

Conditions for the Observation of Excess Power in the D/Pd System

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Abstract

A wide range of experimental results are analyzed in an attempt to find empirical rules for the features of calorimetric experiments that are correlated to the appearance of excess power. In addition to the D/Pd loading, other criteria of importance appear to be: the cathode current and temperature, an initiation process of unknown origin, and a periodic variation of the Pd cathode resistance. This last feature has been interpreted here as arising from a periodic fluctuation of the average cathode D/Pd loading, resulting from a bi-directional flux of deuterons across the cathode/electrolyte interface.

Introduction

Work has been undertaken to test the hypothesis that there is an unexpected and unexplained source of heat in the D/Pd system, which may be observed when deuterium is loaded electrochemically into the palladium lattice, to a sufficient degree. The experiments undertaken fall into two categories:

a) Loading studies in which the means of achieving high D/Pd ratios by electrochemical loading, are studied. The principle methods used are measurements of the resistance ratio¹⁻³ to determine the extent of loading; interfacial impedance techniques²⁻⁷ are used to interrogate the mechanisms and kinetics of electrochemical deuterium atom absorption into palladium.

b) Calorimetry studies. A variety of calorimetric methods have been employed with thermodynamically closed and open electrochemical cells, to determine the rate and extent of "excess" heat production.

The results of these experiments have shown⁷⁻¹² excess heat and excess temperatures in mass flow and heat flow calorimeters, of more than one design and operating principle. The extent of this excess heat is not consistent with the known chemistry of the system components, and is not consistent with any artifact that we have considered.

The experiments have shown that obtaining a high loading ($D/Pd \geq 0.85$) is a necessary condition for excess heat production, but is by no means sufficient. Other criteria of importance appear to be:

a) Current. The electrochemical current or current density which appears also to have a minimum threshold value which is somewhat more variable than that for loading.

b) Temperature. The cathode temperature appears to play an important role in the intensity of excess heat production. Considerable discussion has occurred on the possibility that the mechanism which gives rise to excess heat, whatever it may be, yield a larger effect at higher temperatures; that is, the phenomenon exhibits positive feedback.¹²⁻¹⁵

c) Initiation. For Pd cathodes of large dimension (diameter or width \geq 1 mm), it is necessary not only to attain high loading, but to maintain this loading at large interfacial currents, for appreciable periods of time (typically \gg 200 hours). These times are substantially greater than those needed for the diffusional transport of hydrogen isotopes, and may be associated with the motion of minority and impurity light atom such as Li, Be, B or C or formation of Si or Al surface films.

d) Deuteron Flux. We have observed, a correlation between the rate of excess heat production ("excess power") and the appearance of oscillations in the Pd (cathode) resistance. If we interpret this change in resistance as the change of average cathode loading (at constant temperature), then an oscillating deuteron flux through the interface is implicated.

These results permit us to propose a second hypothesis, that the excess heat originates from an unexpected and unexplained nuclear process. During the past two years we have attempted to establish a quantitative and/or temporal correlation between the rate of production of excess heat and potential products of nuclear reactions with the lattice. Experiments have been performed to search for γ - and x-rays using a germanium detector, for x-rays using a 2π geometry 4-wire proportional counter, for tritium using liquid scintillation methods, and for gas phase ^3He and ^4He using mass spectrometry. As a result of these measurements we are not (presently) able to confirm the existence of a nuclear process correlated to the production of excess heat.¹⁶ The different systems: nuclear, electrochemical and calorimetric, have been difficult to optimize jointly, and it has been difficult to search for more than one potential nuclear products per calorimeter. However, in the search for nuclear products quantitatively correlated to the heat production we can rule out energetic products, such as neutrons, γ -rays, tritium, or any radioactive isotopes. We cannot rule out stable products such as helium (in either isotopic form) or stable isotopes as might be produced by neutron capture, for example on Li, B, Si or Pd.

Experimental

The results which follow were obtained in a mass flow calorimeter, the design and features of which have been described elsewhere.⁸⁻¹² Briefly, the operating principles of this calorimeter are:

a) Proper and accurate integration of all heat flow, independent of source position within the calorimeter.

b) Thermodynamically closed electrochemical cell, using a supported platinum recombiner catalyst, to better define the expected power output.

c) Redundant measurement of all variables critical to the calorimetric determination of heat.

d) Operation under near steady-state conditions with constant input power, mass flow rate and input temperature.

e) Simple non steady-state analysis with single time-constant transient, correction (where needed).

The equations which govern the steady state performance of the calorimeter are:

$$\text{Input Power:} \quad P_{in} = I_e V_e + I_h V_h = K \quad [1]$$

where I is the current and V the voltage measured at the calorimeter boundary, and subscripts e and h refer to the electrochemical power and compensating heater power inputs respectively. K is the constant power setpoint of the calorimeter, which may be varied.

$$\text{Output Power:} \quad P_{out} = \left(\frac{\delta m}{\delta t} C_p + k' \right) (T_{out} - T_{in}) \quad [2]$$

where $\delta m/\delta t$ and C_p are the mass flow rate and heat capacity of the calorimeter fluid (both constant), k' accounts for the conductive loss of heat from the nearly adiabatic calorimeter enclosure (typically $k' \approx 1\%$) and T_{in} and T_{out} are the inlet and outlet temperatures of the calorimeter fluid. These temperatures are measured by two 100Ω platinum resistance temperature devices (RTD's) at the inlet, and two (or more) at the outlet, providing at least two independent pairs of measurements.

$$\text{Excess Power:} \quad P_{xs} = P_{out} - P_{in} \quad [3]$$

Referring to equations [1] - [3], for $P_{in} = K$ and $P_{xs} = 0$, with $\delta m/\delta t$, C_p , k' and T_{in} constant (as is normal in calorimeter operation), we expect T_{out} also to be constant. The first indication of the presence of an unaccounted heat source within the calorimeter volume is, therefore, the observation of an increase in the outlet temperature.

Obviously, P_{xs} may have either sign, but it is observed, in practice, in the steady state, to be either zero (the expected thermal balance) or positive (the "excess power" of which examples are plotted in the accompanying graphs).

Results

Figure 1 shows the typical response of excess power, when it is present. Results are shown from two experiments connected electrically to the same constant current supply and monitored in a multiplexed fashion by the same digital multimeters and microcomputer. The graph shows excess power in watts for experiment P13 (3mm \varnothing x 3 cm Pd cathode in 1.0M LiOH), and P14 (identical cathode in 1.0M LiOD). Also shown is the (common) cathodic current density in $A \text{ cm}^{-2}$ as these cathodes were exercised simultaneously through a sequence of four slow current ramps. For the heavy water cell (P14) the excess power remains sensibly zero until a cathodic current density of $\sim 250 \text{ mA cm}^{-2}$ ($\sim 0.75A$) is reached during the second current ramp. For the light water cell (P13) the calorimeter remains in thermal balance within the calibration accuracy, $P_{xs} = 0 \pm 50 \text{ mW}$, at all currents.

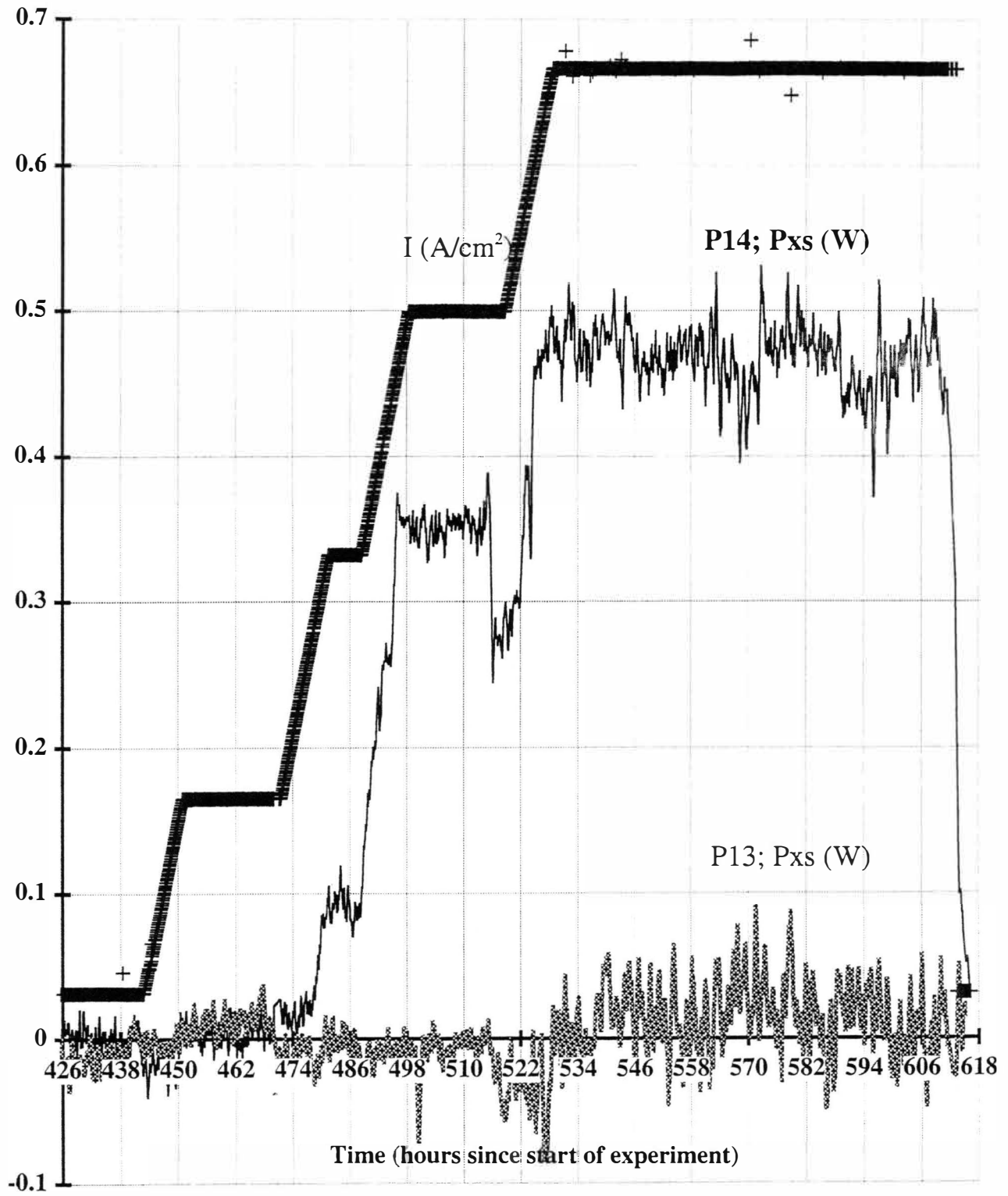


Figure 1 P13 and P14 Excess Power and Current Density versus Time

The results shown in Figure 1 are instructive in that they exhibit clearly some of the features of our excess power observations:

a) Initiation. The ramp sequence shown in Figure 1 was the third such sequence attempted for P14. Previous ramps resulted in similar loadings ($D/Pd \approx 0.95$), but no thermal anomaly. Only after ~ 480 hours of electrolysis was excess power produced.

b) Loading. During the course of the current ramps in Figure 1, the loading of cathode P14 reached a level of $D/Pd \approx 0.95$. For P13, the cathode achieved a higher loading of $H/Pd \approx 0.97$, but no excess power was observed. Excess power appears to be a feature of high deuterium loading in palladium, but not of high hydrogen loading.

c) Current. The excess power in P14 is zero below some critical current threshold, and increases approximately linearly with current (or current density) above this threshold value.

