Experiment M4

Cathode:	JM* (low PGM), 0.1 cm dia., x 10 cm long formed into the shape of a "lasso" (see Figure 3-80).
Anneal:	Oxygen gettered vacuum
Contacts:	Five wire, I contacts across ends, V contacts wrapped and spot welded
Electrolyte:	1.0 M LiOD with 200 ppm Al
Monitors:	2 X-ray films outside PTFE liner
Cell sensors:	Pressure Electrolyte temperature Recombiner gas temperature

Calibration and initial load. The empty cell and calorimeter were placed in the water bath ~ 1 hour before electrolyte addition and the application of cell current. Electrolyte was added through a PTFE catheter, with the electrochemical power supply set to control potentiostatically at 2.0V cathodic. When the electrolyte addition was complete it was determined that one of the electrochemical current wires was broken. The cell was removed from the calorimeter and bath, and the fault corrected. The cell was returned to the calorimeter, and the power set to control galvanostatically at 59 mA (19 mA cm^{-2}), approximately 3 hours later. This time of current initiation is the reference point for experiment duration.

Initial loading of the cathode was performed with flowing D_2 gas (~ 0 psig, ~ 10 cm^3 min^{-1} flow). At ~ 22 h, the cell was pressurized to ~ 5 psig (~ 0.3 atm. gauge) and the cell and manifold sealed.

First ramp. Figure 3-81a shows the initial current ramps for M4 to a final current density of 956 mA cm^{-2}. The loading monotonically increased with current density to a final value of D/Pd = 0.857 at 264 h. The pressure shown in Figure 3-81a first decreases (after the cell is sealed at ~ 22 h) with loading of the cathode, then increases with cell temperature as the input power is increased.

