A STUDY OF THOSE PROPERTIES OF PALLADIUM THAT INFLUENCE EXCESS ENERGY PRODUCTION BY THE "PONS-FLEISCHMANN" EFFECT

Edmund Storms
Energy K Systems
Santa Fe NM, 87501
Storms2@ix,netcom.com

ABSTRACT

A large collection of palladium plates having different treatments were examined to determine the composition limit produced after electrolysis in LiOD-D2O electrolyte, the amount of excess volume produced by the contained deuterium, the open circuit voltage generated by the material referenced to a platinum electrode, and the deloading rate in air. The influence of these properties on the ability to produce excess power from the "Pons-Fleischmann" effect was explored.

The palladium was found to be very nonuniform with respect to the measured properties. Excess power production was associated with a minimum amount of excess volume and an open circuit voltage above 1.0 V. Samples capable of producing excess energy can be reactivated even after deloading or removal of the surface.

INTRODUCTION

Reproducibility has been a major problem for the acceptance and study of the "Cold Fusion" effect. This problem is now recognized to be caused by the difficulty in achieving the required physical and chemical environment[1]. Past work has relied mainly on chance to provide useful palladium. Unfortunately, experience has shown that commercial palladium has a low probability for having the required properties. In addition, there is reason to believe that only rare, isolated regions on the palladium surface become active. These regions are formed where a variety of chemical and physical properties combine to create the necessary local condition. The nature of these properties is still poorly understood, hence difficult to create. Therefore, it is important to develop an easy method to identify useful palladium and to discover which properties need to be enhanced by the manufacturing process.

Past work[2,3,4,5,6] demonstrates that the deuterium content is one of these important properties. Excess energy production is not achieved unless the average composition is above a critical value. Therefore, this behavior needs to be a major part of any pretest method. The other measurements used in this study are related to the properties that influence the achieved composition.

The deuterium content depends on a competition between gain and loss. Gain is determined, in part, by the ease with which deuterium ions can enter a particular surface

region from the solution. Gain from all of the regions combine to produce the measured, overall gain. Loss depends, in part, on the number of cracks that penetrate the surface. These defects provide an easy avenue for escape of deuterium as D_2 gas. Because both of these properties are randomly distributed, their optimal interaction is expected to be rare and random. Only a small number of regions will allow easy gain of deuterium while being sufficiently removed from a surface crack to retain the required very high composition.

Although the detailed surface properties are not easy to measure, the average gross properties can be determined. Presumably, a sample that readily absorbs deuterium and has a smaller number of cracks would achieve the critical composition at a greater number of surface sites, hence produce a larger amount of excess power. Although many of these cracks will not penetrate the surface, consequently not provide an escape path, the presence of fewer cracks should, nevertheless, be of benefit. Unfortunately, the number of cracks can not be directly determined. Instead, the gross volume associated with these cracks is measured and used to monitor changes in the gross crack concentration. A previous study found that excess energy production was influenced by the excess volume concentration[4]. This study extends the discovery.

When the applied voltage is turned off, deuterium immediately begins to leave the palladium as D_2 gas. The loss rate may be used a guide in judging the nature of the surface barrier to both deuterium loss and gain while the sample is being electrolyzed. It is proposed that this loss rate continues largely unchanged even while electrolysis is adding deuterium to the sample.

A potential is generated between the cathode and a reference electrode when the electrolyzing current is briefly interrupted. This potential is produced by chemical reactions occurring within the surface of the cathode. Pure – PdH produces 40-50 mV referenced to pure Pd[7], a value that is consistent with the Gibbs energy of formation of the phase. Much higher potentials are generated in "cold fusion" cells because, it is believed, lithium and other impurities form alloys in which hydrogen is much more stable than in -PdD. Even though the potential is influenced by the presence of these impurities, a change in the voltage is expected to be proportional to a change in the deuterium content of the surface. In addition, this alloy structure is apparently required for the energy producing reaction to occur. Therefore, the open circuit voltage (OCV) provides a means to reveal the presence of the required conditions.

The first part of this study examines eighty pieces of palladium supplied by IMRA Materials R & D Company (Japan) to determine the limiting composition, the excess volume, the deloading rate in air, and the open circuit voltage. Information about the relationship between these properties and their reproducibility between samples is sought. The second part of the study explores the relationship between these properties and the production of excess power. The latter study is still on going. No attempt was made to detect nuclear products.

Part I
Material Properties

EXPERIMENTAL

Supplied palladium samples (20 mm x 10 mm x 1 mm) were cut from a 10 mm wide strip of palladium. The numbering is sequential. All samples were polished using 0.5 μm diamond slurry. Some were given additional treatments. Information supplied by IMRA is listed in Table 1. The samples can be divided into 8 sets based on their pretreatment and chemical composition as shown in Table 2. Each piece was subjected to several measurements before, during, and after pretreatment by electrolysis using a 0.3N LiOD + D_2O electrolyte and a platinum anode. Seleced samples were then studied in a calorimeter.

A. Initial Limiting Deuterium Content:

Electrolysis causes a rapid initial increase in the deuterium content followed by a more gradual approach to a nearly constant value. An example of this behavior is shown in Fig. 1. The constant value is taken as the *composition limit*. Further electrolysis can cause the deuterium content to gradually increase over many days. This process results in a somewhat larger final value which is not addressed here.

The samples were weighted before and after electrolysis to an accuracy of ±0.0001 g. The increased weight was assumed to result from the uptake of deuterium. Values are estimated to have an uncertainty of ±0.002 in the atom ratio. For a few samples, deuterium uptake was monitored during electrolysis by determining the amount of oxygen that accumulated within the closed cell.

TABLE 1
As Delivered Properties of the Palladium Samples

Designation	Surface	Vickers Hardness	Lattice Grain Structure	Parameter, Å
A1-B1	Pd>S=C>O	115	Uneven fiber	3.8954
A1-B2	O>Pd	58	Irregular grain size	3.8896
A1-B3	O>>Si>Pd	60	Irregular grain size	
A2-B1	Pd>C>O>S	219	Uneven fiber	3.8991
A2-B2	O>PD>C	109	200 μm grains	3.8916
A2-B3	O>>SI=Pd	109	200 μm grains	

Palladium powder contained the following in ppm: 20 Pt, 17 Au, 52 Ag, 6 Ca, <10 Cr, 8 Cu, 10 Fe, 1 Mg, <1 Si. The following were sought but not detected: Rh, Ir, Ru, Os, Al, As, Bi, Cd, Co, Mn, Ni, Pb, Sb, Sn, Ti, Zn, W, Zr and Mo.

_____

TABLE 2
Pretreatment of Samples

BASIC PROCESS
       Arc melted
       Cast in vacuum
       Annealed in vacuum at 750° for 1 hr
       Swaged to 8 mm diameter
       Rolled to strip >10 mm wide and 1.2 mm thick
       Cut samples to 10 mm wide and 20 mm long
   Polished using 0.5μm diamond slurry.

ADDITIONAL TREATMENT
       A1-B1, pure palladium + basic process
       A1-B2, pure palladium + basic process+
          annealed in air at 750° for 24 h.
       A1-B3, pure palladium + basic process+
          annealed in vacuum at 750° for 24 h.
       A1-B4, pure palladium + basic process+
          annealed in vacuum at 750° for 24 h,
          etched with Aqua Regia for 10 min,
          annealed in vacuum at 200° for 24 h.

       A2-B1, (palladium + 500 ppm boron) + basic process
       A2-B2, (palladium + 500 ppm boron) + basic process+
          annealed in air at 750° for 24 h.
       A2-B3, (palladium + 500 ppm boron) + basic process+
          annealed in vacuum at 750° for 24 h.
       A2-B4, (palladium + 500 ppm boron) + basic process
          annealed in vacuum at 750° for 24 h,
          etched with Aqua Regia for 10 min,
   annealed in vacuum at 200° for 24 h.

_____

B. Excess Volume:

     Palladium expands as it reacts with hydrogen or deuterium. When the average composition exceeds the lower limit of -PdD, stress produced by additional hydrogen causes a volume expansion beyond that expected from the lattice parameter increase. This effect can be seen in Fig. 2. Much of the expansion is retained when the hydrogen is removed. Most samples show an additional excess volume increase each time the
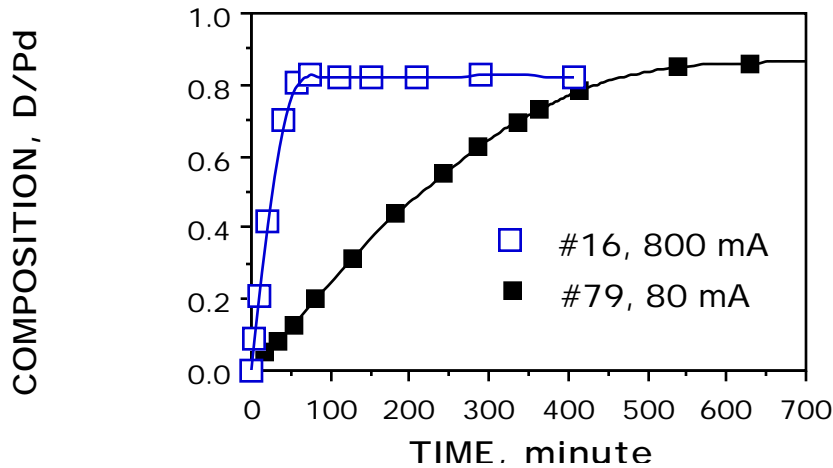
FIGURE 1. Comparison between the loading behavior of two typical samples at currents of 80 mA and 800
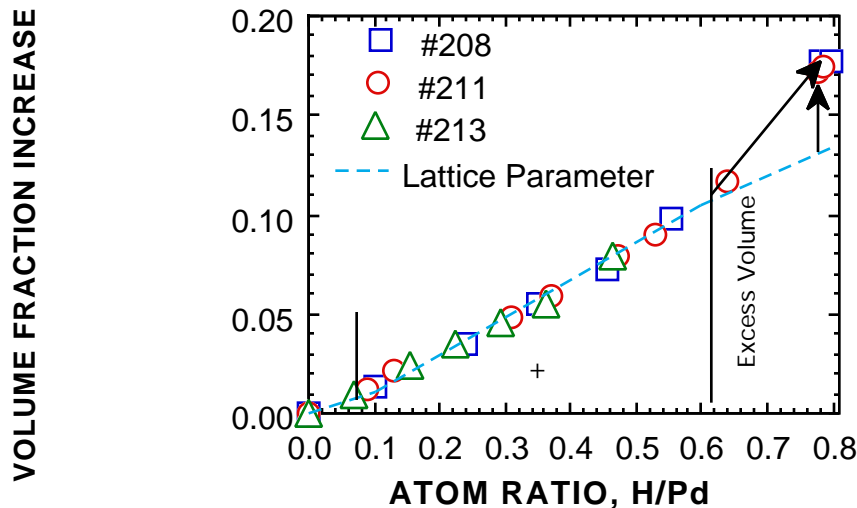
FIGURE 2. The expansion behavior of palladium as hydrogen is added.

loading process is repeated. This excess volume is presumed to be caused by cracks and dislocations within the material.

The dimensions of each piece were measured before and after electrolysis using calipers. The first measurements were made using calipers having a sensitivity of 10 μm while later work used a micrometer having a sensitivity of 1 μm. Measurements were made at 3 positions along each dimension and these were averaged to give the total volume. The uncertainty in the reported percentage is estimated to be ±0.5% for the early measurements and ±0.2% for later studies.

After being electrolyzed, the palladium was again measured. Excess volume fraction was calculated using the following equation[8].

$$EV = [(Final\ Volume)-(Initial\ Volume)]/(Initial\ Volume)-(0.0172+0.14125*D/Pd)$$

This equation applies only to samples having a composition within the -PdD phase. Because the actual EV is sensitive to the D/Pd ratio, all comparisons were made by extrapolating the value to a fixed composition of D/Pd=0.85.

