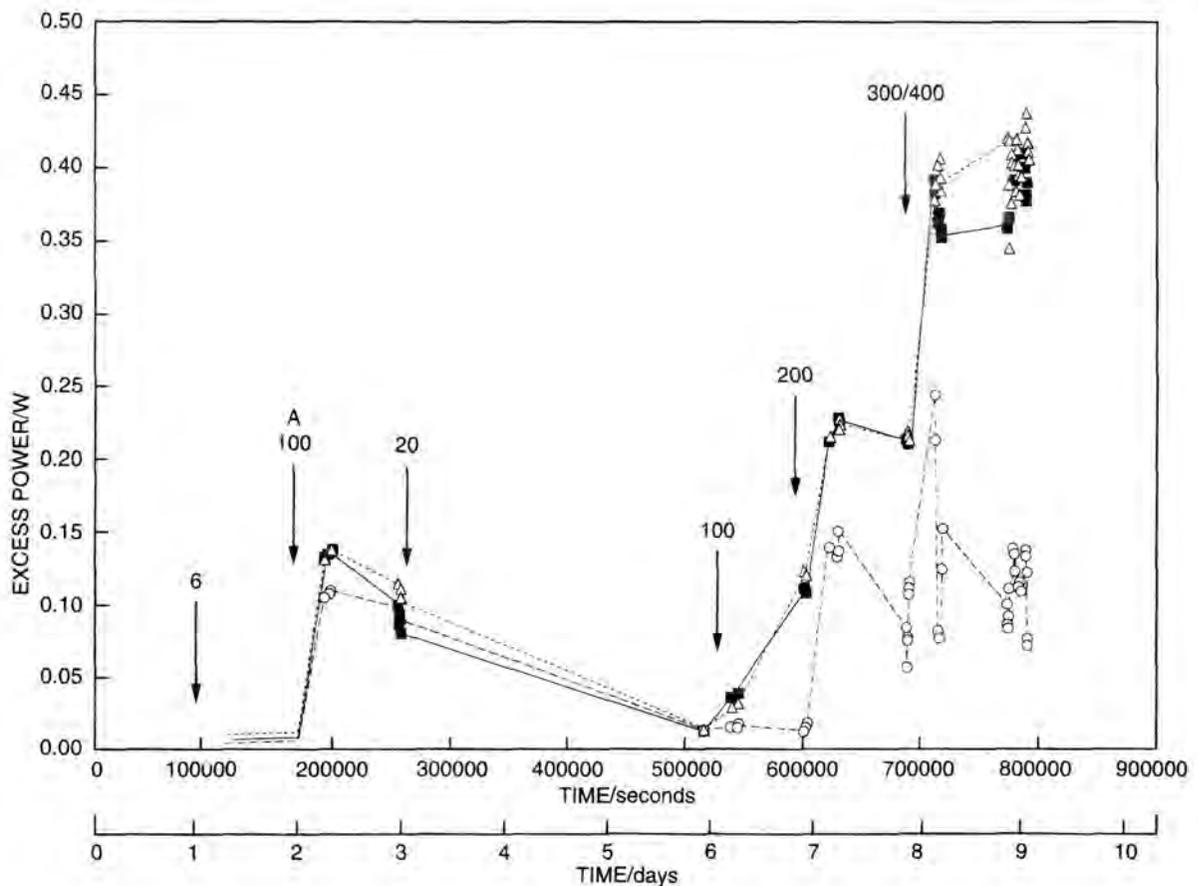
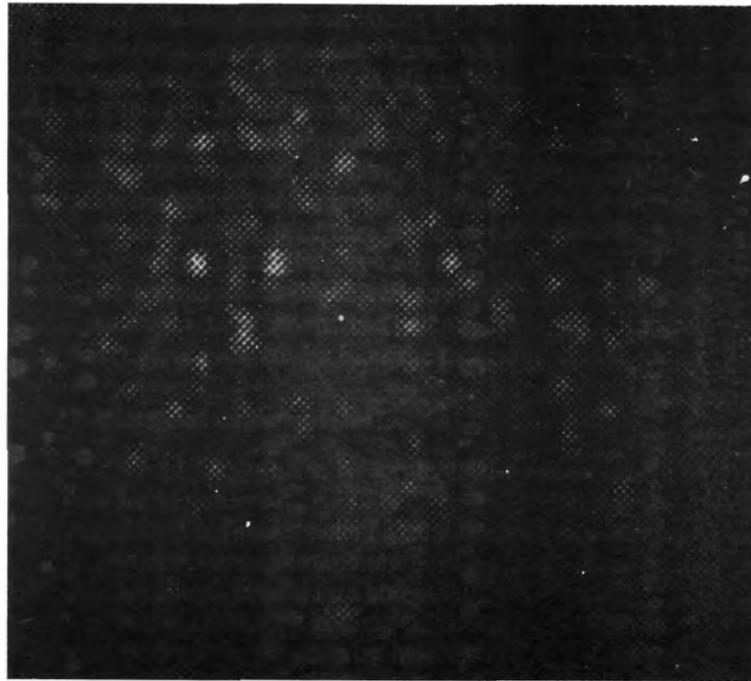
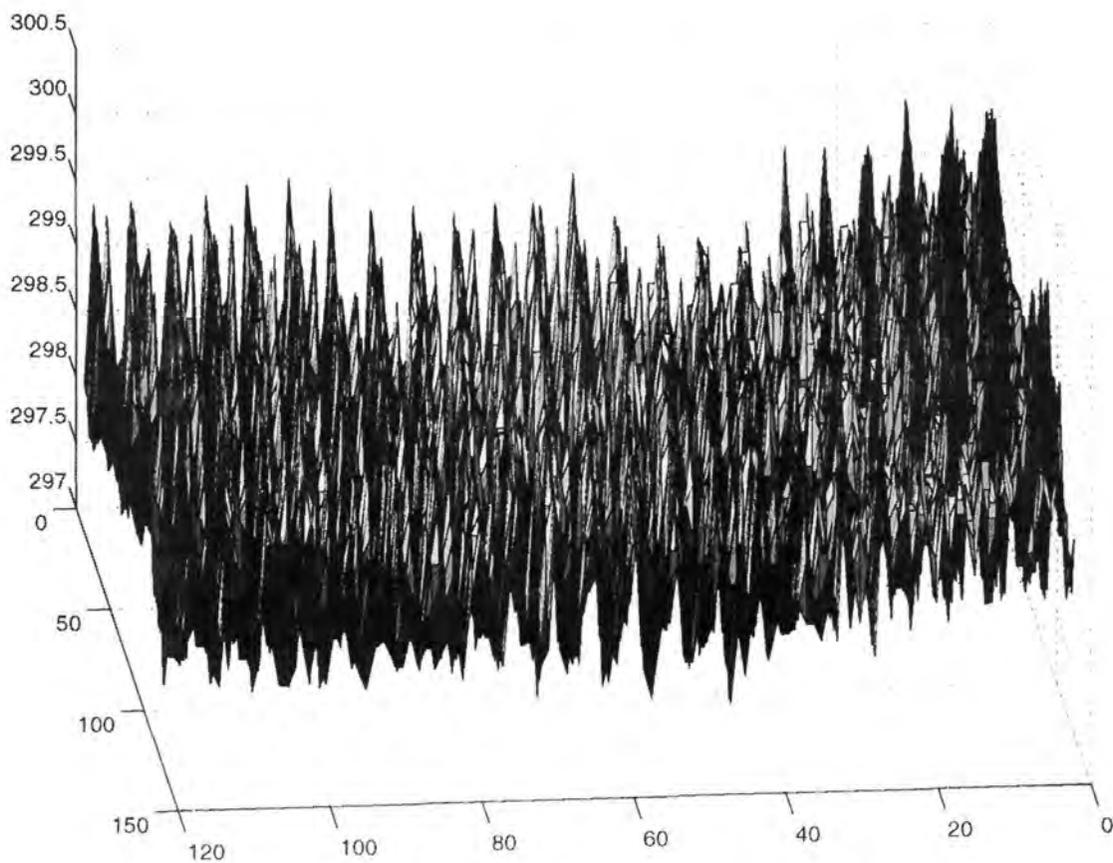