To further expand on point "c", Figure 2a plots measured excess power versus current for a number of different cathodes. The series P12-P15 all were performed with 3mm diameter x 3 cm long cathodes machined from 1/8" Engelhard stock (designated as Engelhard #1). Experiments C1 and M4 will be discussed more fully in the following section (and have been described previously).^{9,17} Both were performed with 1mm diameter Johnson Matthey wire cathodes: C1 30 cm long and M4 10 cm long. The electrolytes in each case were 1.0M LiOD except for P13 which was 1.0M LiOH.

In Figure 2a the linear behavior of excess power with cell current is clearly evident, above some threshold value, and up to some limiting value. There is, however, considerable variability in the threshold value, I° , and in the slope, $\delta P_{xs}/\delta I$. A number of lines are drawn on the data in Figure 2a. These reflect regression fits to sections of each data set in which the response is essentially linear. For P12 and P14, two lines are drawn with common threshold, I° , for each data set, reflecting an apparent step decrease in the slope, at high currents (or at longer time). The initial slope for P12 is very similar to that for P15; the final slope for P12 is very similar to the initial slope for P14. Although very different in cathode geometry, the final slope for P14 is very similar to the initial slope for C1. The slopes for the two Johnson Matthey 1mm wires (C1 and M4) are very similar to each other, but less than those for the 3mm Engelhard cathodes.

While the behavior shown in Figure 2a is to some degree, systematic, we do not understand what phenomenon gives rise to this response. Instead of current, the critical parameter might be current density, which will be different for the "P", "C" and "M" cathodes. Notice, however, that if the phenomenon which gives rise to P_{xs} also is proportional to cathode area, then the data form shown in Figure 2a remains unchanged.

Figure 2b plots the same data as in 2a, but with interfacial current density as the independent variable. This changes the relationships between the data sets very little. One significant difference is that, the response of C1 more closely resembles that for P12 when excess power is plotted versus current density, rather than M4, when plotted versus current.

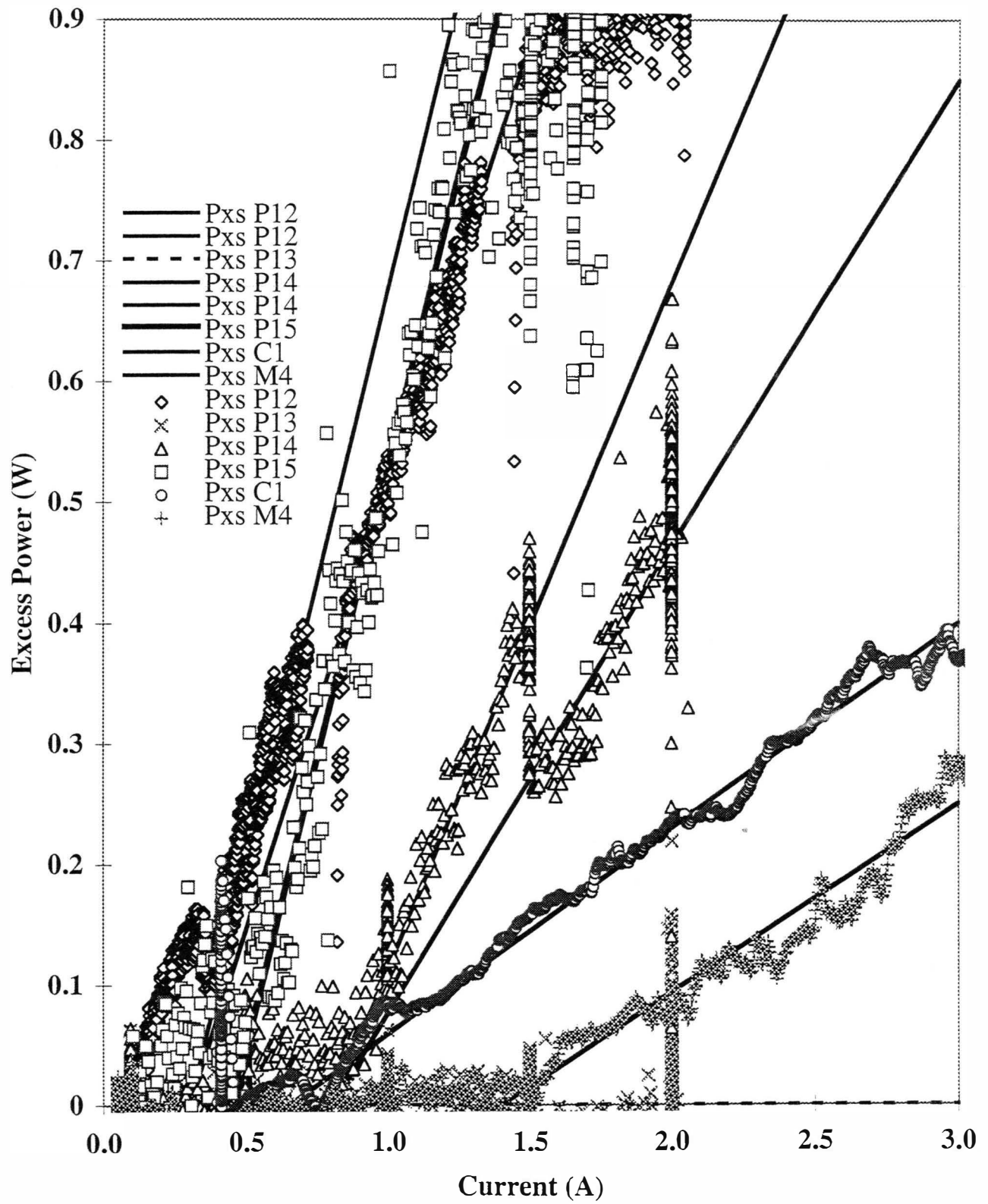


Figure 2a Excess Power versus Current

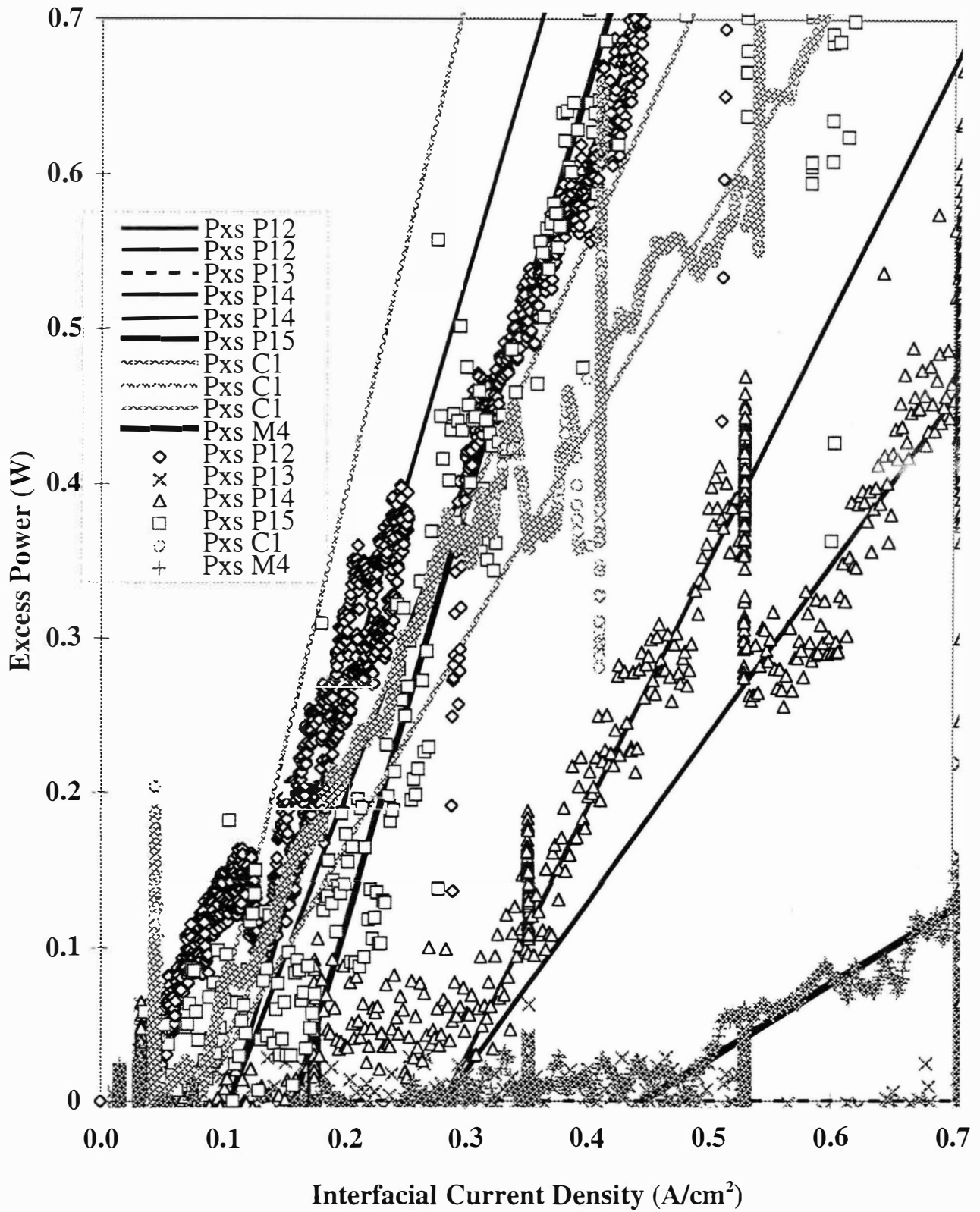


Figure 2b Excess Power versus Cathodic Current Density

Because of the large area of the cathode C1, with the chosen graphing limits, more data are included in Figure 2b than in 2a. This reveals not two regions, but three regions, apparently with a common current threshold, but differing slopes. Three lines are drawn with common origin, which highlight approximately linear regions, with slope decreasing with increasing current (current density or time).