C. Open Circuit Voltage:

Measurement of the voltage developed between the cathode and a platinum reference electrode is made after the applied voltage is interrupted for a brief time. Flame heating the platinum in air allows for a stable, although not an absolute, voltage. A Luggin capillary is used in most cases. This method allows a small region of the cathode to be examined. Some also contain an immersed platinum mesh from which an average voltage is obtained. The voltage is always referenced to the voltage generated between the Pt reference electrode and the palladium cathode before loading starts. This voltage is generally 0.04 ±0.02 V. Measurements are made as a function of average D/Pd atom ratio during the loading and deloading of a few samples.

D. Deloading Rate:

Once the charging current is stopped, deuterium loss commences. The sample is removed from the cell and weighed at regular intervals. The resulting D/Pd ratio is plotted as a function of square root of time and a least squares line is fit to the data. The slope of this line is used to compare the deloading rates and to extrapolate the D/Pd ratio back to the time the current was stopped.

RESULTS

Composition Limit

Values for the various sets of palladium are compared in Fig. 3, 4, 5 and 6. Figure 3 shows the sample set containing pure palladium, which was not annealed. Adjacent samples show a wide variation in this property. A loading current of 800 mA seems to produce a larger average value compared to a current of 80 mA. The effect of temperature during loading is not clear because of the large scatter in the values.

Figure 4 compares samples in set A2-B1, which contained 500 ppm boron and were not annealed. This set shows a wider variation in values but contains samples having a higher limiting composition compared to the set not containing boron. As before, the effect of loading temperature is uncertain because of the general scatter in values.

Figure 5. compares three sets, A1-B2, A1-B3 and A1-B4, which contain pure palladium and are annealed. Because set A1-B2 was annealed in air, the samples showed a gray layer of oxide on the surface. Bits of this layer would flake off after loading, thereby biasing the compositions in the low direction by an unknown amount. Although set A1-B3 was annealed in vacuum, an oxide layer was also evident. Only set A1-B4 of this group had a bright metallic surface. This set had been etched in Aqua Regia following by a low temperature anneal. Although the treat Figure. 6 shows the annealed samples that contain 500 ppm boron. These samples also were coated by an oxide layer that flaked off on a few occasions. However, the thickness of this layer was less on

samples in set A2-B3, a factor that may have caused the higher limiting composition. As previously noted, the Aqua Regia treatment improved reproducibility.
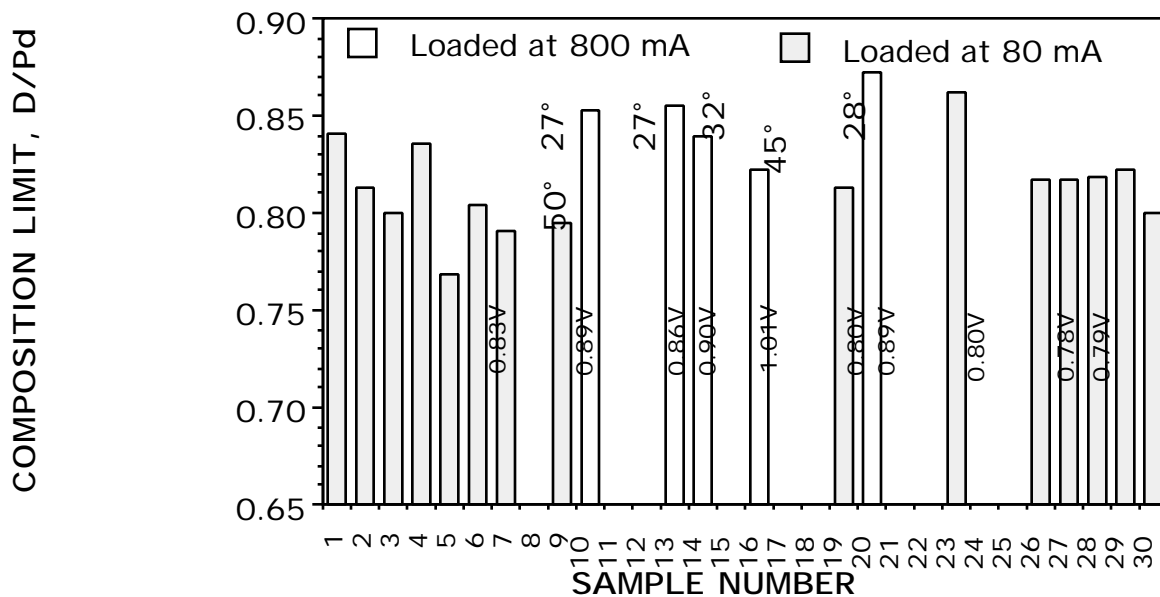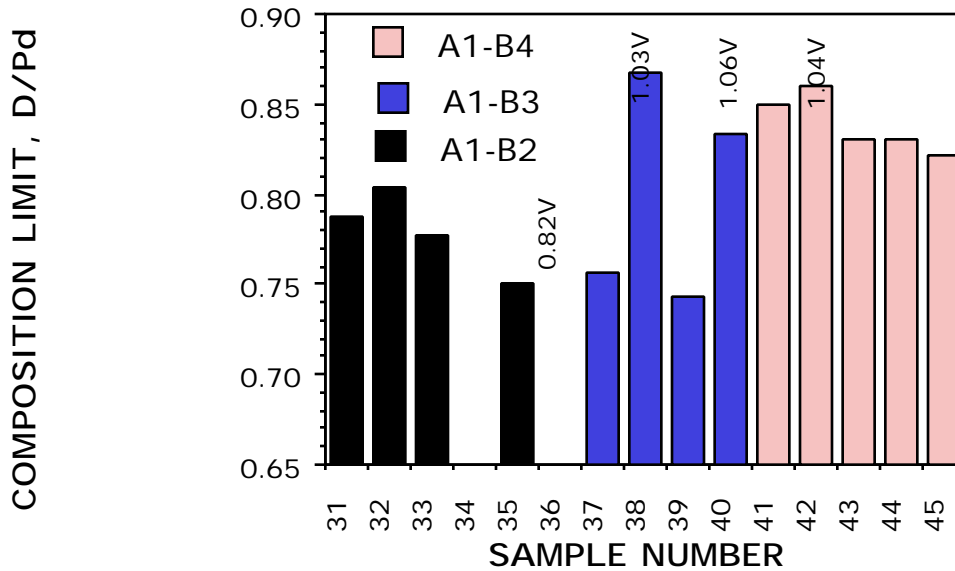

FIGURE 3. Composition limit of sample set A1-B1. Initial OCV is indicated. Temperature 20-23° except where noted.
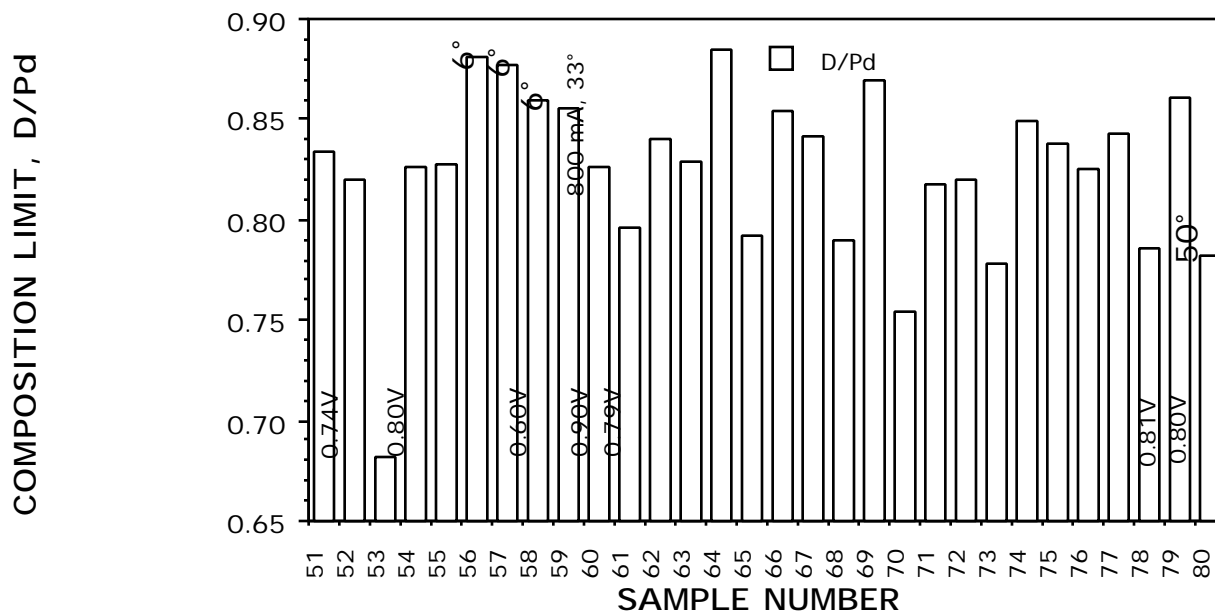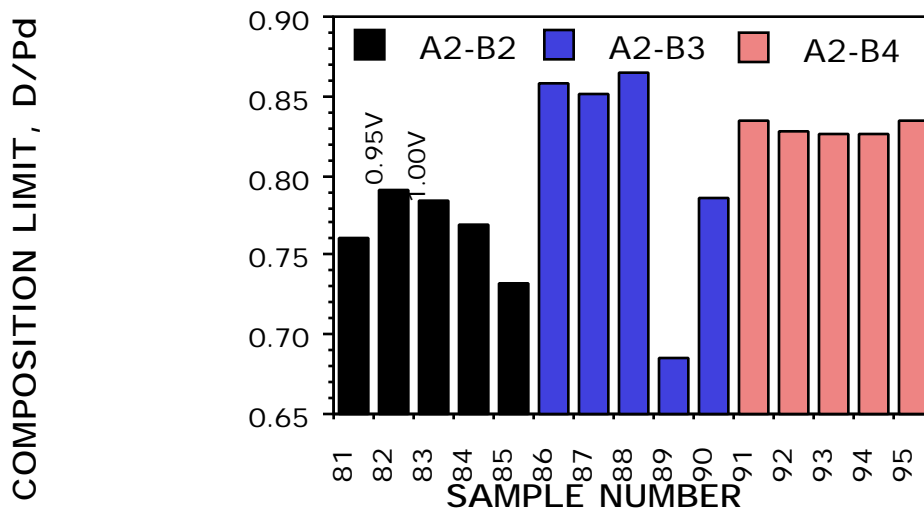

FIGURE 4. Composition limit of sample set A2-B1. Initial OCV is indicated. Temperature 20-23° except where noted.

Excess Volume (EV):

In general, an increase in excess volume results in a reduction of the composition limit (Fig. 7). Part of the large variation is thought to result from the presence of two

FIGURE 5. Composition limit of sample sets A1-B2, A1-B3, and A1-B4.

FIGURE 6. Composition limit for sample sets A2-B2, A2-B3 and A2-B4. Initial OCV is indicated.

types of cracks. Type 1 is proposed to intersect the surface and, therefore, have a large effect on the retention of deuterium. In contrast, Type 2 cracks are proposed to exist completely within the solid material. Their effect is small because they can only change the local magnitude of the composition gradient. Although, the relative concentration of these two types can not be determined, many samples appear to contain a nearly equal mixture. Regardless of this uncertainty, a low excess volume appears to produce a benefit. Figure 8. compares the EV for sample set A1-B1. The samples loaded at 800 mA have a lower average than those loaded using 80 mA. The annealed samples shown in Fig. 9 all have a similar behavior with most values falling between 4% and 7%. The extremes shown by the unannealed material are not present.