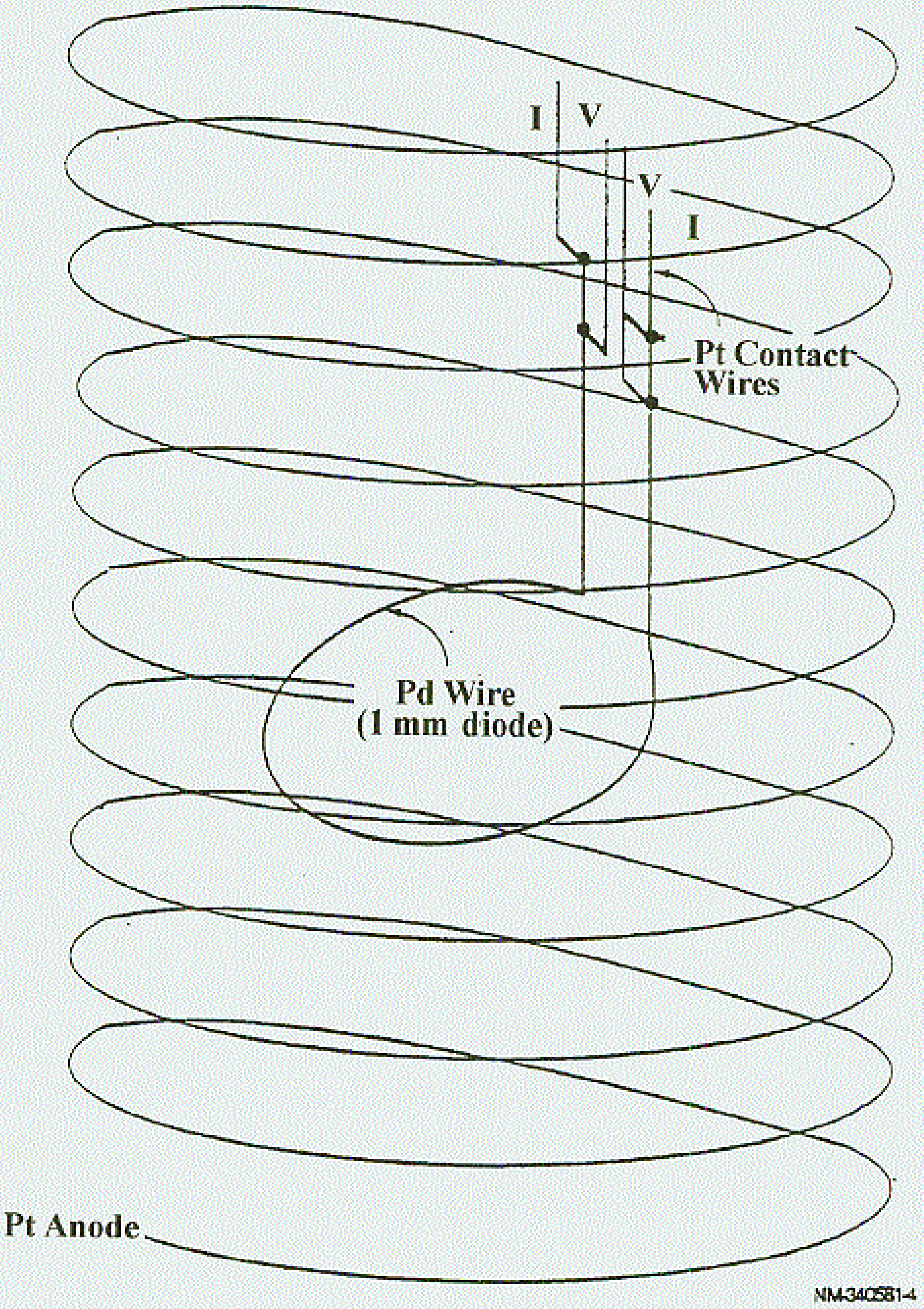

Figure 3-80
M3 Loading

2

Figure 3-81b shows the input, output and excess power observed during this period. The input and output power, referenced to the left axis, monotonically increase with current density and time. The excess power, referenced to the right hand axis, is shown both as raw data (light) and with application of a non-steady state correction. A small exotherm is observed during the rapid loading phase at $t \leq 20$ h. Apart from this, the calorimeter appears to be in thermal balance, and thus well calibrated. At the highest levels of loading, there is an indication of very small levels of excess power, with $P_{xs} \leq 70 \pm 25$ mW.

For the period shown in Figure 3-81, $0\,^{2}\,t \leq 264$ h,

$$E_{xs} = 12 \pm 18 \text{ kJ}$$

$$P_{xs} = 12 \pm 21 \text{ mW}$$

The response of the cathode loading to current density for this cell was slightly unusual. Figures 3-81c and d show loading plotted against current density as both linear and logarithmic plots. It can be seen that, for $i \leq 0.5$ A cm^{-2}, the loading increases linearly with current density;

$$D/Pd = 0.805 + 0.061\ I \qquad r^2 = 0.997$$

For $i \geq 0.5$ A cm^{-2}, the loading increases logarithmically with current density, as is more normally observed (see discussion of M1, Figure 3-68).

$$D/Pd = 0.857 + 0.074\ \text{Log}\ [i] \qquad r^2 = 0.991$$

Strips, Cu addition, second ramp. At ~ 308 h the cell current density was reduced from 956 to 16 mA cm^{-2}, and shortly thereafter reversed in polarity to strip the Pd surface. During the period of the anodic strip, the cell manifold was opened and 2 ml of 1 M LiOD containing 200 ppm (wt) Cu was added to the cell with D_2 gas flowing. The copper-containing LiOD was followed with 1.5 ml D_2O. The pressure was then set to ~ 5 psig, the cell and manifold sealed, and the current reversed to 16 mA cm^{-2} cathodic.

The cell was held at 16 and then 32 mA cm^{-2}, and then given a brief current ramp to 670 mA cm^{-2}. At ~ 400 h the current was reduced to 16 mA cm^{-2}, and the strip and Cu addition procedure described above was repeated.