The data in Figures 2a and 2b show some scatter and these figures appear complex. In part this is due to the very large amount of data presented, nearly 21,000 data points; over 1,600 hours of continuous data recording, or 67 days. An attempt is made to summarize the linear responses of these experiments in Table 1.

Table 1

Experiment	Cathode Area (cm ²)	Region	Current I ^o (A)	Current $\delta P_{xs}/\delta I$	Current i ^o (A cm ⁻²)	Density $\delta P_{xs}/\delta i$
P12	2.83	Low	0.30	7.8	0.11	2.7
		High		5.9		2.1
P13	2.83	--	--	0.0	--	0.0
P14	2.83	Low	0.8	4.5	0.28	1.6
		High		3.1		1.1
P15	2.83	Low	0.45	7.7	0.16	2.7
C1	9.42	Low	0.75	31	0.08	3.3
		Middle		16		1.7
		High		13		1.4
M4	3.14	Low	1.40	1.5	0.45	0.49

The functionality of excess power with loading is more difficult to assess, as we have very little control over the loading, in the high loading state. Figure 3 shows the results of experiment C1, employing a 1mm x 30 cm Pd wire in 1.0M LiOD. The excess power appears to increase, in a non-linear manner, with D/Pd loading above a threshold value of D/Pd ~ 0.83 to 0.85. Unfortunately, the data have insufficient precision to characterize uniquely the dependence of P_{xs} on loading. In Figure 3, three regression curves are drawn through the data:

a) An asymptotic dependence which might be expected if excess power were related to the deuterium activity.

$$\text{For } x > x^{\circ}: P_{xs} \sim (x - x^{\circ})/(1-x); \text{ where } x^{\circ} = 0.85.$$

b) An exponential dependence presuming that excess power is caused by populating a state or phase of high energy.

$$\text{For } x > x^{\circ}: P_{xs} \sim \exp [x - x^{\circ}] - 1; \text{ where } x^{\circ} = 0.85$$

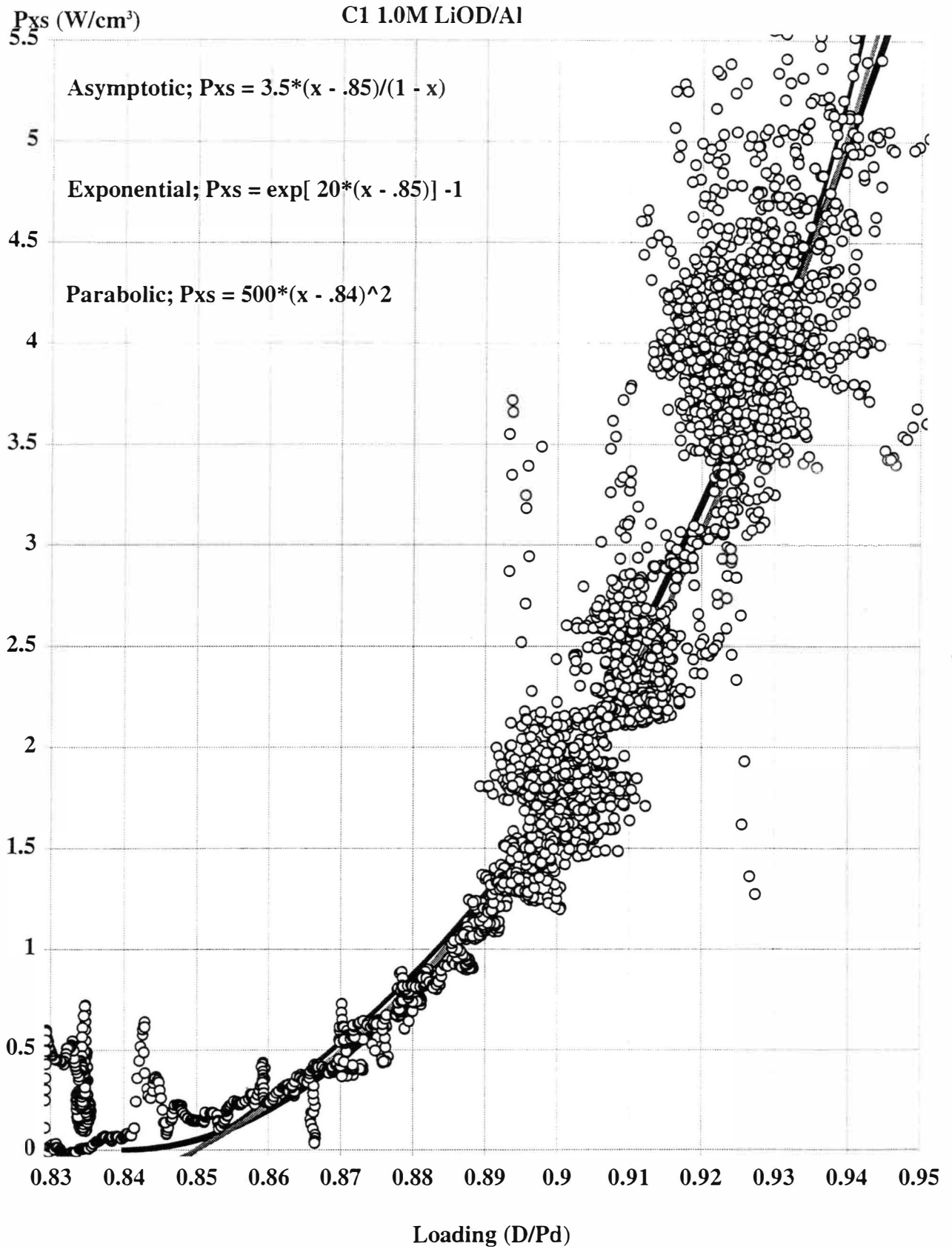


Figure 3 Cell C1 Excess Power versus Loading

c) A parabolic dependence which might originate from a number of processes, one of which is discussed in the following section.

$$\text{For } x > x^\circ: P_{xs} \sim (x - x^\circ)^2; \text{ where } x^\circ = 0.84$$

In the subsequent discussion, excess power data from electrodes of varying dimension are normalized by the volume of the Pd cathode. We have not yet demonstrated, however, that the phenomenon scales in this way.

Discussion

Although the form of the dependence of excess power on D/Pd loading is not accurately defined, it appears from the data in Figure 3 and from data of numerous other experiments^{3,16,17} including those of other researchers^{18,19} that there exists a threshold in average loading, below which excess power is not observed. At least one of the theories that have been developed to explain excess heat generation in metal-deuteride lattices, predicts such a threshold effect.

The model proposed by Hagelstein²⁰ postulates that a phonon laser operates to initiate solid state neutron transfer, and to couple the nuclear energy produced, to the lattice, as heat. The details of this model are presented in Reference 20 and in preceding papers cited therein. This model makes two predictions that are relevant in the discussion:

- a) No excess power will be observed at deuterium loadings below that at which the partial molar enthalpy change for desorption becomes exothermic.
- b) The rate of excess heat release (excess power) will increase with the desorption flux.

The first (threshold) criterion establishes the point at which a phonon laser may begin to operate. In a previous paper²¹ we have attempted to define the position of this loading threshold based on literature data for the Pd-D system. By extrapolating the literature data at lower loadings, we estimate that the threshold value for the exothermic desorption of deuterium from palladium to be $0.83 \leq x^\circ \leq 0.85$, a value closely in accord with our observed value of x° as a threshold for excess power production.

The second (flux) criterion is associated with the rate of phonon excitation. This flux can be measured as the rate of change of the average loading; in the Hagelstein model only the desorption flux plays a role.

Taking together our empirical observation and the predictions of the Hagelstein theory, we can propose a simplified predictive function for P_{xs} , and test this against the experimentally derived time series data. Understanding that considerable simplification is involved, we have constructed a test function for P_{xs} which is a simple combination of the known or expected variables.

$$P_{x_s, \text{test}} = M (i - i_a) (x - x^\circ)^2 |\delta x / \delta t| \quad [4]$$

where: M is a proportionality constant, which may include other variables such as cathode area volume and the effects of temperature; i° and x° are threshold values to be determined, and $\delta x / \delta t$ is the measure of the net rate of adsorption and desorption of deuterons through the cathode/electrolyte interface. The term $|\delta x / \delta t|$ assumes the importance of flux to be independent of sign, and gives no weight to a steady state flux.

This test was first applied to the results of an experiment performed in August 1994, experiment M4, employing a 1 mm dia., 10 cm long Pd cathode. The palladium was obtained from Johnson Matthey, and was formed into the shape of a horizontal "lasso", and annealed by using published procedures.¹ The electrolyte was 1.0M LiOD containing 200 ppm Al at the outset. Sufficient Cu was added, dissolved in LiOD, 156 hours before the data shown in Figure 4 to make the concentration ~ 3 ppm in the electrolyte.

Figure 4a shows, initially, the normal response of a cell producing excess power: P_{x_s} rising with increasing current density and loading above threshold values. After ~ 2 days, however, the response of P_{x_s} at constant current density and (generally) decreasing loading, is unexpectedly dynamic. Furthermore excess power was observed in this cell at an unusually low maximum loading ($D/Pd \approx 0.88$).

Examining closely the loading plotted in Figure 4a we see that this too is unexpectedly dynamic. For the first and last 24 hours shown, the amplitude of the variation in x is small, in the period around 608 h intermediate, but for the rest of the time the average loading shows a significant variation about the mean, with standard deviation $\sim \pm 0.002$. These periods of greater dynamism in x correlate with those for which $P_{x_s} > 0$.

Figure 4b shows, in detail, the period of transition between low and modest excess power after 608 hours of electrolysis. While the frequency of the oscillation in loading does not change significantly, during the time of increasing P_{x_s} (at $t > 620$ h), the amplitude of this oscillation increases by a factor of 3 or more. When converted to a flux the rate of change of net loading could be accommodated by an adsorption and desorption current density, of $\sim 0.1 - 1 \text{ mA cm}^{-2}$.