As can be seen in Figs. 10 and 11, the presence of boron introduces extremes in both the annealed and unannealed material.
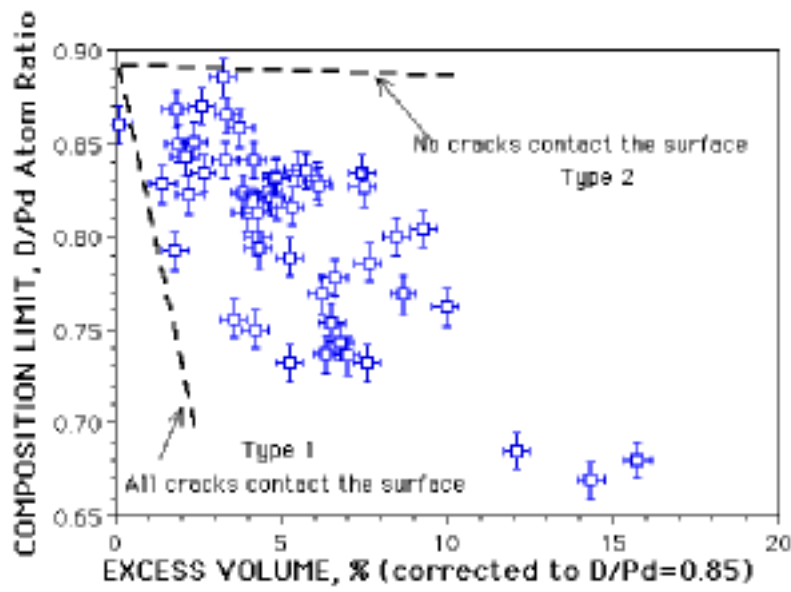
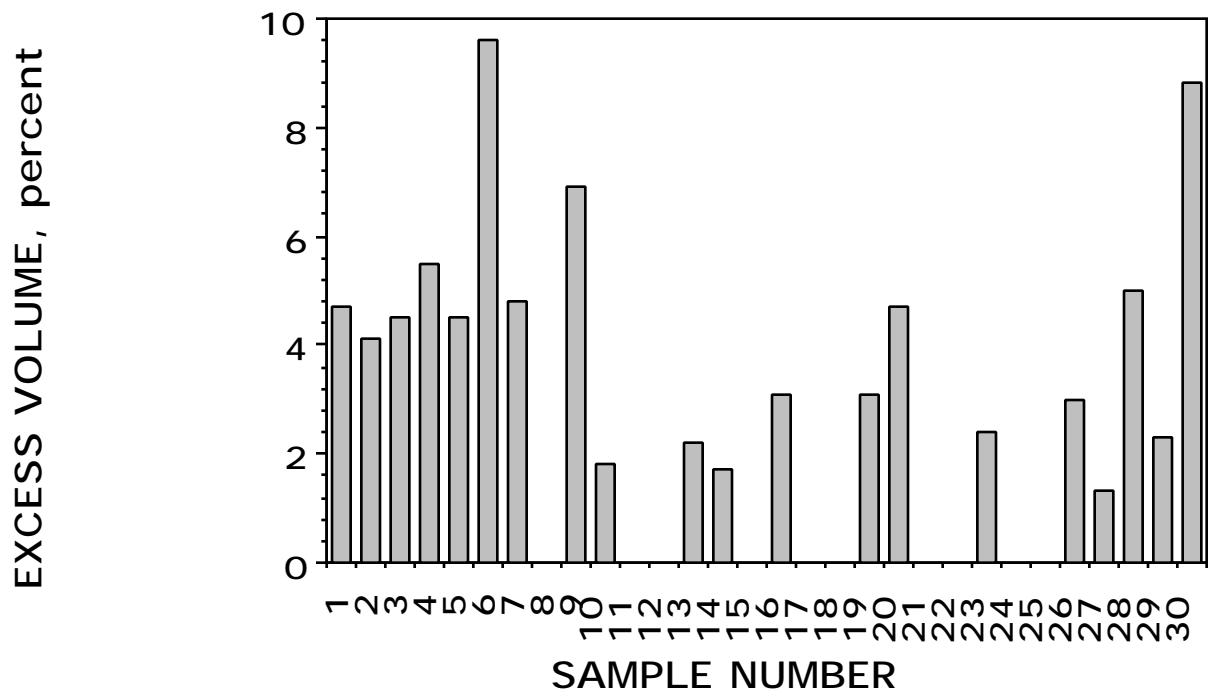**FIGURE 7.** Effect of excess volume on the composition limit.

FIGURE 8. Comparison of excess volume for sample set A1-B1.

Deloading Rate:

The deloading rate is expressed as D/Pd divided by the square root of time in minutes. Values between 1×10^{-3} and 22×10^{-3} were measured. No relationship to the composition limit was apparent. On the other hand, in spite of considerate scatter, the

deloading rate seems to be larger for samples having a lower excess volume as shown in Fig. 12. The presence of 500 ppm boron has no apparent effect.

Open Circuit Voltage (OCV):
        The OCV at the conclusion of the loading varied between 1.01 V and 0.74 V as can be seen in Fig. 13. No relationship emerged to show the effect of boron. However, the use of 800 mA produced generally larger values compared to 80 mA.
        On the other hand, the OCV gradually increased as the average composition increased during loading. Fig. 14 compares this behavior for several typical samples.
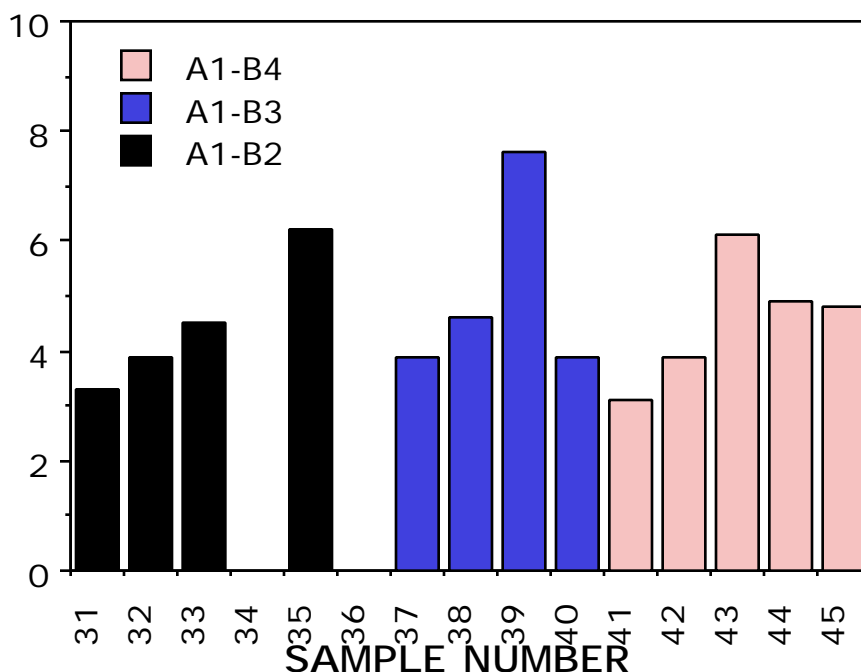
FIGURE 9. Comparison of excess volume for sample sets A1-B2, A1-B3 and A1-B4.