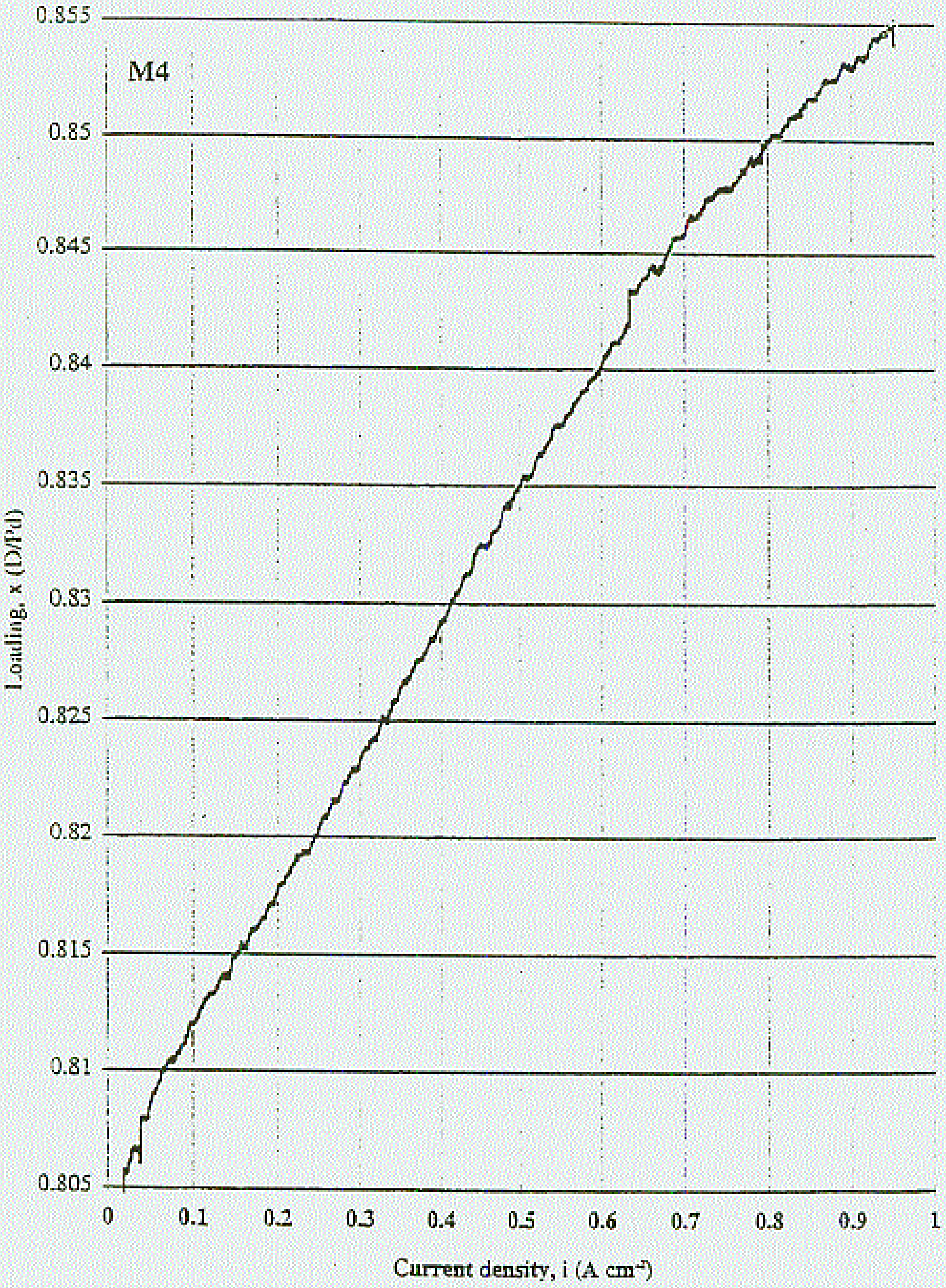

Figure 3-81c
M4 Loading

4

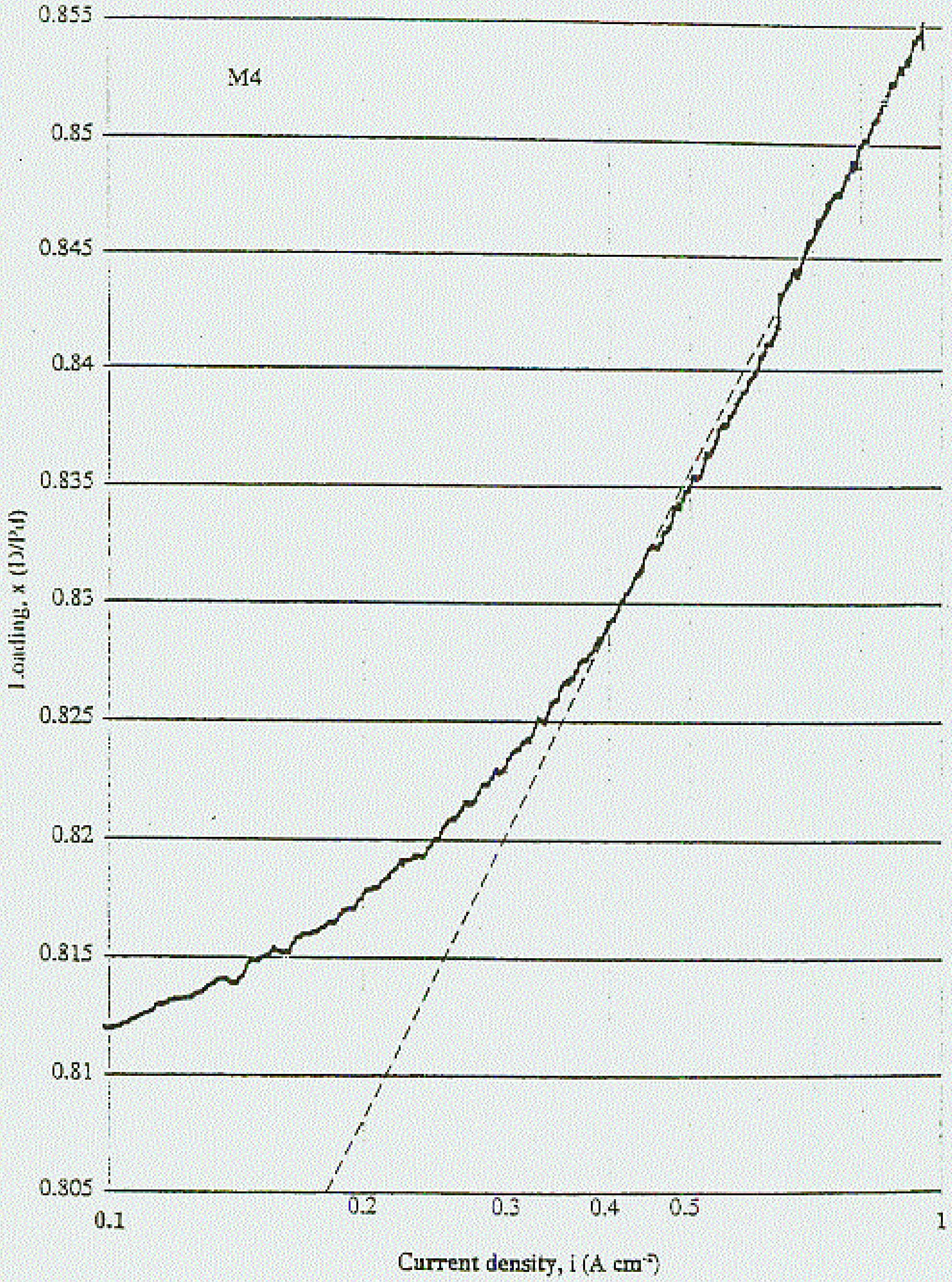

Figure 3-81d
M4 Loading

5

Figure 3-82a shows the current profile, steps, strips and Cu additions. Following the first strip and Cu addition, the Pd cathode achieved a slightly improved loading (over the first attempt) of D/Pd = 0.862 at 32 mA cm^{-2}. During the current ramp the loading improved to D/Pd = 0.867 at $i \approx 150$ mA cm^{-2}, but declined as the ramp continued.

Following the second strip and Cu addition, the Pd cathode demonstrated a further improvement in loading, and obtained a loading D/Pd = 0.854 at 16 mA cm^{-2}, and D/Pd = 0.864 at 32 mA cm^{-2}.

In very close association with the current step from 16 to 32 mA cm^{-2} at 472 h, a possibly important change was observed in the properties of the measured resistance ratio (and, consequently, in the inferred loading); the measured resistance exhibited spontaneous fluctuations. No change was made (knowingly) to the electrical circuit at this time, other than repeating a previously made current step. We will discuss this observation further in the analysis of ramp 3.

Figure 3-82b shows the input, output and excess powers for the period 264-504 hours. Until the time of the current reduction at 306h,

$P_{xs} = 53 \pm 25$ mW

During the subsequent current step, ramp and hold periods,

$P_{xs} = 0 \pm 13$ mW

The second ramp therefore shows the calorimeter to be extremely well calibrated and operating with very good accuracy and precision. The excess power observed at 956 mA cm^{-2} which persists from 220 to 306, must therefore be treated as a real, although small effect. During this period (220-306 h),

$E_{xs} = 17 \pm 8$ kJ

This is only a 0.24% response, which is the limit of calorimeter accuracy.

It should be noted that no measurable excess power was observed during the second ramp to 670 mA cm^{-2}, even though the loading achieved was higher than that obtained on the previous ramp at 956 mA cm^{-2}.