Figure 5 shows the test function defined by equation [4], compared with the measured excess power. Two functions are tested. In Figure 5a, the full function is tested with values of x° and i° determined by maximizing the correlation between the test and observed excess power functions. For the two data sets in Figure 5a, the correlation coefficient $r = 0.854$ with $x^\circ = 0.832$ and $i^\circ = 400 \text{ mA cm}^{-2}$ ($= 1.26 \text{ A}$). In Figure 5b, we apply the same test, with the same threshold values, but without the variable $|\delta x / \delta t|$, to test the importance of the flux variable. For this case, the correlation coefficient $r = 0.696$.

A value of 0.854 for the functions plotted in Figure 5a indicates that $\sim 73\%$ of the excess power is related linearly to our test function. Other variables may be involved (the test function is not complete) or the coefficients may not be precisely right or the component variables strictly independent (the test function is not completely correct); this is nevertheless a remarkable degree of correlation when the approximations and implications involved in generating the test function are considered.

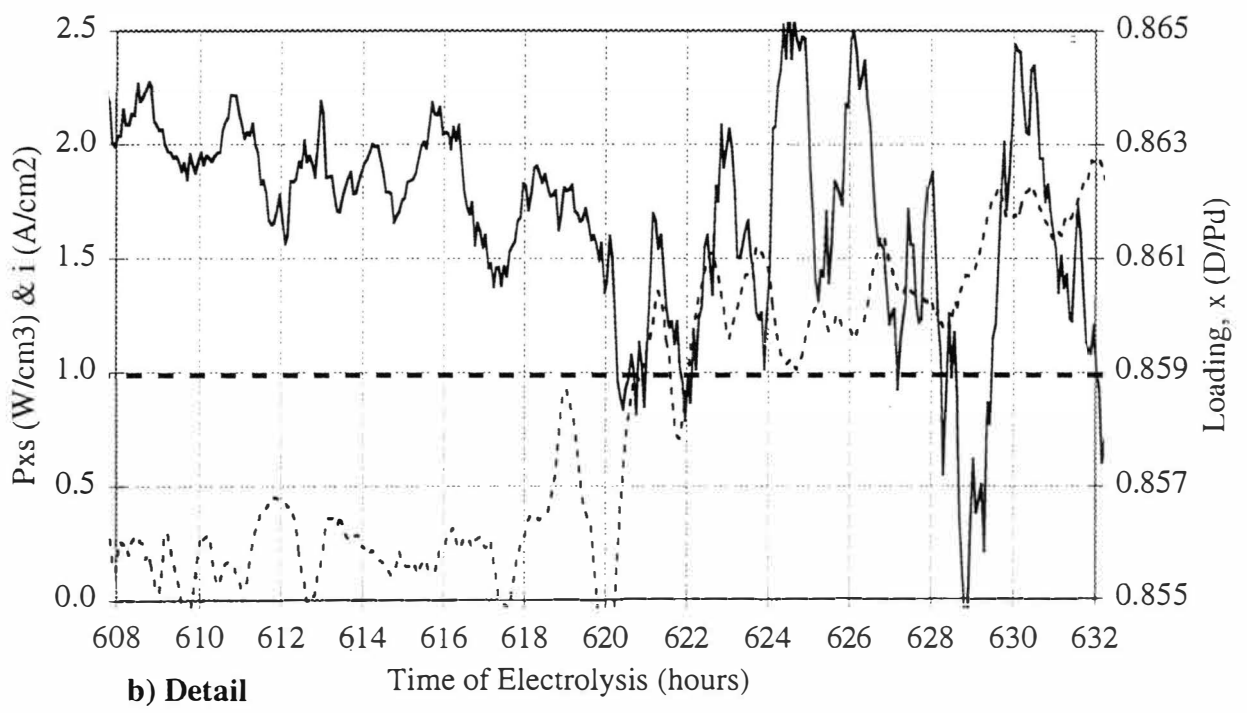
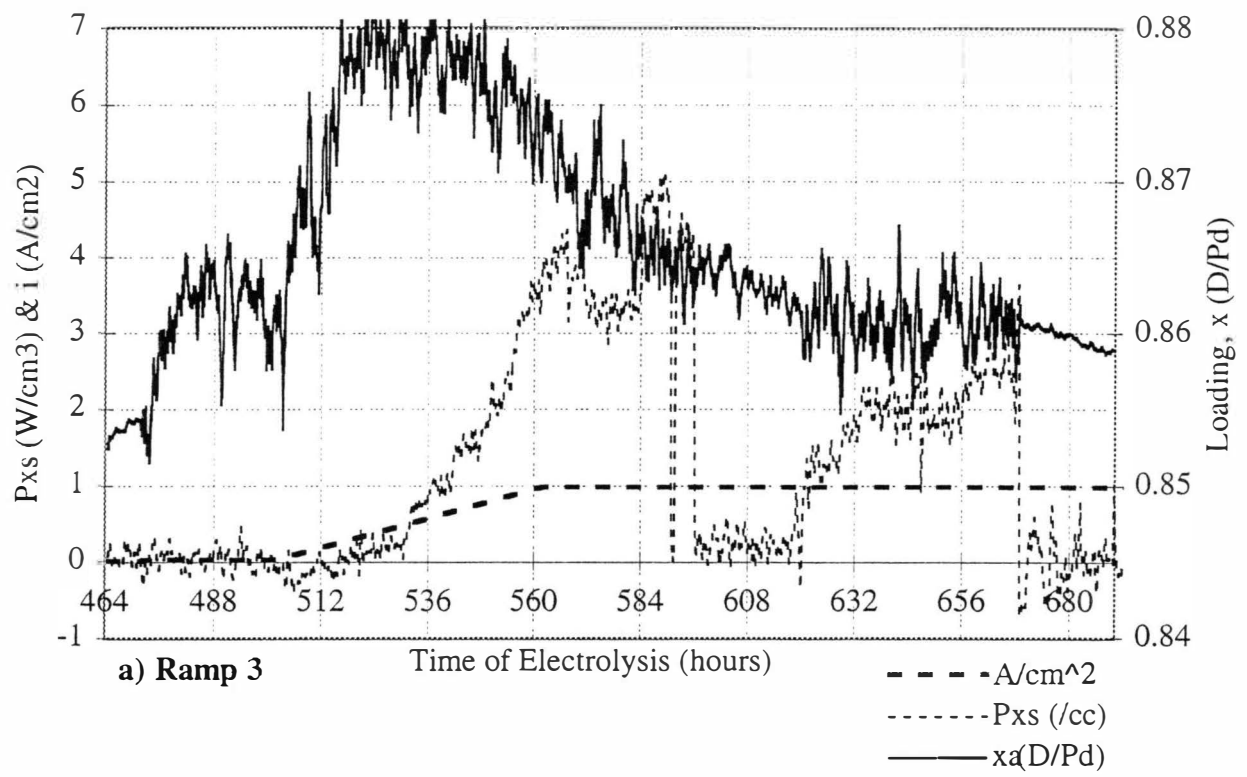


Figure 4 M4 Excess Power Current Density and Loading

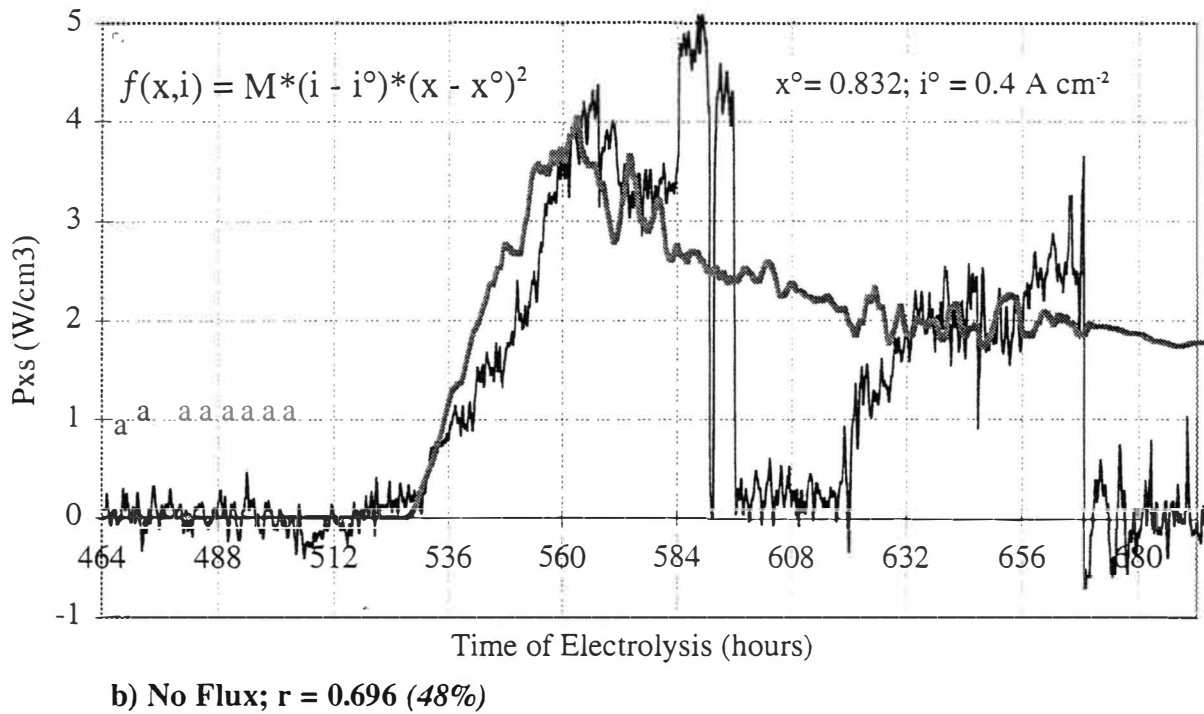
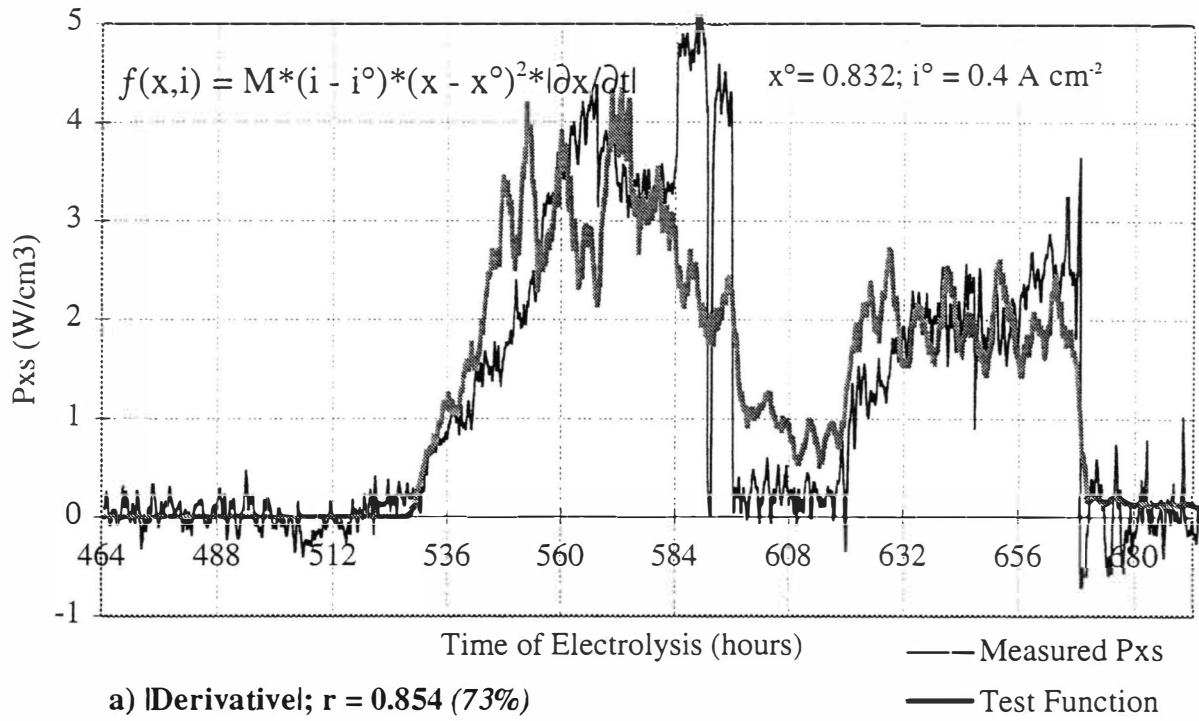