<div align="center">

PART II
Excess Energy Study

</div>

EXPERIMENTAL

Method
        An isoperibolic-type calorimeter was used to measure energy production during electrolysis after the pretest had been run. The electrolyte, consisting of 0.3 N LiOD in D_2O, was precleaned using platinum as the cathode during the initial checkout procedure. A detailed description is given in the next section.
   Typically, a fixed current was applied which was interrupted every 0.5 -1 h for about 10 sec. The OCV was measured during this interval. Every 24 hour, the current was stepped using arbitrary intervals from 50 mA to 3 A several times. The calorimeter was allowed to come to steady-state after each current change whereupon measurement of temperature, applied voltage and current were made. These measurements are identified by Set numbers in the following discussion.
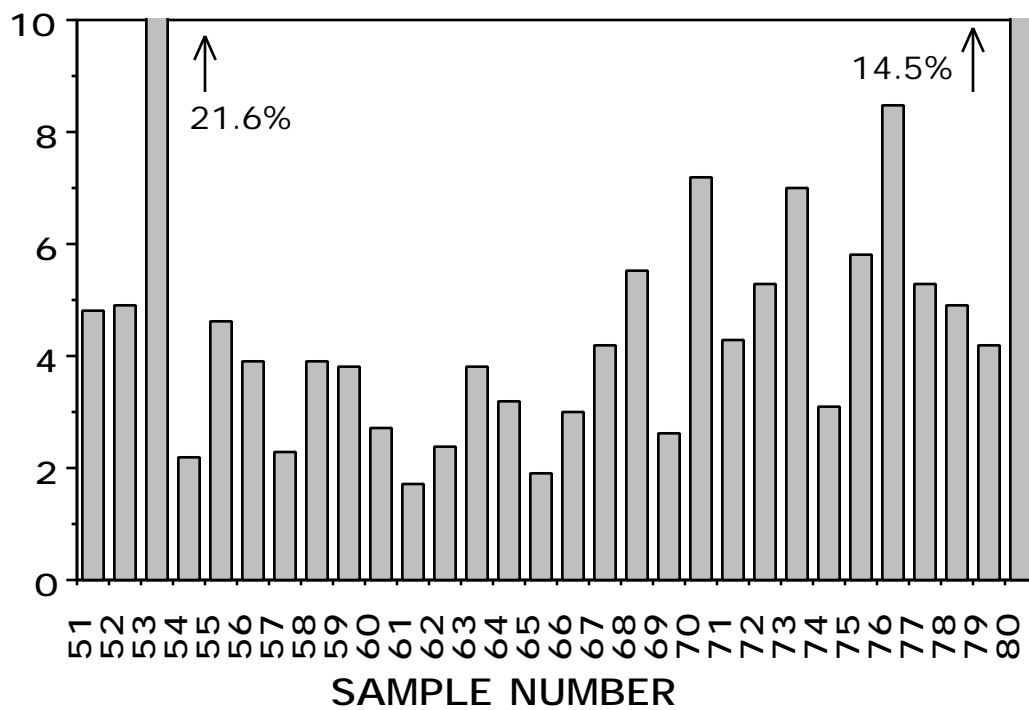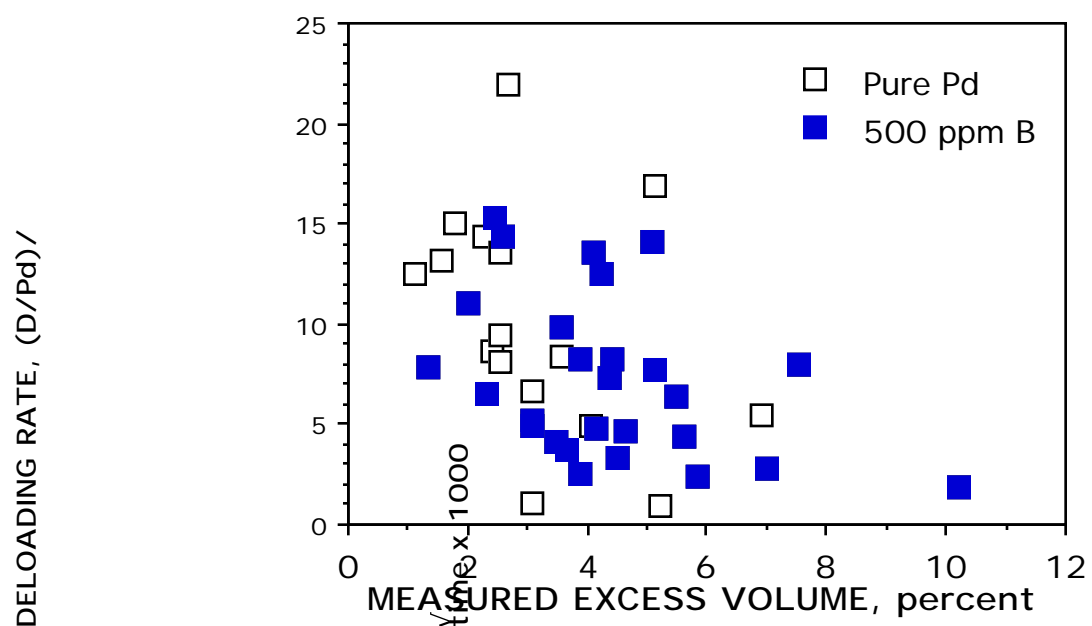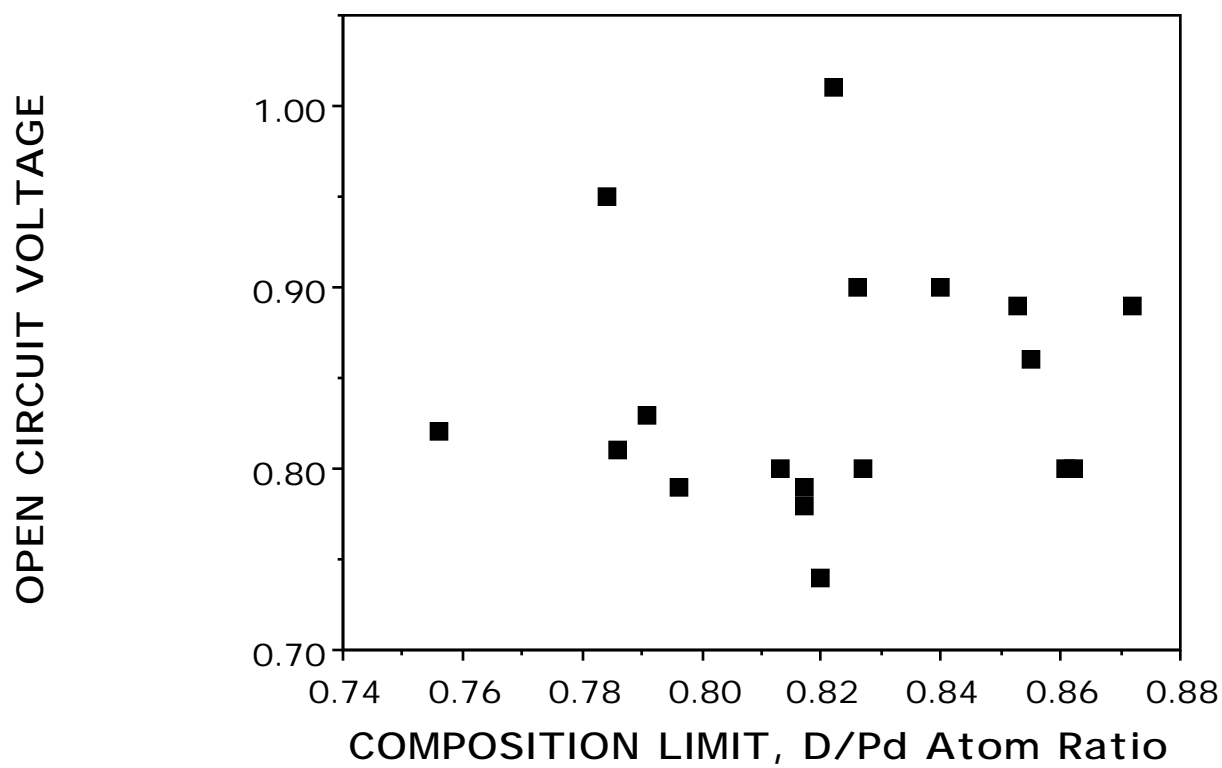
FIGURE 10. Comparison of excess volume for sample set A2-B1.
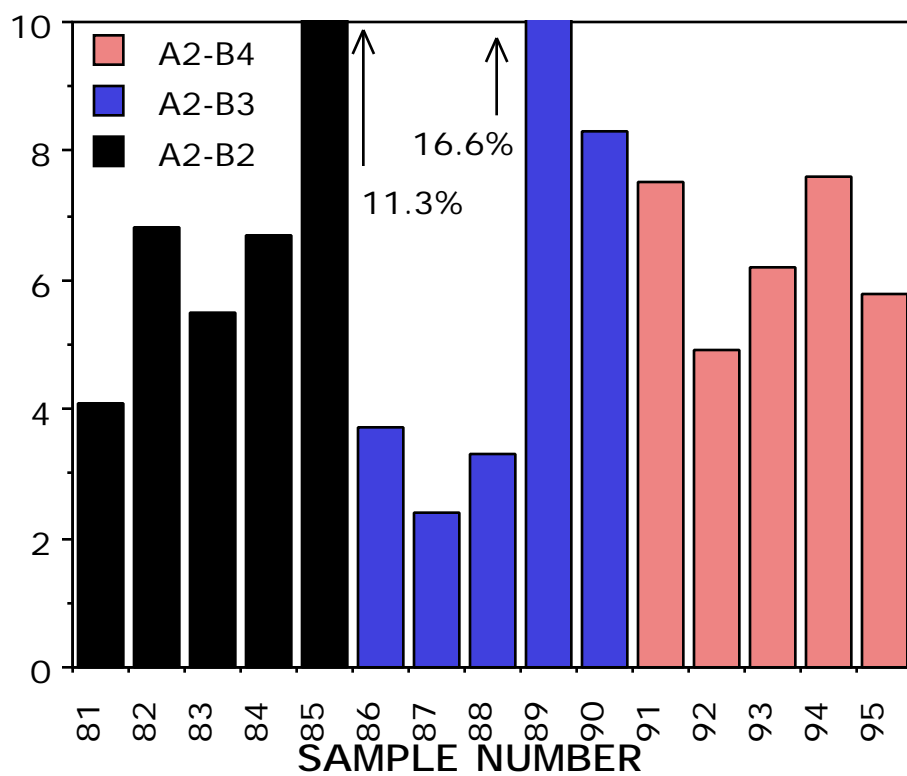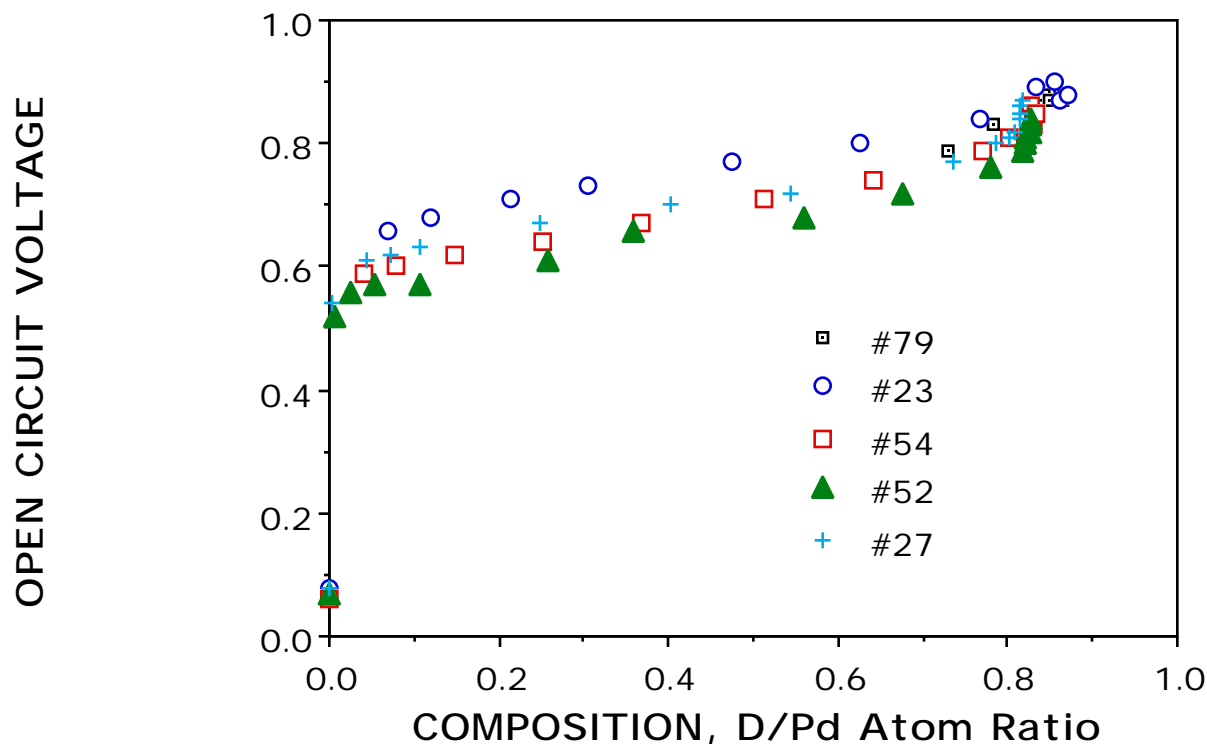

FIGURE 11. Comparison of excess volume for sample sets A2-B2, A2-B3 and A2-B4.

FIGURE 12. Relationship between deloading rate and excess volume for all samples.

FIGURE 13. Open circuit voltage at the conclusion of loading.

**FIGURE 14**. Open circuit voltage change during loading.

The cathode temperature was continuously monitored and used to indicate when production of excess power first started.

Calorimeter

The general configuration of the Pyrex Isoperibolic calorimeter is shown in Fig. 15. It consists of an inner, stirred cell and a surrounding jacket through which constant temperature ($\pm 0.02°$) water flows. Temperature ($\pm 0.01°$) was measured at three locations within the cell — at the top of the anode, at the bottom of the anode, and at a glass enclosed thermistor pressed against the cathode. Temperature is also measured where the fluid enters the jacket and where it leaves. The temperature difference across the cell wall is determined by subtracting the average jacket temperature from the average inner temperature based on the top and bottom temperatures. Applied power is calculated by multiplying the applied current ($\pm 0.01A$) by the cell voltage (± 0.01 V) measured by the 4-wire technique within the calorimeter.

The OCV was measured in two ways. A Luggin capillary using an external platinum electrode allowed the OCV to be measured at a region involving perhaps 4 mm^2 of the cathode surface. The overall OCV produced by one side of the cathode was measured using an immersed platinum electrode located outside of the anode structure.