Ramp 3. At ~ 504 h a current ramp was started at 32 mA cm^{-2}. Figure 3-83a shows the current density, cell pressure and loading response of the Pd cathode. Also shown numerically at the top of the graph is the calorimetric mass flow rate, which was varied to permit additional calibration with the calorimeter operating at high input and output power. This graph displays the following features:

i. The overall envelope of loading responds to the current steps and ramp, but declines with time.

ii. A maximum loading of 0.88 ± 0.01 was achieved at a current density of ~ 376 mA cm^{-2}.

iii. The amplitude of the loading variations, $|\delta x/\delta t|$, varies with time and applied current density. The amplitude increases markedly at 472 h in association with the current step to 32 mA cm^{-2} as noted above. The amplitude $|\delta x/\delta t|$ then generally increases with time but is relatively small during the 24 hour period from ~ 594 to 618 h. The amplitude $|\delta x/\delta t|$ then markedly decreases in close association with the gas sampling at 667 h, and the consequent reduction in cell pressure.

Figure 3-83b shows the input, output and excess power for the period of the third ramp. This plot shows several interesting features.

iv. Excess power appears in two "bursts", each of ~ 2.5 days duration, separated by ~ 1 day.

v. In the first instance, excess power appears to initiate with the current ramp at a current density $i \approx 425$ mA cm^{-2}.

vi. The excess power reaches a local maximum of ~ 340 mW, shortly following the end of the current ramp at 562 h.

vii. At constant current, the excess power is highly variable, displaying a minimum of 0 ± 50 mW, and a maximum of 400 ± 25 mW.

viii. In some instances, changes in excess power appear to be anti-correlated with changes in input power; that is, when the excess power steps down, the input power steps up, and vice versa. [While these changes appear in Figure 3-83b as abrupt steps, they are in fact not. The data reflect a period of 11 days].

ix. Deliberate mass flow variations at the times noted in Figure 3-83a, result in no apparent change in the excess power, in the presence or absence of excess power. The calorimeter thus appears well calibrated, and the effect insensitive to mass flow rate.

At constant current, the variability in input power noted in viii above, is reflected in the cell voltage. Figure 3-83c presents the cell voltage and the excess energy (the integral of excess power from t^o = 464 h). The total excess energy observed during ramp 3 was 82.45 ± 27 kJ, or 9.27 MJ/Mole of Pd.

The implications of these data are discussed more fully in the Conclusions to this section. In subsequent experiments with the M4 cell attention was paid to an apparent correlation between excess power and the variation in loading $|\delta x/\delta t|$. Experiments were designed to enhance this variable loading, in an attempt to stimulate excess power production.

Third Cu addition and Ramp 4. At 740 h, the cell was stripped and a third Cu addition made. At 758 h a series of three, six hour heater power steps were made at 5.5, 11 and 22 W, to verify calorimeter calibration, with the cell current at 16 mA cm^{-2}. The current was then stepped to 32 mA cm^{-2} for a period of 12 hours, and the fourth current ramp commenced.

Figure 3-84a shows the current density, cell pressure and cathode loading response. The loading achieved a maximum of 0.898 ± 0.001, shortly into the current ramp, at a current density of ~ 150 mA cm^{-2}. It is clear from Figure 3-84a that the loading variability manifest during ramp 3 (at i ≥ 32 mA cm^{-2}), is not present during ramp 4.

At 1000 h, with the cell current at 3.1 A (956 mA cm^{-2}), an attempt was made to induce a fluctuation in loading with the hope of stimulating excess power production. A current bias of increasing amplitude and alternating sign was applied to the electrochemical current, immediately following the collection of data for each measurement (period 240 s). The increase in amplitude was stopped at a perturbation current of 3.1 ± 1 A; this condition was maintained for ~ 24 hours.

At 1054 h a new pulsing regime was started during which the power supply was controlled to set the cell current to zero for 477 ms every 240 s, immediately following data collection. It is clear from Figure 3-84a that current perturbation of this form did not result in a measurable increase in $|\delta x/\delta t|$; the loading monotonically (and smoothly) declines with time, before, during and following the period of current oscillation. [The measured pressure, temperatures and output power do reflect the current oscillations].

Figure 3-84b shows the input, output and excess power for ramp 4. The raw data are not shown for P_{xs} because, without non-steady state correction, these are unintelligible. However, the fact that we are able, using the non-steady state correction, to maintain a calorimetric measurement accurate to 50 mW, in the presence of an input power source oscillating by 18W (from ~ 13 to ~ 31 W), is a substantial tribute to the design, execution, performance and accuracy of this calorimeter.