Figure 5 M4 Excess Power and Fit Functions

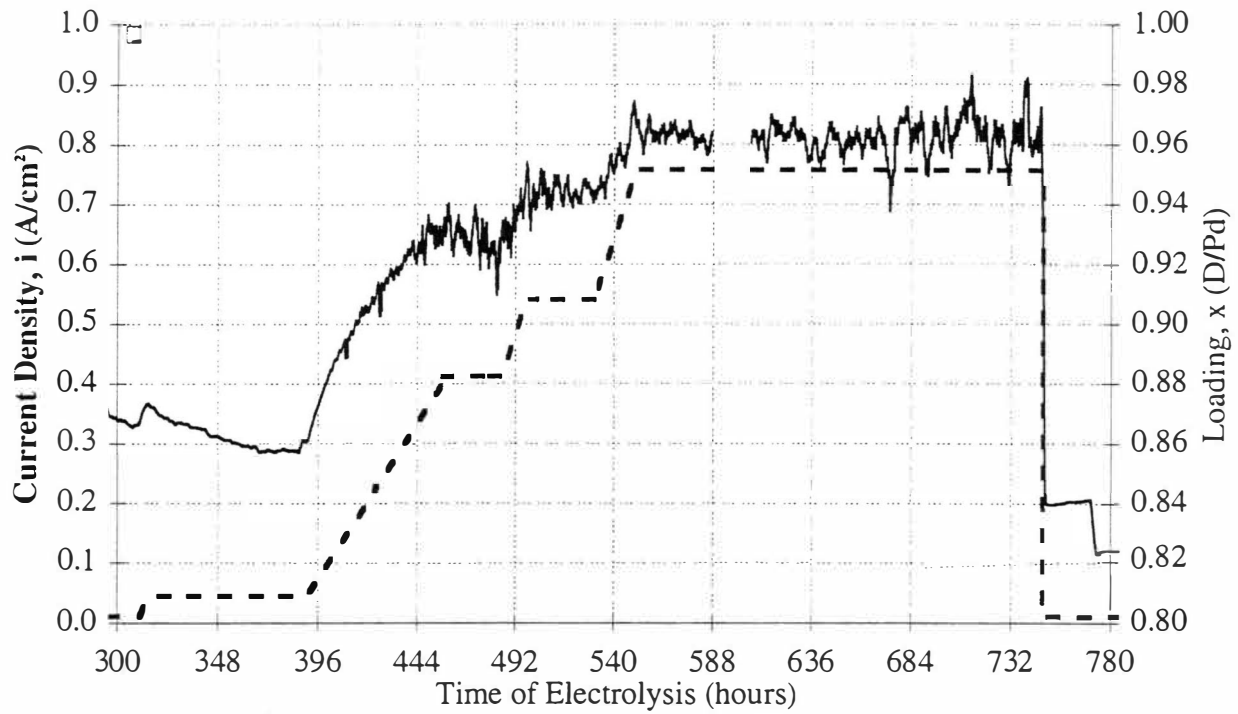
A factor not taken into account in the simple correlation function is the possibility of temporal displacement between the two data sets. If one imagines that the test function is a generating function and the measured excess power is the response (that our test function is causal) then one might expect $P_{xs}(t)$ to be delayed with respect to $P_{xs.test}(t)$, and to have large amplitude (high frequency) features somewhat smoothed. Close inspection of Figure 5a reveals that this may indeed be the case. An analysis of the cross correlation function will be presented elsewhere, together with a more rigorous description of the treatment of the variable $|\delta x/\delta t|$. However, the relatively poor correlation of the functions plotted in Figure 5b suggest that the variable $|\delta x/\delta t|$ is strongly associated with the production of apparent excess power.

Important questions are raised by the success of our test function:

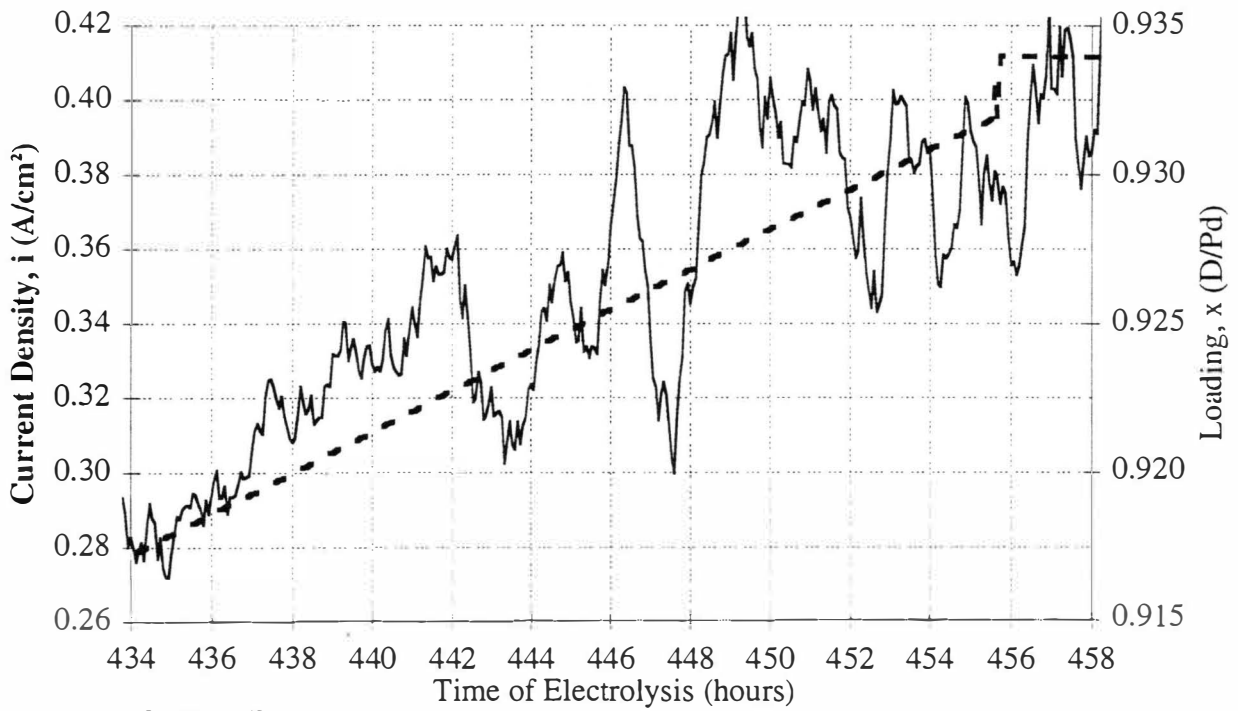
- a) how generally applicable is this function?
- b) is the function predictive or responsive to other (possibly hidden) variables?
- c) can the function be used to explain the appearance of excess power in some experiments and its non-appearance in others?
- d) can the function variables be used to induce controllable excess power?
- e) what can this function teach us about the phenomenon under test?

On the question of general applicability, we are limited in our choice of comparative experiments. It would be desirable to select reference experiments having the same cathode geometry and dimension as the M4 cathode. Very few of our experiments have been performed with 1 mm wires, and none, previously, with the "lasso" geometry employed in M4. In practice, we are more constrained in our choice by the need for high data quality in resistance measurements, so that random measurement errors are not introduced into the values of $\delta x/\delta t$. Simply because the signal-to-noise ratio for 1 mm wires is better than the 3 or 4 mm diameter wires more typically (and successfully) employed, we are reduced in our selection of comparative experiments to one only: C1.

Experiment C1 has been described previously.⁹ Figure 6a presents the loading and current density data for the first current ramp of C1. As for M4, the loading inferred from the measured resistance initially shows little perturbation, first decreasing with time at low current density, then increasing with the current ramp. Some time after initiation of the current ramp, an oscillation appears in x , which builds in amplitude. Figure 6b shows a 24 hour detail in the vicinity of 444 h. While generally increasing with increasing current density, before 442 h the loading shows small fluctuation. After ~ 442 h the loading exhibits a superimposed somewhat sinusoidal oscillation of period ~ 2 h, as seen for M4. Perhaps significantly, the rate of increase in loading with increasing current density decreases at this point, suggesting the initiation of a transient de-loading (desorption) process, superimposed on the steady state loading.



a) Ramp 1



b) Detail

Figure 6 C1 Current Density (A/cm²) & Loading (D/Pd)

Figure 7 shows the excess power measured during C1; ramp 1, compared to the test function employed previously for the M4 data (Figure 5). In this case, the value of x° was chosen to be the same as previously used for the M4 data (0.832); this value is also consistent with the number found by direct regression of P_{xs} vs. $(x - x^\circ)^2$. The maximum correlation is, however, found with a significantly lower current density threshold for C1 (0.1 A cm^{-2}) than for M4 (0.4 A cm^{-2}). Perhaps significantly, however, the threshold current, I° , for the two experiments are not markedly different: for M4, $I^\circ \approx 1.26 \text{ A}$; for C1, $I^\circ \approx 0.95 \text{ A}$. For the two data sets shown in Figure 7, the correlation coefficient $r = 0.94$, with $x^\circ = 0.832$ and $i^\circ = 0.100 \text{ A cm}^{-2}$. This correlation suggests that 88% of the function $P_{xs.test}(t)$ is reflected linearly in $P_{xs}(t)$.