A recombining catalyst was located in the gas space. Consequently all D_2 and O_2 were recombined except that O_2 remaining after the D_2 had reacted with the palladium. A small tube carried the excess oxygen into a vessel containing oil. As the amount of excess oxygen increased, the oil was displaced on to a balance where the amount of oil
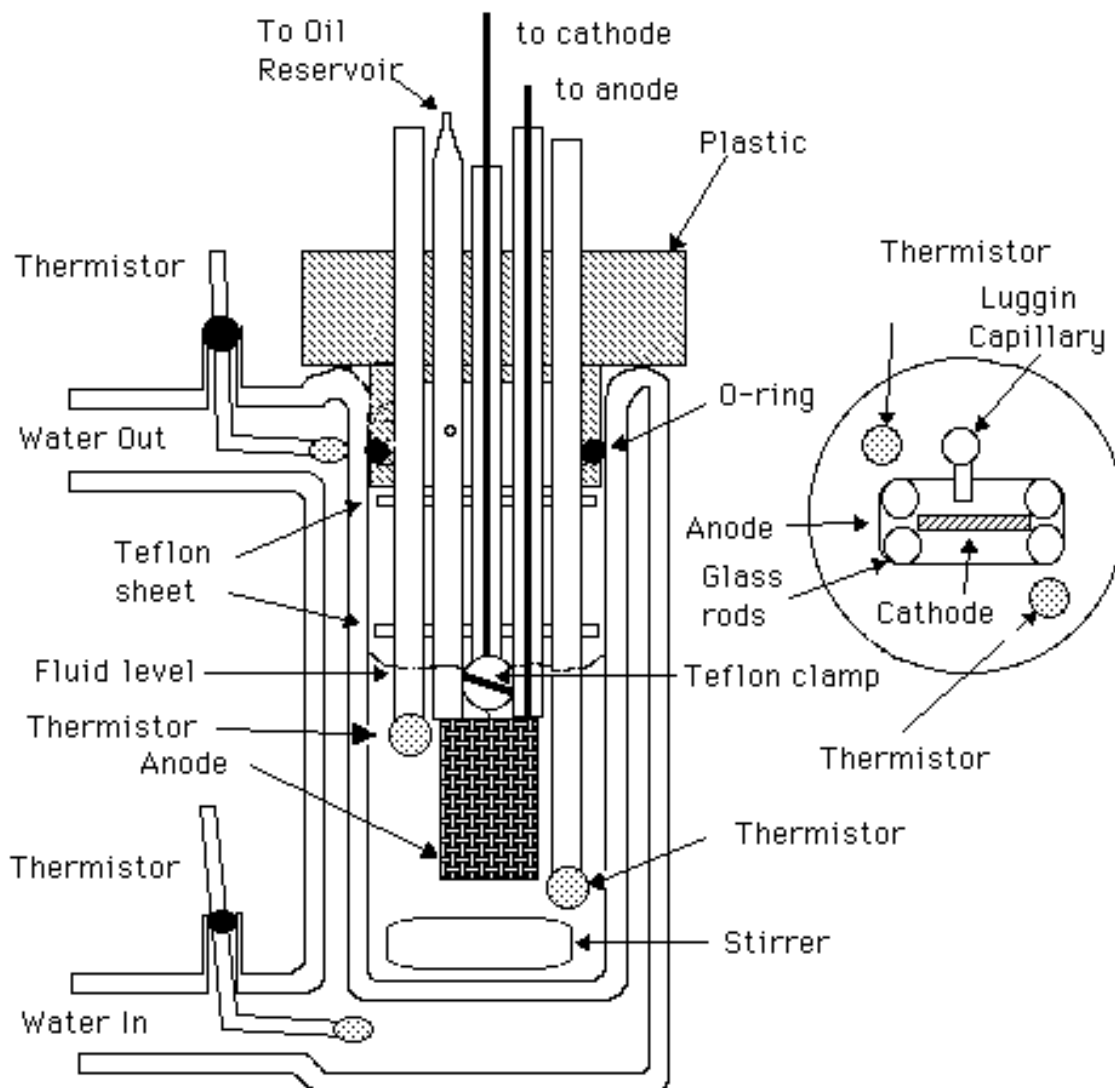
FIGURE 15. Cross-section of the calorimeter. The thermistor that contacts the cathode is not shown. The recombiner is located within a well in the Lucite lid and protected from electrolyte spray by the Teflon sheets. Variations on this design were used as described below.

was weighed to ±0.01 g. After suitable calibration, this weight was used to determine the D/Pd ratio during the experiment. An additional tube containing recombiner was located within the oxygen transfer tube. The temperature of this recombiner was monitored in order to demonstrate that all D_2 had been recombined within the calorimeter.

       Several variations of the design were used involving mainly a change in the anode structure. Both platinum and palladium metals were used as the anode in separate experiments. The platinum was in the form of a wire mesh surrounding the cathode while the palladium was in the form of a wire spiral.

The cathode is crimped to a short piece of platinum wire after it was passed through a small hole. This wire is attached to the fixed platinum lead wire using a Teflon clamp, thereby allowing easy removal for weighing.

Calibration was performed using the electrolytic method during the first few days of electrolysis, before the palladium showed signs of energy production. This process involved increasing the current in steps between 80 mA and 3 A while measuring ΔT and applied power after the calorimeter had achieved steady values (≈7 min). A linear least squares line was fit to the data. The resulting equation was used to convert the measured ΔT to the amount of power being generated within the cell. Excess power resulted when the measured power was greater than the applied power. Although random variations of 200 mW were common, excess power was not claimed unless sustained values above 1000 mW were observed.

An additional indication of excess power resulted from a comparison between the top temperature and the temperature of the cathode. Normal electrolysis caused the cathode temperature to be hotter than the top of the fluid, in proportion to the applied power. In contrast, excess power production caused the cathode to become significantly hotter than expected. In addition, excess power production caused the cathode temperature to become erratic.

RESULTS

Sample #42a

The sample was placed in the calorimeter containing a platinum anode, and loaded at 0.4 A and 45°. The OCV was 1.04-1.06 V. After the jacket temperature had stabilized at 9°, the calorimeter was calibrated by changing the applied power as shown in Fig. 16. The sample was removed and found to have a composition of D/Pd=0.866 with an EV of 1%. An additional 30 h of electrolysis produced a composition of D/Pd=0.891. During subsequent electrolysis, periodic changes in applied current resulted in the behavior shown in Fig. 17.

The data show the characteristic critical onset current as observed by other workers[1,4,5,6,9.10,11]. In addition, the consistent lack of apparent excess power below this critical value demonstrates that the apparent power production above this current is not caused by a change in calibration constant.

Between sets #6 and #7, the applied voltage was interrupted for 1 hr while the OCV was measured. As can be seen in Fig. 18, the OCV rose slightly as the cell cooled after the applied power was turned off. After 30 min, an arrest in the voltage was apparent. Later studies showed the same effect following by an approach to a constant value near 1.02 V that lasted for several hours. Samples not producing excess power show a much different behavior.

The time history of the excess power at 3 A is shown in Fig. 19. In spite of two occasions when the sample was removed from the cell for brief periods, the amount of excess power continued to increase. Only power interruptions for 1 h at 177 h and again for 1.5 h at 216 h caused a reduction in excess power.

After Set #12, the D/Pd ratio was found to be 0.879. The sample was washed with Aqua Regia, polished with 400-600 mesh silicon carbide paper, heated to 110° in air, and again washed with Aqua Regia. This process was done in an attempt to eliminate
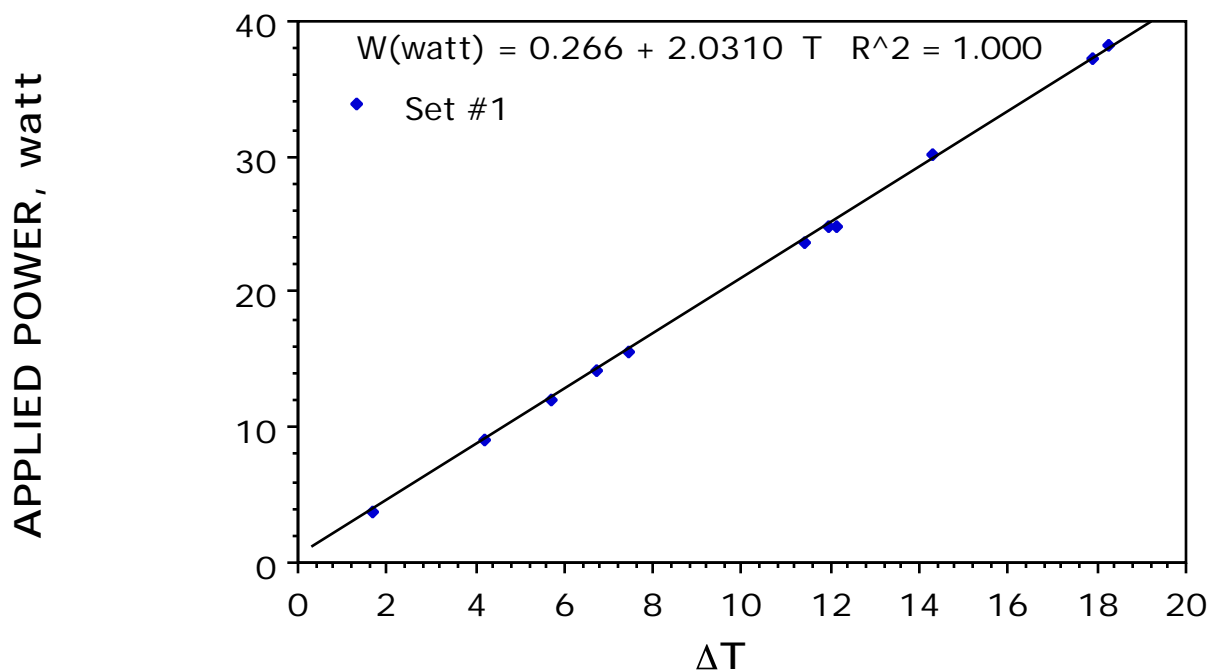
**FIGURE 16.** First calibration of sample #42.
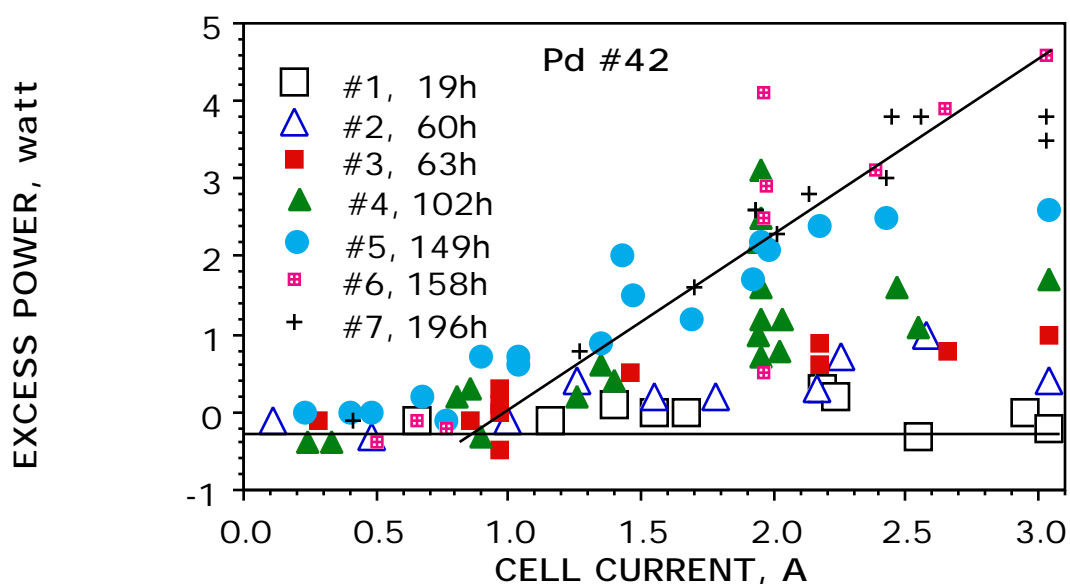
FIGURE 17. Effect of applied current on the excess power at various intervals during electrolysis. The line is based on the data taken in Set #7.

the effect and to determine whether the effect could be reproduced in a previously "good" sample.

A fresh electrolyte was used in the calorimeter, the Luggin capillary tip was modified, and an internal reference electrode was placed in the cell.