Despite the higher maximum loading, and identical current densities, the cell M4 exhibited no detectable excess power during ramp 4 either in the presence or absence of induced current oscillations. For the period 728-1076 h (when the current was reduced back to 16 mA cm^{-2})

$$P_{xs} = 0 \pm 40 \text{ mW}$$

$$E_{xs} = 4 \pm 26 \text{ kJ}$$

Al addition and Ramp 5. At 1077 h the cell was stripped and 2 cm^3 of 1 M LiOD with 200 ppm Al was added to the cell, followed by 1 cm^3 D_2O, with flowing D_2. At 1078 h the cell was pressurized to ~ 5 psig, the D_2 flow stopped and manifold sealed, and the current was returned to 16 mA cm^{-2}.

At 1154 h the manifold was opened and D_2 gas flow started at ~ 10 cm^3/hour. At 1174 h, a gas sample was taken while D_2 was still flowing. The cell was sealed and pressurized to ~ 5 psig and a current ramp started from 0.1 A to 3.1 A at 25 mA/hour.

At 1336 h a further attempt was made to induce loading variation by switching the current on alternate measurement cycles between 3.1 A cathodic and 0.001 A anodic. Figure 3-85a shows the current, cell pressure and cathode loading response for the current ramps, steps and pulse sequence described above. During the initial ramp the loading reached a maximum of D/Pd = 0.918 ± 0.001 at a current density of ~ 175 mA cm^{-2}. The cathode de-loads monotonically with current density and time. With the introduction of the first cathodic/anodic pulsing at 1334 h, the cathode briefly loads and then de-loads, roughly to its initial value. There is, however, a small indication that this pulse sequence somewhat reversed the trend of slow de-loading; it also introduced a variability in loading, as desired, but the response was small.

On terminating the current pulses and re-establishing a constant cathodic current of 3.1 A (956 mA cm^{-2}), the cathode loaded rapidly, and then de-loaded when the current was dropped to 50 mA cathodic (16 mA cm^{-2}). The implications of this observation, and the success of attempts to reproduce the effect which gave rise to rapid loading are discussed subsequently in the section in **M-Series Conclusions.**

Figure 3-85b plots the input, output and excess power for the period of ramp 5. The raw data are calculated as the average of adjacent pairs of data points to somewhat remove the effect of the imposed power oscillation. As for ramp 4, the excess power initially shows a small endothermic response that is not fully corrected for by the non-steady state correction. During periods of current oscillation the calorimeter appears to be slightly endothermic; this effect is due to asymmetric voltage transients associated with switching to and from high current. It is clear, however, from Figure 3-85b that the cell M4 exhibited no detectable positive excess power during ramp 5 (as for ramp 4), either in the presence or absence of induced current oscillations. For the period 1076-1408 hours.

$$P_{xs} = -25 \pm 25 \text{ mW}$$

$$E_{xs} = -4 \pm 24 \text{ kJ}$$

Attempts at pulsed loading. A series of experiments was performed to determine the conditions under which loading enhancement might be achieved by a variety of anodic strips, current interrupts, and anodic/cathodic pulse sequences. Table 3-4 summarizes the procedures employed, and the results achieved. Figure 3-86a plots the current density, cell pressure and cathode loading obtained during the period covered by Table 3-4. Figure 3-86b plots the input, output and excess power for the same period. R9

After T 1408

It is clear from Table 3-4 that a benefit is obtained in achieving enhanced loading after the following procedures:

i. Maintaining the cell at open circuit for a period of time (operation 17 in Table 3-4).

ii. Anodic/cathodic pulsing, with the anodic limit ~ 1 mA cm^{-2} (operations 1, 3, 5, 7, 9, 21 and 24 in Table 3-4).

iii. Brief anodic strips at ~ 1 mA cm^{-2} (increasing benefit with increasing hold time; operations 11, 13, 15).