An important question is whether, or not, the empirical fitting function can be used to predict the occurrence of excess power in some experiments, and explain the absence of observable heat, in others. To this end, it is, or will be, critical to understand the causes and consequences of the variable which we have represented as $\delta x/\delta t$.

In an attempt to understand the phenomenology of the temporal variations in $\delta x/\delta t$, a Fourier transform analysis has been performed of the M4 data presented in Figure 4a(x). A sequence of FFT's were calculated for successive intervals of 132 points (= 131 x 4 minutes or 8.7 hours) in the data range $464 \leq t \leq 686$ hours. Figure 8 shows an eleven point average of every tenth spectrum thus calculated, as a function of the time of electrolysis. This graph indicates the presence of a periodic function, with fundamental frequency ~ 0.5 cycles per hour and with considerable harmonic structure. The amplitude of this periodic variation in x varies appreciably with electrolysis time, t , although the percentage and character of the harmonic distortion remains rather constant.

The three dimensional representation in Figure 8 makes it somewhat difficult to interpret quantitatively, and to compare to the time series data (e.g. Figure 4). Figure 9 plots the average amplitude of the frequency domain perturbation assessed in the following intervals:

1. $0.18 \leq f \leq 0.8$ cph
2. $1.3 \leq f \leq 1.9$ cph
3. $2.5 \leq f \leq 3.1$ cph
4. $3.7 \leq f \leq 4.3$ cph

Figure 9 shows the temporal (as well as harmonic) structure of the modulation, in particular, a maximum is observed in the perturbation at ~ 500 h, a minimum at ~ 600 h, and an abrupt termination at ~ 670 h. When present, the modulation takes the form,

$$x = |x| \sum_{h=1}^{h_{\max}} A_h \text{Sin} (2\pi h f + \theta_h) \quad [5]$$

where h is the harmonic number and f the fundamental frequency. No information is conveyed about the relative phase relationships (θ_h), but the relative amplitudes can be described approximately as

$$A_h = 1/(2h-1) \quad [6]$$

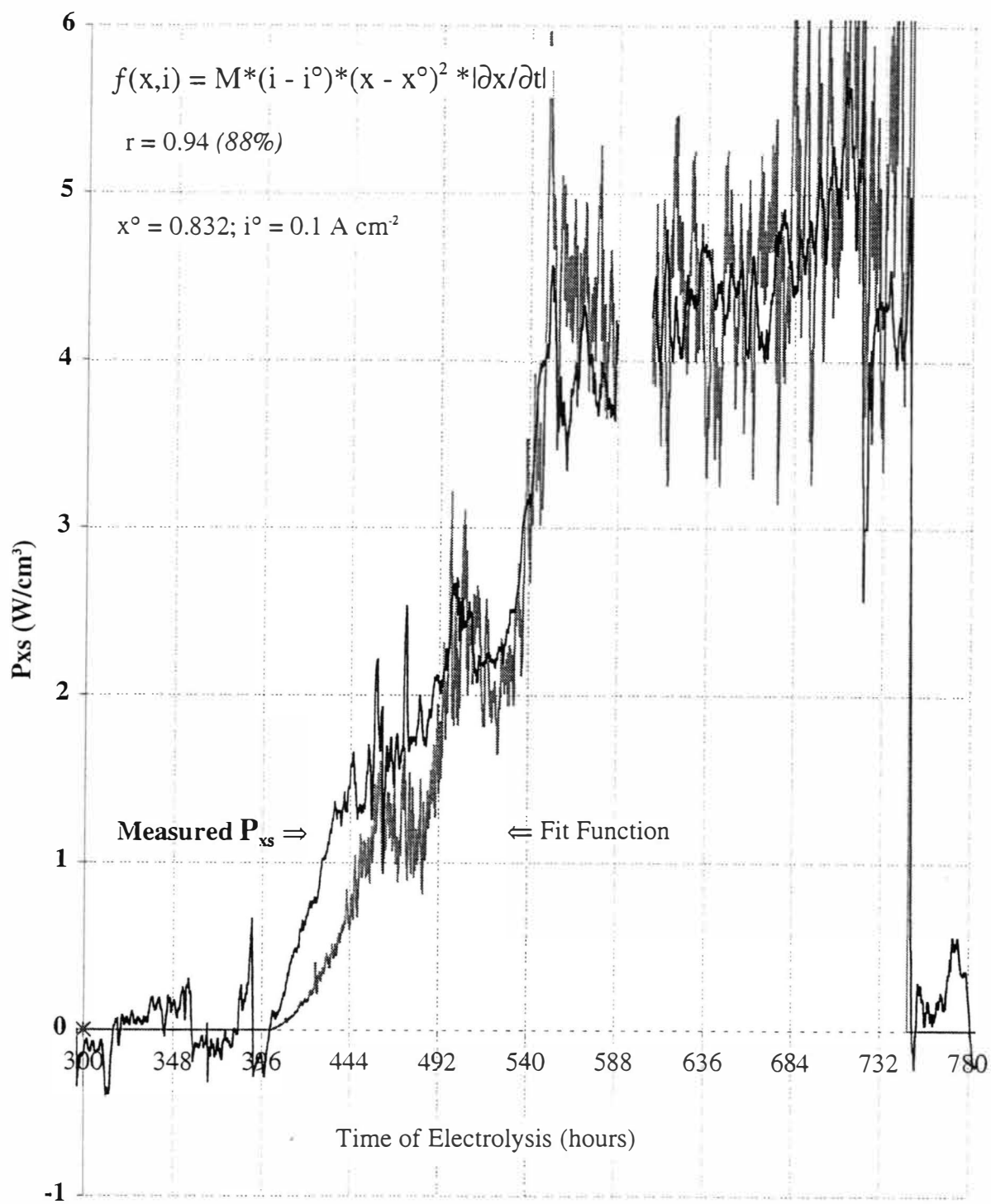


Figure 7 C1 Excess Power and Fit Function

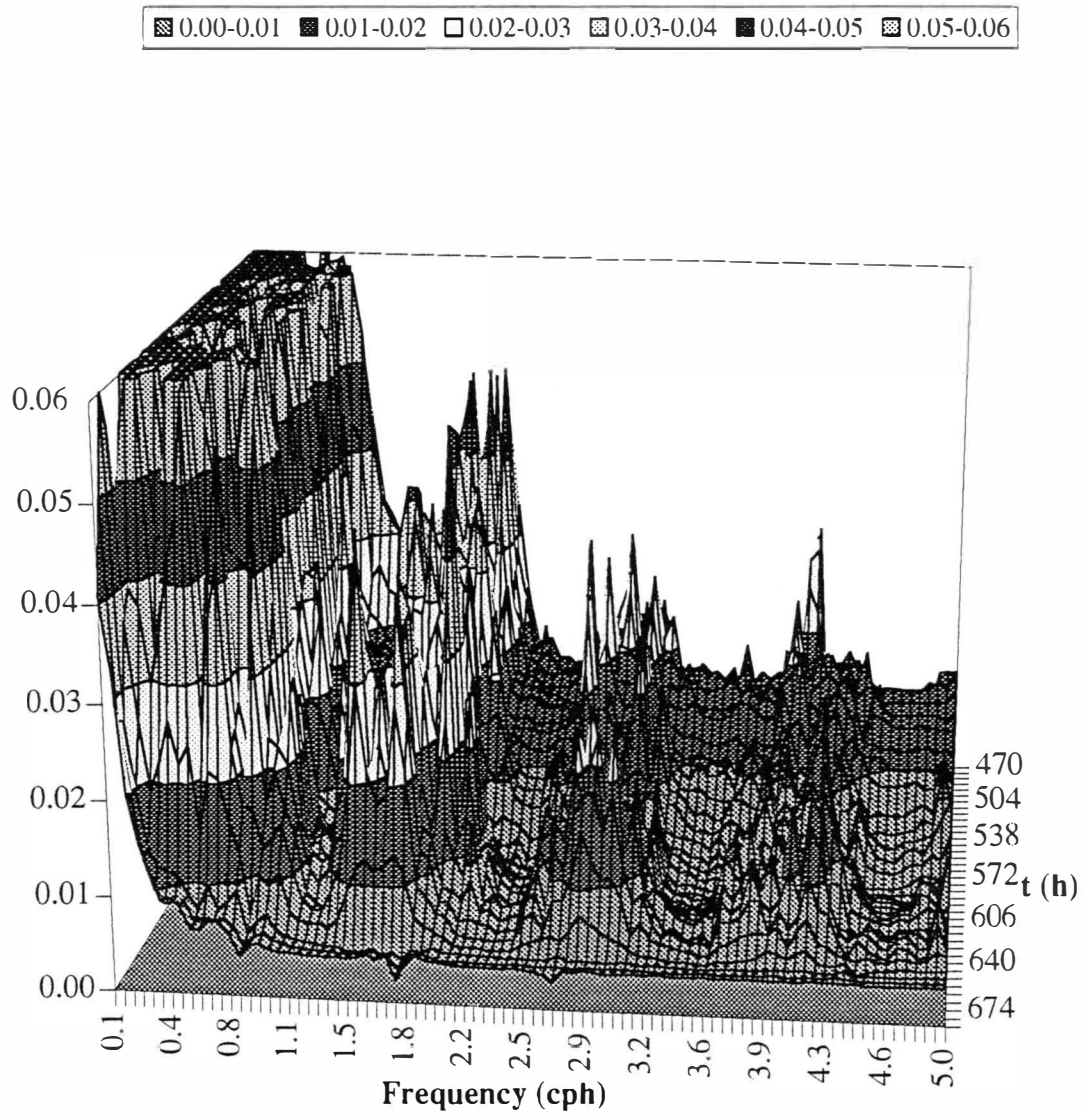


Figure 8 Fourier Transform of time series data for Average Loading in experiment M4