Fig. 3. Excess power generated during prolonged D₂O electrolysis on electrodes prepared by codeposition. Electrolyte composition: 0.025 PdCl₂ + 0.15 M ND₄C1 + ND₄OD in D₂O. Note that for the final two days, the cell current was 400 mA in cells indicated by open circles and triangles and 300 mA in cells indicated by solid squares.



(a)



(b)

Fig. 4. Infrared photographs of the electrode surface: (a) view perpendicular to the surface showing distribution of hot spots and (b) view parallel to the electrode surface showing temperature gradients. The photographs were taken by an infrared camera manufactured by Lynx Real-Time Systems, Los Gatos, California 95030.

The development of instabilities and/or oscillatory behavior is expected in nonlinear systems, of which an operating electrochemical cell is a prime example.⁸ The development of such instabilities is consistent with ideas advanced recently by Fleischmann et al.⁹ They postulated that production of excess enthalpy can be expressed in terms of a number of time and space dependent variables and their differentials, $Q = f[E_s, dE_s, d; d, X, dX, , d]$. These variables are: cell voltage, cathodic overpotential (in particular its Volta component), surface coverage, deuterium content (expressed as D/Pd atomic ratio), and the formation of the gamma phase. Some of these variables can be controlled by an experimenter; others cannot (so called "hidden variables"). Because these variables are interconnected, they can lead to the development of instabilities of the type illustrated in Figs. 4a and 4b.

V. CLOSING COMMENTS

Experimental evidence concerning thermal activities generated by the electrochemical compression of deuterium within the Pd lattice on electrodes prepared by codeposition has led us to the following conclusions:

1. The major impediment in accepting the excess enthalpy production by electrochemical compression of deuterium generated by electrolysis of heavy water on Pd electrodes is removed, i.e., the excess enthalpy production is reproducible.
2. The excess enthalpy generated in cells where the cathode is prepared by codeposition is, on the average, higher than that produced in cells employing solid Pd rods.
3. The heat sources are highly localized, and judging from the steepness of temperature gradients, they are located in close proximity to the electrode solution contact surface.

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