Table 3-4
Summary of Pulse Procedures

	Time		Duration (h) Expt.	Duration (h) Process	i low (mA/cm²)	i high (mA/cm²)	D/Pd	Max	Min
1	9/16/94	10:24	1408.6	1.3	-0.001	0.987 pulse	0.818		0.817
2	9/16/94	11:44	1410.0	72.3	0.987	0.987 dc	0.818	0.909	
3	9/19/94	12:04	1482.3	6.1	-0.001	0.987 pulse	0.879		0.816
4	9/19/94	18:12	1488.4	5.9	0.987	0.987 dc	0.817	0.900	
5	9/20/94	0:04	1494.3	6.1	-0.001	0.987 pulse	0.900		0.819
6	9/20/94	6:12	1500.4	5.9	0.987	0.987 dc	0.822	0.901	
7	9/20/94	12:04	1506.3	1.1	-0.001	0.987 pulse	0.900		0.846
8	9/20/94	13:12	1507.4	4.9	0.987	0.987 dc	0.845	0.900	
9	9/20/94	18:04	1512.3	1.1	-0.001	0.987 pulse	0.895		0.848
10	9/20/94	19:08	1513.4	16.9	0.987	0.987 dc	0.848	0.902	
11	9/21/94	12:00	1530.2	0.1	-0.001	4 min. anodic	0.896		
12	9/21/94	12:04	1530.3	1.8	0.987		0.892	0.882	
13	9/21/94	13:54	1532.1	0.2	-0.001	10 min. anodic	0.880		
14	9/21/94	14:04	1532.3	3.2	0.987		0.870	0.887	
15	9/21/94	17:17	1535.5	0.3	-0.001	16 minutes anodic	0.885		
16	9/21/94	17:33	1535.8	20.9	0.987		0.865	0.894	
17	9/22/94	14:24	1556.6	2.5	0.000	Open Circuit	0.888		0.814
18	9/22/94	16:52	1559.1	16.9	0.985	Close Circuit	0.818	0.894	
19	9/23/94	9:444	1576.0	2.1	-0.016	Anodic Strip	0.890		0.560
20	9/23/94	11:52	1578.1	72.2	0.987	Cathodic	0.576	0.929	
21	9/26/94	12:04	1650.3	2.0	-0.001	0.987 pulse	0.891		0.819
22	9/26/94	14:04	1652.3	0.0	0.987	0.987 dc	0.819	0.857	
23	9/26/94	15:48	1652.3	3.7	-0.013	Strip at -0.8V	0.819		0.545
24	9/26/94	17:44	1656.0	21.2	-0.001	0.987 pulse	0.551	0.843	
25	9/27/94	14:56	1677.2	23.9	-0.988	0.987 oscillation	0.599		
26	9/28/94	14:48	1701.0		0.987	0.987 dc	0.817		

iv. A more extended anodic strip under galvanostatic conditions at ~ 16 mA cm^{-2} (operation 19)

v. A constant voltage anodic strip, up at ~ -0.8V (operation 23).

The benefits achieved by these processes, thought to clean or refurbish the Pd surface, appear to increase with increasingly aggressive procedures. That is, the larger the anodic current (or voltage) and the longer the procedure, the greater the benefit observed in subsequent re-load steps. None of the procedures attempted, however, yielded the benefits observed following the initial pulsing sequence from 1336-1362 h. This first instance of pulsing, also, was the only one which did not result in net cathode de-loading.

One procedure which did not yield a beneficial effect on loading was the ~ ± 1A cm^{-2} oscillation (25 in Table 3-4). This oscillation did appear to have profound effects on the cathode which are discussed more fully below.

Because of the large number of power steps in the period covered by Table 3-4, an accurate determination of the total excess energy cannot be made. Figure 3-86b shows the input, output and excess power calculated for this period; the raw data for P_{xs} are offset slightly for clarity. From observation of Figure 3-86b it is clear that no appreciable amount of excess power was observed, even at times when the loading was as high as D/Pd ≈ 0.929. For the period 1408-1672 h we estimate

$$E_{xs} = 0 \pm 35 \text{ kJ}$$

At 1701 h the pulsing was stopped and the power supply was set to deliver a 3.1 A continuous cathodic current. At 1718 h the current was reversed in polarity for nearly 30 h in order to strip all D from the Pd and re-determine a value for R°. At 1744 h the cathode was re-loaded, and attained a (modest) loading of 0.83 at 3.1 A (956 mA cm^{-2}).

Figure 3-87a shows the current density, cell pressure, calorimetric mass flow and resistance ratio until the termination of M4. At 1672 h, under the influence of alternating current pulses ~ 1 A cm^{-2} cathodic and ~ 1 mA cm^{-2} anodic, the resistance ratio was stable at ~ 1.93 on the right side of the maximum; a loading of D/Pd ≈ 0.83. When the pulsing begins, at the point indicated by the first arrow in Figure 3-87a, several interesting features are observed in the measured resistance.

i. Unlike the preceding pulse regime, under the influence of ± 1 A cm^{-2} current oscillation, the cathode displays marked loading and de-loading on alternate cycles, as shown by the divergence of the R/R^o trace in Figure 3-87a.