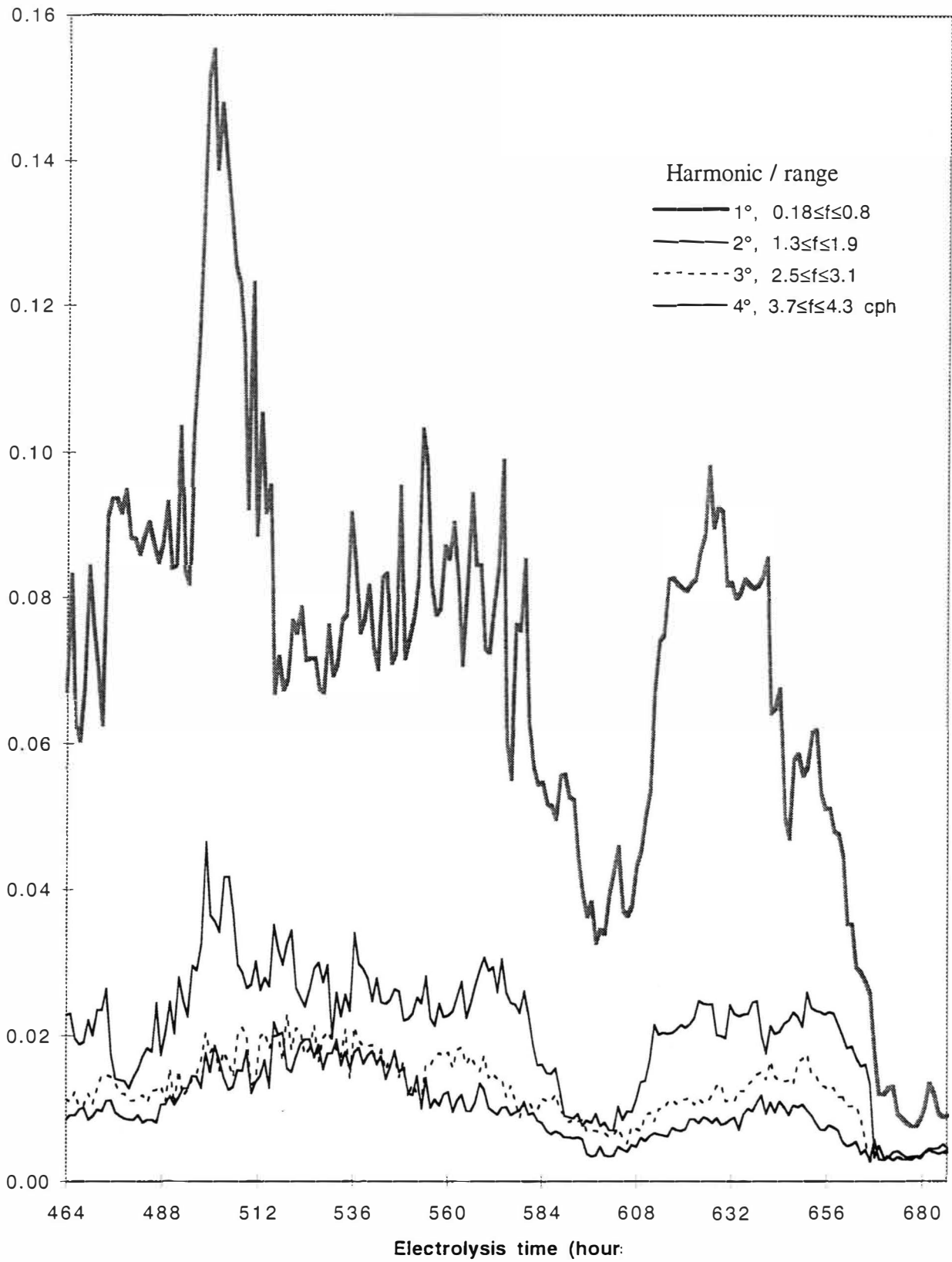


Figure 9 Eleven point average of the Fourier spectra determined from M4 time-series data of loading, in the designated intervals.

If we assign random values for the phases ($-\pi \leq \theta_h \leq \pi$), then we can calculate a single period time-series "snapshot" of the modulation, with the hope that this might provide information about the underlying physical process. Figure 10 shows an example of this calculation performed with the following parameter values:

$$\begin{aligned} f &= 0.9 \text{ cph} && (= 2.5 \text{ mHz}) \\ h_{\max} &= 20 && (f_{\max} = 0.5 \text{ Hz}) \\ |x| &= 0.01 \end{aligned}$$

characteristic of the periods exhibiting higher levels of modulation. The heavy line in Figure 10 referenced to the left abscissa, shows an example of the synthesized waveform variation of the average loading, x , about the mean value, x° for a single cycle, according to the parameters and assumptions stated above.

If,

- i) the observed variation in resistance is due to a change the average loading (at constant temperature), and,
- ii) the form of this variation is accurately reflected in equations [5], [6], and the assignment of random phases for the harmonic components,

then we can use the calculated waveforms to access information about the driving force for change in average loading, the net adsorption and desorption flux of deuterons across the cathode/electrolyte interface. Under an imposed cathodic bias, the net adsorption of deuterons originates from a (change in) electrochemical process, and can be quantified as a partial current. The thin line in Figure 10 shows the net deuteron absorption, expressed as an interfacial partial current density, necessary to yield the calculated average loading variation.

The results of calculation, plotted in Figure 10, reveal an unexpectedly dynamic, but physically achievable variation in the electrochemical character of the Pd surface. The partial current density associated with adsorption varies by $\sim \pm 3 \text{ mA cm}^{-2}$. This number is consistent with mass transport constraints, and represents a very small percentage of the overall interfacial current density of 1 A cm^{-2} . Thus the observed change in resistance may very well be associated with a fluctuation in average loading; the cause of the necessary variation in surface condition which gives rise to a changing adsorption partial current, remains unclear.

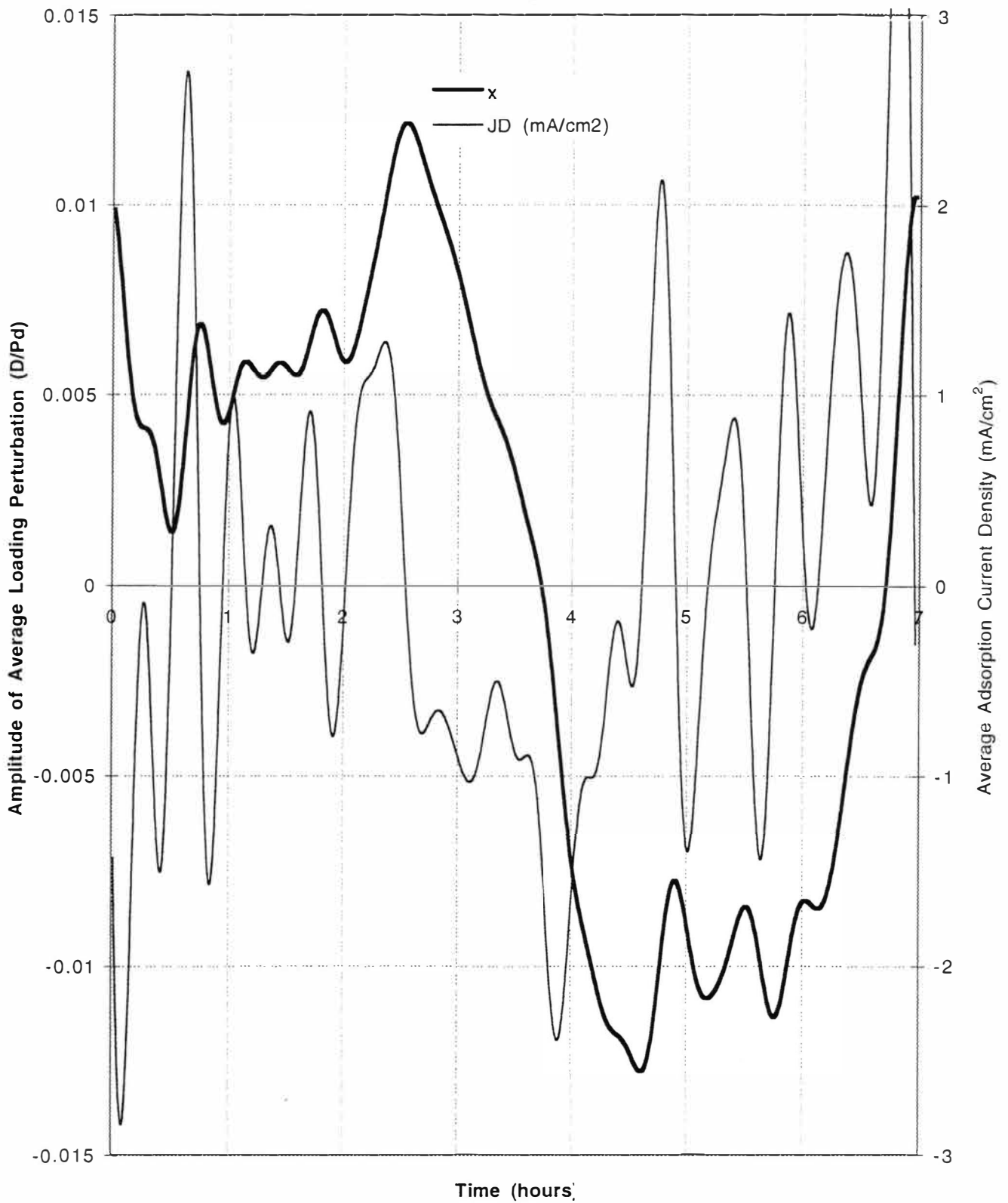


Figure 10 Average Loading Perturbation and Adsorption Current Density for Cathode M4, during periods of large perturbation.

Conclusions

We may conclude that the appearance of excess power is controlled by at least four variables:

- a) Initiation; ($t > t^\circ$)

While not explicit in equation [4], the appearance of excess power requires an initiation process; for M4 as much as 520 hours, for C1 as much as 440 hours. The results of this initiation do not affect i or x ; and do not obviously affect $|\delta x / \delta t|$ or x° . It seems likely that whatever process is involved with initiation, its results are manifest the scaling factor, in M (increasing with time), the critical current decreasing with time.