Upon being returned to the cell, the OCV to the Luggin capillary was 0.00 V and 0.02 V to the internal reference electrode. Loading was commenced at 200 mA. After
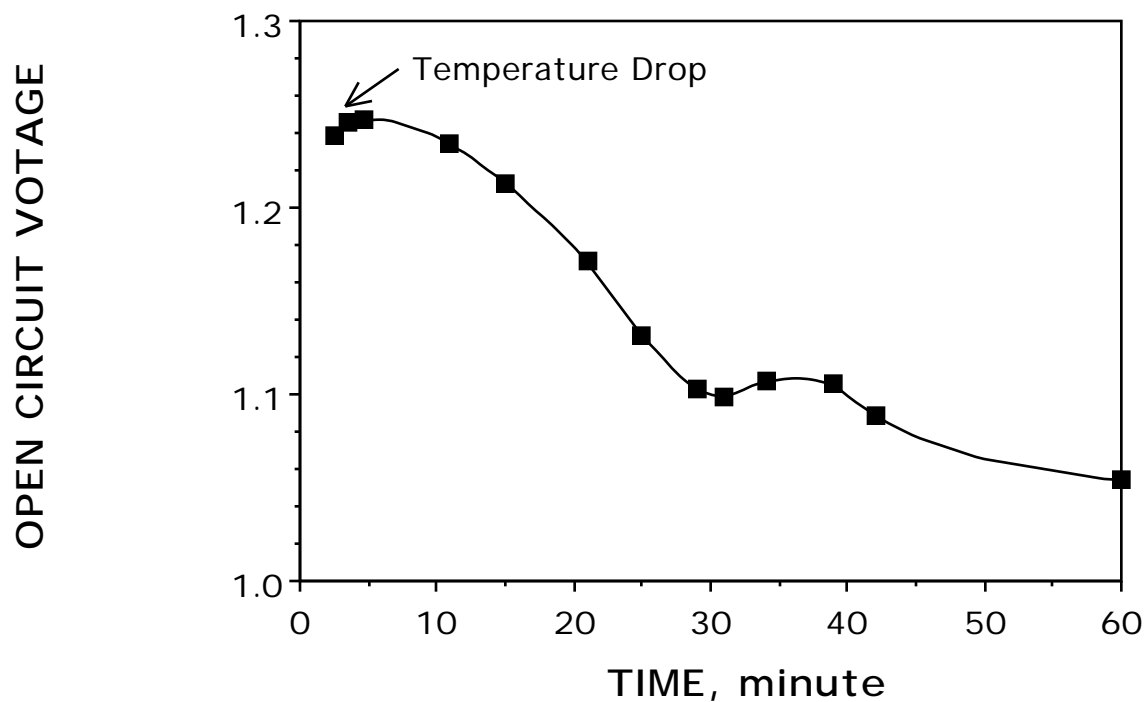
FIGURE 18. Open circuit voltage measured after applied voltage was interrupted between. Sets #6 and #7. The initial rise occurred while the cell temperature dropped from 15° to 9°.
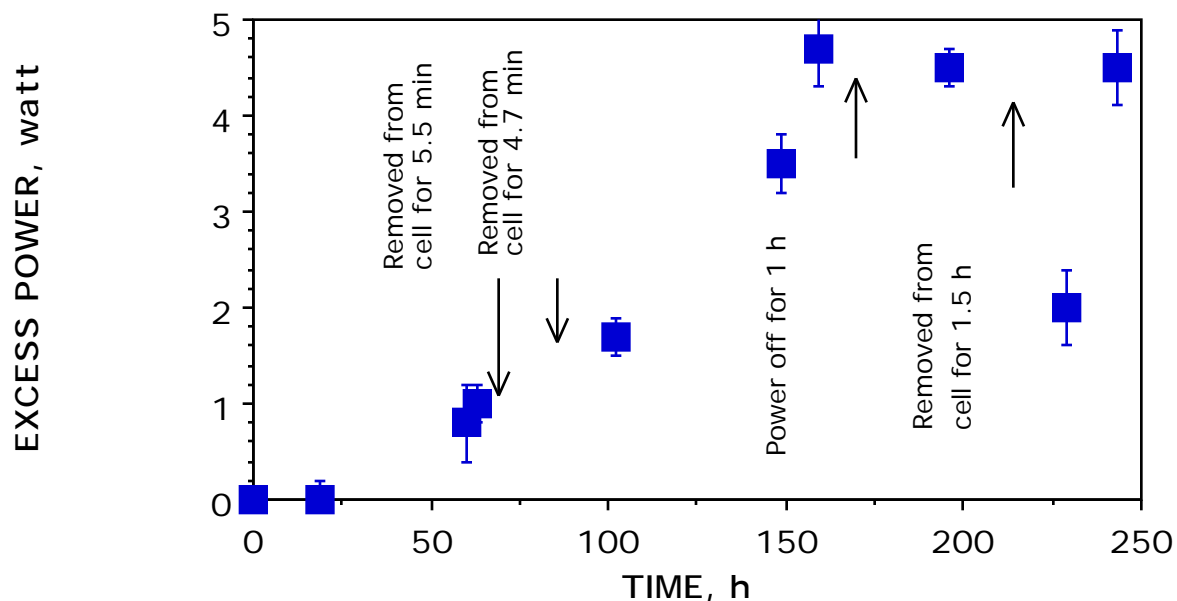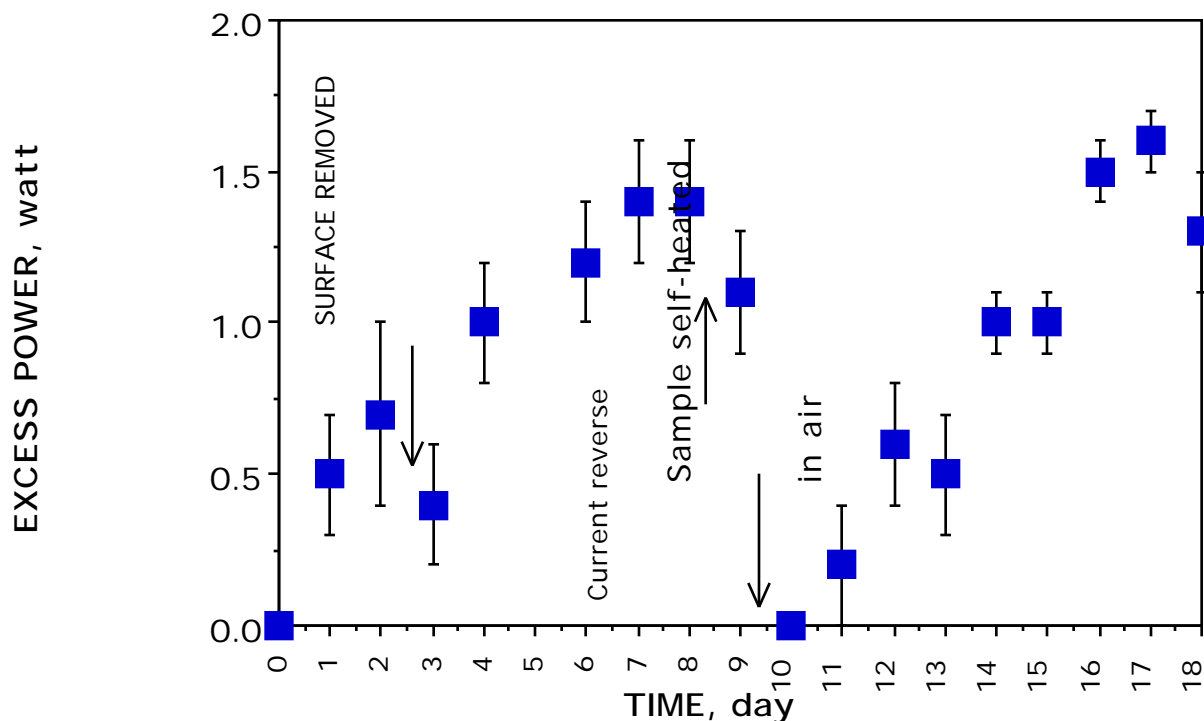

FIGURE 19. Time history of excess power for Sets #1-#12. Current equal 3.0 A

the loading process was finished, the cell was calibrated as previously described. After being electrolyzed at 2 A for 4 days, no excess power was apparent even though the OCV was as high as 1.13 V. The sample was removed from the cell and found to have a

composition of 0.841 and an excess volume of 2%. After the sample was returned to the cell, regular bursts of excess energy were seen that caused abrupt increases in the cathode temperature along with increases in T. The effect of applied current was much less significant and less reproducible than previously observed.

After day six (Fig. 20), the electrolyte was replaced by D_2O containing 3N Li_2SO_4. Additional electrolysis at 1 A caused a modest increase in excess energy and

FIGURE 20. Time history of excess power for Sets #1 to #19.

 the power bursts continued. The sample was removed and major changes were made in the calorimeter and the sample was modified.
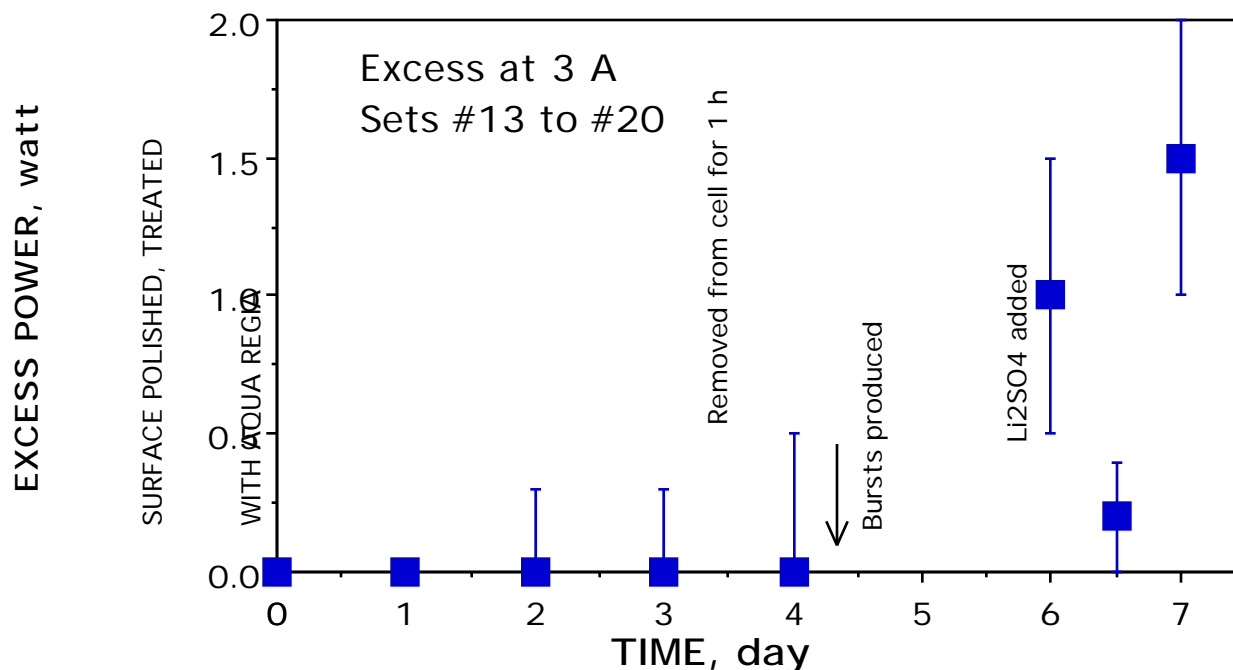
Sample #42b
The calorimeter was made larger in diameter, the anode was changed to a single spiral of
1 mm palladium wire; two Luggin capillaries were placed in the cell, one looking at a spot and one looking at the average voltage of one side; the recombiner was placed in a thin-walled glass tube above the liquid rather than being exposed; and the electrolyte was changed to 0.4 N LiOD in D2O. Use of a constant speed stirrer reduced the random variation in excess power.

The sample was polished with diamond to 1800 mesh, washed with Aqua Regia, and heated in air to 325°C. The OCV before electrolysis was 0.04 V. Loading was done at 80 mA and
9° C. After loading, the composition was D/Pd=0.816 with 2.8% excess volume.

Figure 21 shows the time history of excess power at 3 A. The cell was calibrated at day 0. Electrolysis at 1.5 A produced a steady increase in excess power until day 8. A current reverse on day eight produced a slight reduction on day 9. When the sample was

FIGURE 21. Time history of Sets #13to #20 after the surface was removed from sample #42.

removed on day 10 for weighing, the sudden reaction of the evolving deuterium with the air caused the sample to rapidly self-heat. This process caused loss of deuterium to D/Pd = 0.33. The sample was returned to the calorimeter, a new calibration was made, and electrolysis was continued at 1.5 A. Again, a steady increase in excess power was produced. During this time the OCV was 1.04 to 1.06 V.