ii. The resistance of the branch measured at the end of the cathodic half cycle (the upper branch between the arrows in Figure 3-87a) increases from the initial value, passes through a maximum and begins to decrease.

iii. The resistance of the branch measured at the end of the anodic half cycle (the lower branch between the arrows in Figure 3-87a) increases in value, essentially monotonically, by ~ 13%.

iv. When the current was restored to ~ 1 A cm^{-2} cathodic, the resistance ratio rises to a roughly constant value of $R/R^o \approx 2.22$. When stripped completely, at 1744 h, the measured resistance ratio $R/R^o \approx 1.133$.

v. When this cycle was repeated, the resistance ratio rises on loading to $R/R^o \approx 2.13$, and when fully stripped falls to $R/R^o \approx 1.09$.

Provided that the Pd electrode does not undergo mechanical change, and is influenced only by the absorption and desorption of D, we expect the resistance ratio to be bounded such that $1 \leq R/R^o \leq 2$. Clearly, something unusual must have happened to the Pd electrode.

Figure 3-87b shows the input, output and excess power from 1072 - 1840 h. During the period of ± 1 A cm^{-2} current oscillation, the calorimeter appears to be operating endothermically by about 0.5 W. In fact, this is due to the asymmetric transient voltage responses to the up-going and down-going current steps. These transients were integrated completely by digitizing the transient waveform to calculate the net power for each cycle. The open squares plotted in Figure 3-87b show the results of this calculation for a selected set of data. Clearly, these data coincide with the alorimetrically determined endotherm. We can conclude, therefore, that, during the period of current oscillation and up until the experiment end at 1840 h, $P_{xs} = 0 \pm 50$ mW and $E_{xs} = 0 \pm 17$ kJ.

Table 3-5 summarizes the measured resistances during this period. In the column labeled "$R^{o\prime}$", we calculate the presumed value based on the measured R/R^o, with the following assumptions:

a. All temperature corrections have been correctly handled.

b. The value of R^o before the current oscillations is the same as that measured at the start of the experiment.

c. The maximum described by the cathodic branch during the period of oscillation, is a de-loading maximum (point ii, above).

d. The rise in R/R^o described by the anodic branch during the period of oscillation (point iii, above) is due to an increase in R^o, and not due to increased loading.

e. The Pd cathode at 1720 and 1818 h is loaded approximately to the resistance maximum, for which $R/R^o \approx 1.95$ (the largest value observed for this cathode).

f. The Pd cathode at 1744 and 1840 h is fully stripped ($R/R^o = 1.00$)

The final column in Table 3-5 shows the rise in this estimated resistance as a percentage of the initial value. This percentage is plotted in Figure 3-87c; these data points are shown as squares, connected by straight lines. Also plotted in Figure 3-87c is the resistance rise during the period of oscillation, calculated on the basis of assumption (d), alone.

Table 3-6
Loading Response to Current Ramps in Experiment M1, M2 and M4

Expt. #	Ramp #	Rate (mA/hour)	Maximum (D/Pd)	at i (mA cm^{-2})	at t - t° (h)	Additive†
JM* 2mm x 3 cm					0	
M1	1	20	0.927	900	250	Al[1]
M1	2	25	0.900	800[2]	552	None
M1	3	50	0.867	800	844	None
M1	4	50[5]	0.877[6]	30[4]	1000	B[3]
E#1 2.8mm x 3cm						None
M2	1	50	0.829	580[2]	144	None
M2	2	50	0.840	490	280	Al
M2	3	50	0.854	525	460	Si
M2	4	50	8.846	280	542	B[7]
JM* 1 mm x 10 cm						
M4	1	25	0.857	956[2]	264	Al[1]
M4	2	25	0.867	150[5]	360	Cu
M4	3	25	0.880	376	524	Cu
M4	4	25	0.898	150[5]	872	Cu
M4	5	25	0.918	175[5]	1184	Al
M4	Step to	956	0.929[8]		1580	None

[1] 200 ppm Al in starting electrolyte, (2) Highest current density obtained on this ramp

[3]. 15 mg H_3BO_3, containing 7.3 x 10^{-4} moles of H (4) Maximum loading obtained at start of ramp

[5]. Loading declined markedly with increasing current density, (6) D/Pd not well known due to influence of H and B

[7]. 3 mg B_2O_3, (8). Loading declined markedly with time

† Unless otherwise noted, chemical species additions were made by adding the element dissolved in 1.0 M LiOD