We have very little information about the mechanism of initiation. Known processes which occur in the lattice with comparable time constants are the diffusion of light elements, (other than hydrogen isotopes, which diffuse more rapidly), and the generation and diffusion of vacancies. Both are consistent with the Hagelstein model in that Si is a candidate impurity nucleus for the production of excess heat by a neutron transfer reaction, and a high population of vacancies are required for phonon interactions to couple energy to and from the lattice.

- b) Current; $(I - I^\circ) = A (i - i^\circ)$.

The requirement for current in the production of apparent excess power is clear and mathematically simple; the reasons for such a requirement are obscure or complex. At the most elementary level, on the basis of the experiments we have performed thus far, we are not able to distinguish between the effects of cell current, and interfacial current density. If the former, then we might focus attention on electromigration effects in enhancing local deuteron activity, or, possibly, in inducing phonon excitation. If the latter, then attention is drawn to near surface and interfacial electrochemical effects, possibly enhancing a transient flux by fluctuating or oscillating surface conditions at high current densities. Alternatively, one might consider the appearance or enhancement of a steady state flux, associated with surface heterogeneities, in which adjacent zones absorb and desorb deuterium.

The threshold value (whether I° or i°) is extremely variable; from experiment-to-experiment, and with time in a single experiment; suggesting that the interaction of current with the supposed heat producing process, is oblique or indirect.

- c) Loading; $f(x - x^\circ)$.

In the correlation analysis that we have presented, we have assumed for simplicity that excess power is related parabolically to the loading above a loading threshold, x° . From our data it is not clear that the relationship is second order: it may be the higher order, exponential, asymptotic, or have another undetermined functionality. The existence of a threshold value of loading is more clearly evident. As was pointed out by Fukai²² and Fleischmann,¹⁴ this threshold value $0.83 \leq x \leq 0.85$, is very close to the loading at which the partial molar enthalpy of adsorption of deuterium into palladium changes from being exothermic to endothermic.²¹ One conjecture, therefore, is that subtle effects of chemical potential within the PdD_x lattice act as a trigger for excess heat production. A more exotic, but more rigorously argued view is that of Hagelstein, in

which the transition from the condition of endothermic to exothermic desorption (at $x > x^\circ$) signals the point at which a phonon laser may operate to couple nuclear energy from and to the lattice.

d) Flux: $J_D \sim \delta x / \delta t$.

Evidence is presented in this paper of a correlation empirically deduced between the rate of excess heat generation ("excess power") and the rate of change of the cathode resistance. Such a resistance change is most directly attributable to a change in the average cathode loading ($\delta x / \delta t$), or a change in the cathode temperature ($\delta T_c / \delta t$). We may therefore interpret our results in one of two ways: a change in average loading at constant temperature, signaling the net absorption or desorption of deuterium via a flux of deuterons through the interface; or a change of cathode temperature at constant loading, due to processes occurring with the PdD_x lattice. We have chosen to favor the first interpretation as it has at least partial theoretical support in the model of Hagelstein,²⁰ in which the desorption flux (for $x > x^\circ$) drives a phonon laser coupling energy into a lattice induced nuclear process. From our available data, however, we cannot eliminate the second possibility in which the observed resistance fluctuations reflect a change in the cathode temperature. We expect, and have other evidence to suggest, that the cathode is the source of the heat that we measure as excess power. Thus, a rise in cathode temperature, correlated with excess power seems necessary and obvious. However, the 1 mm diameter cathodes in M4 and C1 are coupled thermally very effectively to the bathing electrolyte, particularly in the presence of evolving deuterium gas. For the resistance fluctuations to originate with changes in the average temperature of the Pd wire cathode, requires a roughly sinusoidal temperature oscillation of period ~ 2 hours and amplitude 2-4K. This amplitude is at least an order of magnitude larger than that which might reasonably be induced by a homogeneous thermal power source of the magnitude measured as P_{xs} in the calorimeter. We cannot, however, rule out the possibility that the measured resistance rise is due to a much larger but more localized temperature rise at some point or points along the length of the wire cathode, due to a more intense but confined excess power source, or small number of sources.

We have demonstrated a mathematical correlation between excess power and the product of three variables: the excess current or current density; the excess loading, squared, $(x - x^\circ)^2$; and the rate of change of the Pd cathode resistance. While we have demonstrated this correlation only for two experiments, M4 and C1, we have no reason to suppose that this correlation is not general. In one of two possible interpretations we have associated the rate of change of resistance with the rate of change of cathode deuterium loading, $\delta x / \delta t$, at constant temperature.

References

1. D. Macdonald, M. McKubre, A. Scott and P. Wentrcek, "Continuous *In-Situ* Method for the Measurement of Dissolved Hydrogen in High Temperature Aqueous Systems", *I&EC Fundamentals* **20**, p. 290, (1981).
2. M. McKubre, S. Smedley, F. Tanzella, B. Chexal, T. Passell and J. Santucci, "Measurements of Excess Heat in D/Pd System", Proceedings of the NSF/EPRI Workshop on Cold Fusion, Washington DC, October (1989).
3. M. McKubre, S. Crouch-Baker, S. Smedley, F. Tanzella, M. Maly-Schreiber, R. Rocha-Filho, P. Searson, J. Pronko and D. Kohler, "Development of Advanced Concepts for Nuclear Processes in Deuterated Metals", Final Report on EPRI Contract 3170-01, (1994, TR104195, August (1994).
4. M. McKubre and D. Macdonald, "Electronic Instrumentation for Electrochemical Studies," in A Comprehensive Treatise of Electrochemistry, J. O'M. Bockris, B. E. Conway, and R. E. White, Eds., Vol. 6, p. 1, Plenum, New York (1984).
5. M. McKubre and D. Macdonald, "Impedance Measurement Techniques," Chapter in Electrochemical Impedance Methods, edited by J. R. Macdonald, Wiley-Interscience, New York (1987).
6. M. McKubre, S. Crouch-Baker, R. Rocha-Filho, S. Smedley, F. Tanzella, T. Passell, and J. Santucci "Isothermal Flow Calorimetric Investigations of the D/Pd System" *J. Electroanal. Chem.*, **368**, p. 55 (1994).
7. M. McKubre, R. Rocha-Filho, S. Smedley, F. Tanzella, J. Chao, B. Chexal, T. Passell, and J. Santucci "Calorimetry and Electrochemistry in the D/Pd System" in *Proceedings of the First Annual Conference on Cold Fusion*, National Cold Fusion Institute, Salt Lake City, UT, p. 20, (1990)
8. M. McKubre, R. Rocha-Filho, S. Smedley, F. Tanzella, S. Crouch-Baker, T. Passell, and J. Santucci "Isothermal Flow Calorimetric Investigations of the D/Pd System" in *The Science of Cold Fusion*, Eds. T. Bressani, E. Del Giudice, and G. Preparata, Conference Proceedings Vol. 33, Italian Physical Society, Bologna, p. 419, (1992)
9. M. McKubre, S. Crouch-Baker, A. Riley, S. Smedley and F. Tanzella "Excess Power Observations in Electrochemical Studies of the D/Pd System: Proceedings of 3rd International Conference on Cold Fusion, *Frontiers of Cold Fusion*", ed. H. Ikegami, Universal Academy Press, Inc., Tokyo p. 139 (1993).
10. M. McKubre, S. Crouch-Baker, S. Smedley and F. Tanzella, "An Overview of Calorimetric Studies on the D/Pd System, at SRI; May 1989 to October 1993. Proceedings of the Russian Conference on Cold Fusion (RCCF), Abrau Durso, September (1993).
11. M. McKubre, S. Crouch-Baker, R. Rocha-Filho, S. Smedley, F. Tanzella, T. Passell, and J. Santucci "Isothermal Flow Calorimetric Investigations of the D/Pd System" *J. Electroanal. Chem.*, **368** p. 55 (1994)

12. M. McKubre, S. Crouch-Baker, A. Hauser; N. Jevtic, S. Smedley, M. Srinivasan, T. Passell and F. Tanzella, "Loading, Calorimetric and Nuclear Investigation of the D/Pd System", Presented at the Fourth International Conference on Cold Fusion, Maui Hawaii (1993), TR104188V1-V4, July (1994).
13. First speculated on publicly by M. Fleischmann and M. McKubre during formal discussion of presentations at The 3rd International Conference on Cold Fusion, Nagoya (1992).
14. S. Pons and M. Fleischmann (IMRA Europe, S.A., Valbonne, France), "Heat after Death," Proceedings of the Fourth International Conference on Cold Fusion, Maui Hawaii pp. 8-1 to 8-26, (1993).
15. S. Pons and M. Fleischmann, "More About Positive Feedback, More About Boiling," Proceedings of the Fifth International Conference on Cold Fusion, Monte Carlo (1995).
16. M. McKubre, S. Crouch-Baker, A. Hauser, N. Jevtic, S. I. Smedley, F. L. Tanzella, M. Williams, S. Wing, "Development of Energy Production Systems from Heat Produced in Deuterated Metals," Final Report on EPRI Contract 3170-23, (1995).
17. M. McKubre, S. Crouch-Baker, A. Hauser, S. Smedley, F. Tanzella, M. Williams, S. Wing, "Concerning Reproducibility of Excess Power Production," Proceedings of the Fifth International Conference on Cold Fusion, Monte Carlo (1995).
18. K. Kunitatsu, "Deuterium Loading Ratio and Excess Heat Generation," Proceedings of 3rd International Conference on Cold Fusion, "*Frontiers of Cold Fusion*", ed. H. Ikegami, Universal Academy Press, Inc., Tokyo p. 139 (1993).
19. N. Hasegawa and N. Hayakawa, "Observation of Excess Heat During Electrolysis of 1M LiOD in a Fuel Cell Type Closed Cell," Proceedings of the 4th International Conference on Cold Fusion, Maui Hawaii (1993), TR104188V1-V4, July 1994. Also Trans. of Fusion Technology Vol. 26, Number 4T Part 2 FUSTE 8(4) 1-540 (1994).
20. P. Hagelstein, "An Update on Neutron Transfer Reactions," Proceedings of the Fifth International Conference on Cold Fusion, Monte Carlo (1995).
21. S. Crouch-Baker M. McKubre, and F. Tanzella, "Some Thermodynamic Properties of the H(D)-Pd System," Proceedings of the Fifth International Conference on Cold Fusion, Monte Carlo (1995).
22. Y. Fukai, "The ABC's of the Hydrogen-Metal Systems," Proceedings of the 3rd International Conference on Cold Fusion, "*Frontiers of Cold Fusion*", ed. H. Ikegami, Universal Academy Press, Inc., Tokyo p. 265 (1993).