Excess power production caused changes in the temperature gradients between the cathode and the top of the fluid, and between the top and bottom of the cell. Figure 22 compares these temperature differences when excess power was being measured and when it was not. No power was detected during Sets #11 and #12 (Days 10 and 11 in Fig. 21). Excess power production at Set #18 (Day 17) caused both the cathode and top temperatures to be hotter than expected.
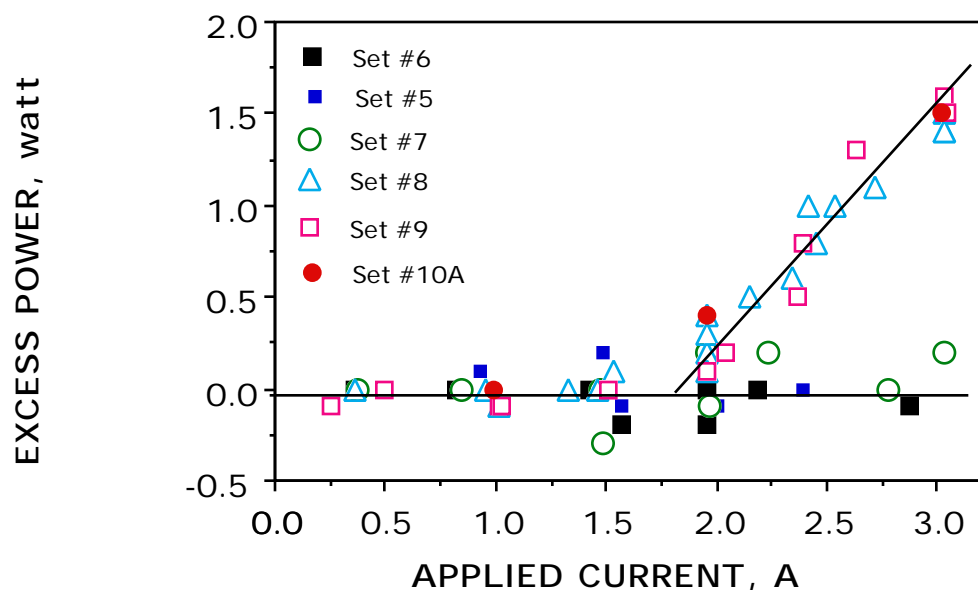
Sample #84
When placed in the calorimeter, the sample had a D/Pd ratio of 0.30 and was loaded at 0.5 A. After loading the D/Pd = 0.752 with an EV of 6.7% and an OCV of 1.00 V. Electrolysis was continued for 4 days with no sign of excess power. Excess power was seen on the sixth day as shown in Fig. 23 as Set #8. A critical onset current was apparent but was larger than needed for sample #42.

Sample #38
This study was made without using the stirrer in order to determine the effect of stirring on the apparent production of excess power. As can be seen in Fig. 24, the calibration constant shifted but remained sufficiently stable in the absence of stirring.
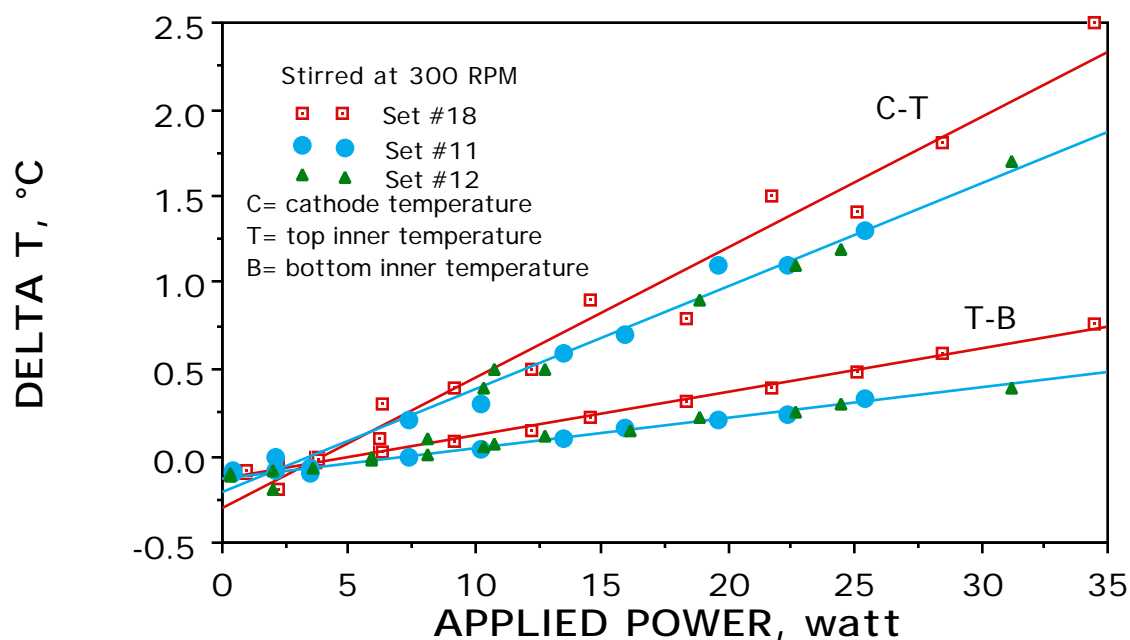
FIGURE 22. Temperature difference between the cathode and the top of the electrolyte and between the top and the bottom of the anode structure. No excess power was detected during Sets #11 and #12. Excess power was detected during Set #18.

FIGURE 23. Excess power as a function of applied current for sample #84.

The sample was loaded at 80 mA and 9°. After loading, the composition was D/Pd=0.875 with EV=2.8% and OCV=1.03 V. Excess power production became apparent after 3 days while being electrolyzed at 1.5 A. Figure 25 shows the rather scattered growth in excess power over 15 days. Part of this scatter is caused by the

amount of excess power being influenced by whether the current was being increased or decreased. As can be seen in Fig. 26, the excess power for Sets #10, #11, sand #12 increased as the current was increased to 3 A. Once at 3 A, the excess power continued to increase. A reduction in current caused the excess power to follow a different line. This behavior was seen many times during the study of this sample.
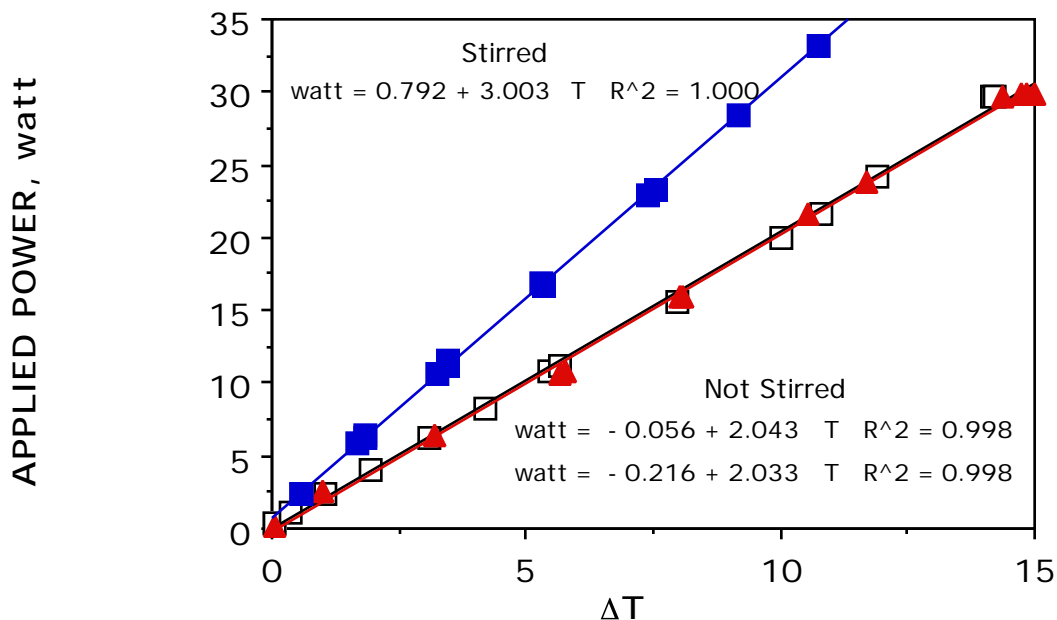

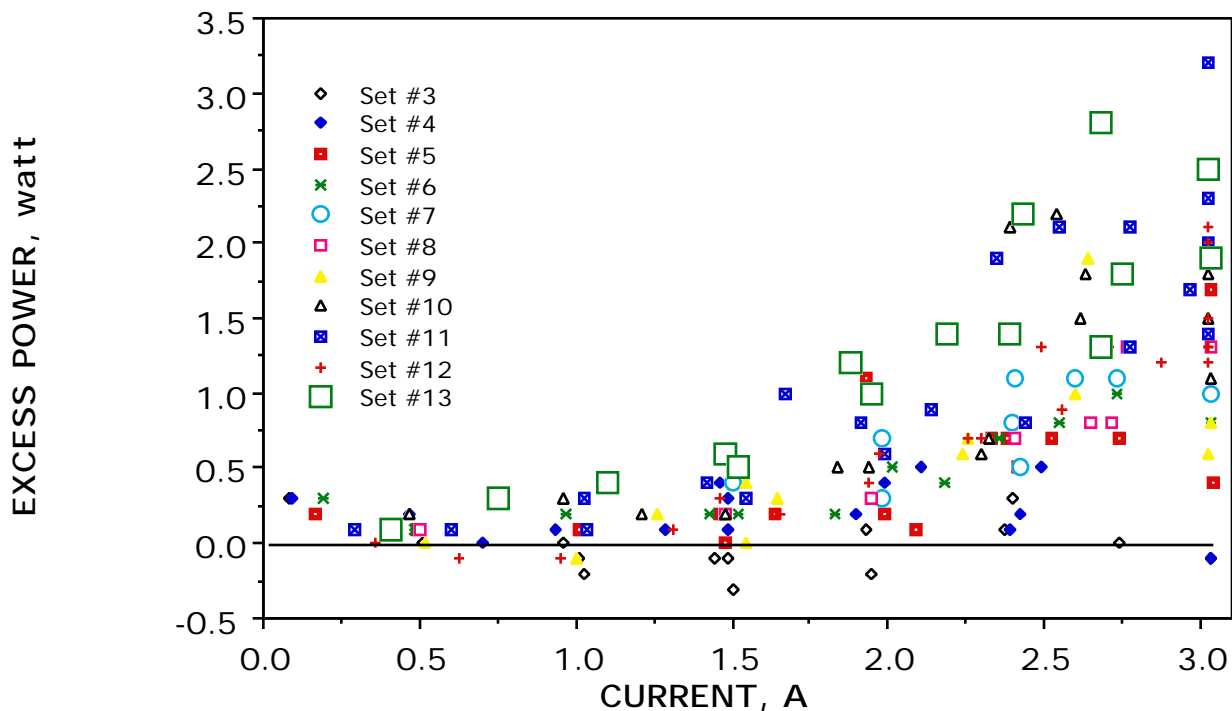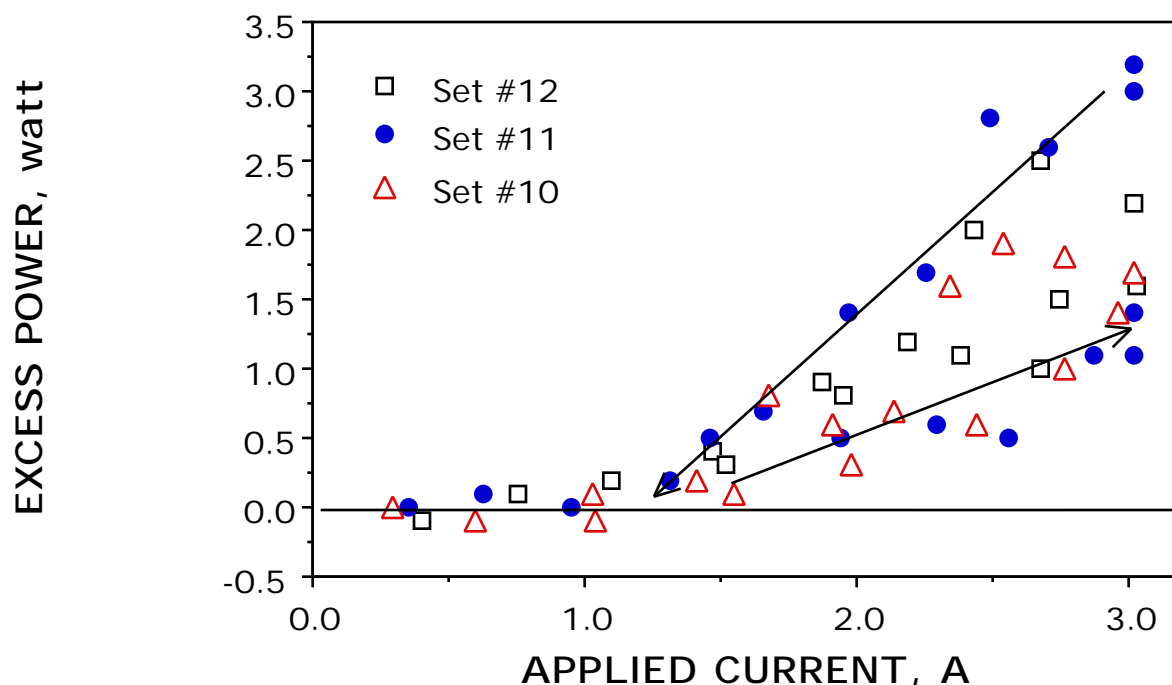**FIGURE 24.** Effect of stirring on the calibration equation for sample #38.

FIGURE 25. Growth of excess power in sample #38.

FIGURE 26. A comparison showing how excess power changed during current increase and current decrease during Sets #10, #11 and #12 of sample #38.

As was seen during the studies of other samples, the temperature difference between the cathode and the top of the electrolyte was greater while excess power was being produced compared to the value in the absence of excess power. This behavior was also seen when the temperature at the top of the electrolyte was compared to the bottom of the anode (Fig. 27). Because stirring was not used in this study, the behavior was more pronounced.

Sample #58
The sample was washed with concentrated HCl, and loaded at 80 mA and 5°. After loading the composition was D/Pd=0.833 with EV=4.1%. Electrolysis was continued at 1.5 A in the calorimeter for 13 days. The OCV never rose above 0.6 V and excess power was not observed. After being removed from the calorimeter, the composition was D/Pd=0.792 with EV=4.8%.

DISCUSSION

Property Measurement
All of the physical measurements show a variation between samples that is well outside of the errors in the measurements. Large differences are even seen between adjacent samples cut from the same rolled strip. This behavior strongly suggests that this same property variation is also present in each sample. Consequently, the average properties reported here are expected to have a wide variation within each sample as well. This realization helps explain why the "Pons-Fleischmann" effect is so difficult to
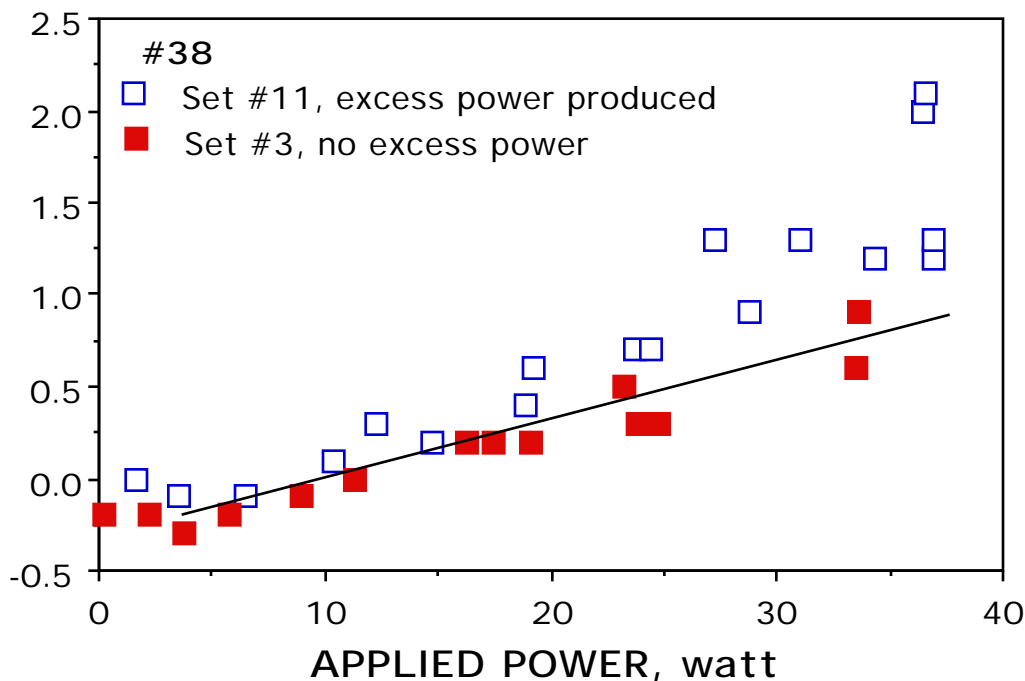
FIGURE 27. A comparison between the temperature difference between the cathode and the top of the electrolyte while excess power was being made and while it was not.

reproduce. In addition, this wide variation in properties makes conclusions based on the behavior of a few samples very uncertain, even after they are given what seems to be identical treatment.

Annealing and surface treatments produce variable results. Only an etch using Aqua Regia seems to make the composition limit somewhat more uniform without a significant effect on the other properties. Annealing at 750° causes grain growth and a more uniform structure. However, a variable oxide layer was created on many samples by the process. In addition, the vacuum annealed material also shows evidence for attack by silicon pump oil in addition to oxygen. These effects are difficult to sort out because the batch size is too small.

The presence of boron results in an increased variation in the measured properties. Consequently, more potentially good as well as bad pieces are created. These extremes may be of benefit if a pretest method is used to remove bad samples.

The presence of excess volume causes a reduction in the composition limit. Because both values are averaged over the whole piece, the local behavior is not revealed. These local variations are expected to impact on the local conditions that are required to produce excess energy, thereby producing a very uneven energy source.

The maximum detected excess power is compared to the various properties in Table 3. Although the data set is still too small to make quantitative conclusions possible, excess power production seems to be related to the average composition, the amount of excess volume, and the open circuit voltage. One exception is found when the

sample has a thick oxide layer. Perhaps a thin region next to the electrolyte is reduced to PdD and this layer produces energy without the need for a high average composition.

The behavior of sample #42 reveals a very important property of "good" material. Partial deloading results in excess power production just as soon as loading has been restored. Even after the surface has been removed, excess power production starts again after a somewhat longer delay. Apparently, "good" palladium remains good in spite of the removal of deuterium and major changes to the surface. Consequently, when the bulk material has the "correct" properties, a suitable surface will form and reform after removal.   This behavior suggests that once suitable material has been identified, subsequent measurements will be reproducible.

The open circuit voltage of samples producing excess power show two characteristics. The values are above 1.0 V and an arrest or break in slope is seen as the value changes after the applied power is interrupted. This discontinuity in the time variation suggest a phase change in the surface region. As argued previously[12], this behavior suggests the formation of a phase having a higher deuterium content than is possible in b-PdD. Impurities are expected to have an additional effect.

_____

TABLE 3
Comparison between measured properties and excess power production

Sample Number	Designation	Excess Volume, %	Composition D/Pd	OVC	Excess Power, W (at 3 A)
Tanaka 1*		1.7	0.82		7.5
IMRA #38	A1-B3	2.8	0.875	1.03	3.2
Tanaka 4*		2	0.84		2
IMRA #42	A1-B4	1 to 2	0.891	1.25	4.6
IMRA #84**	A2-B2	6.7	0.752	1.00	1.5
IMRA #58	A2-B1	4.1	0.833	0.60	0.0
Tanaka 2*		13.5	0.75		0.0

* Tanaka samples from Refs. [4,11]
** Oxide surface layer

Calorimetry

Claims for excess energy from the "Pons-Fleischmann" effect are very difficult for some people to believe. Therefore, the calorimetric studies need to be done using special care. Although the calorimeter used in this study was not especially sensitive, several methods were used to demonstrate that excess energy was actually being made.

Unlike many efforts, absolute heat measurements were not attempted.   The claimed excess power is always relative to the power being produced by electrolysis in the absence of the effect. The effect is absent early in the study, after the current has been reduced below a critical value, or after the sample has been deloaded. Power production during each of these conditions was compared before, during, and after

apparent excess power production. No significant change in the calibration constant was detected.

An additional indication of excess power can be obtained by measuring changes in temperature gradient within the cell. In particular, the temperature at the cathode is always found to increase while excess power is being made. Although this gradient change could introduce errors in the calculated amount of the excess power, it is too small to be the initial cause of the excess.

ACKNOWLEDGEMENTS

References

[1] McKubre, M. C. H., Crouch-Baker, S., Hauser, A. K., Smedley, S. I., Tanzella, F. L., Williams, M. S., and Wing, S. S., Concerning Reproducibility of Excess Power Production, Proceedings of the 5th International Conference on Cold Fusion, Monte-Carlo, Monaco April 9 - 13, 1995, IMRA Europe, France (1995), p. 17.

[2] Fleischmann, M., Pons, S., Anderson, M. W., Li , L. J. and Hawkins, M., Calorimetry of the Palladium-Deuterium-Heavy Water System, J. Electroanal. Chem. **287** (1990) 293.

[3] McKubre, M. C. H., Crouch-Baker, S., Riley, A. M., Smedley, S. I. and Tanzella, F. L., Excess Power Observations in Electrochemical Studies of the D/Pd System; The Influence of Loading, Proc. Third International Conference on Cold Fusion, October 21-25, 1992, Nagoya Japan, "Frontiers of Cold Fusion", (H. Ikegami, ed), p. 5.

[4] Storms, E., Measurements of Excess Heat From a Pons-Fleischmann-Type Electrolytic Cell Using Palladium Sheet, Fusion Technol. **23** (1993) 230.

[5] Storms, E., Review of Experimental Observations About the Cold Fusion Effect, Fusion Technol. **20** (1991) 433.

[6] Hasegawa, N., Hayakawa, H., Tsuchida, Y., Yamamoto, Y. and Kunimatsu, K., Observation of Excess Heat During Electrolysis of 1M LiOD in a Fuel Cell Type Closed Cell, Proc. Fourth International Conference on Cold Fusion, Lahaina, Maui, Dec. 6-9, 1993. EPRI TR-104188-V1 (1994), p. 3.

[7] Green, J. A. S., and F. A. Lewis, "Overvoltage Component at Palladized Cathodes of Palladium and Palladium Alloys Prior to and During Bubble Evolution", Trans. Faraday Soc. **60** (1964) 2334.

[8] Storms, E. and Talcott-Storms, C., The Effect of Hydriding on the Physical Structure of Palladium and on the Release of Contained Tritium, Fusion Technol. **20** (1991) 246.

[9] Pons, S., Private communication (1990).

[10] Kainthla, R. C.,Velev, O. , Kaba, L., Lin, G.H., Packham, N., Bockris, J., Szklarczyk, M. and Wass, J., Sporadic Observation of the Fleischmann-Pons Effect, Electrochimica Acta **34** (1989) 1315.

[11] Storms, E., Some Characteristics of Heat Production Using the "Cold Fusion" Effect, Proc. Fourth International Conference on Cold Fusion, , Lahaina, Maui, Dec. 6-9, 1993, EPRI TR-104188-V2 (1994), p. 4. Electric Power Research Institute, Palo Alto ; Ibid , Trans. Fusion Technol. **26** (1994) 96.

[12] Storms, E., The Nature of the Energy-Active State in Pd-D, Infinite Energy, **1**, #5 & 6, (1996) 77.