The Effect of Hydriding on the Physical Structure of Palladium and on the Release of Contained Tritium

by

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ABSTRACT

The behavior of tritium released from a contaminated, palladium cathode has been determined and compared to the pattern found in cells claimed to produce tritium by a cold fusion reaction.

Void space is produced in palladium when it is subjected to hydrogen adsorption and desorption cycles. This void space can produce channels through which hydrogen can be lost from the cathode, thereby reducing the hydrogen concentration. This effect is influenced, in part, by impurities, the shape of the electrode, the charging rate, the achieved concentration of hydrogen and the length of time the maximum concentration is present.

I. INTRODUCTION

Reports of significant tritium found in electrolytic cells using a palladium cathode raise questions concerning the origin of this isotope[1; 2; 3; 4; 5; 6; 7; 8; 9; 10; 11; 12; [13][1].

Chemiluminescence in the detector and enrichment by electrolytic action can produce an apparent presence of excess tritium. However these processes are well known and

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1. This list does not contain all of the reported observations of tritium production but only those known to the authors in sufficient detail to make an evaluation possible. Many workers who find excess heat or neutron emission do not observe tritium production.

their effects on the conclusion can be eliminated. If the tritium was not in the cell as contamination or did not enter the cell from the environment, then it must have been produced by a nuclear reaction. This conclusion is so important and so controversial that great care must be taken to learn whether the tritium might have entered the cell from an external source. Unfortunately, this knowledge is difficult to obtain with certainty. Another approach is to determine the behavior pattern when tritium is caused to enter an electrolytic cell from the outside on purpose and compare this with the pattern observed in cold fusion cells. A similar pattern would give a strong indication that the same process was occurring in both cases. This paper will concentrate on the behavior pattern when entry occurs as contamination in the palladium cathode.[2] Such a study would make possible an evaluation of the claim that inadvertent contamination of the cathode might explain some results that have been attributed to cold fusion.[14; [15] In the process, tritium was used as a tracer to determine how hydrogen interacts with a palladium cathode and how the production of excess volume affects this interaction.

Previous work[16] has shown that when Pd is cycled between hydrogen[3] uptake and removal, the sample thickness shows an increases while the other dimensions decrease after all the hydrogen is removed. This process appears to continue without limit up to at least 90 cycles[16]. The result is an increase in measured volume over that calculated using the lattice parameter increase, called in this paper "volume excess" and given as a volume fraction. Such behavior indicates that void volume can form in palladium when it reacts with hydrogen. To the extent that this void space produces channels, the ability to achieve a high D/Pd ratio on the surface of an electrode would be reduced, much like trying to fill a leaky bucket. The question that we have attempted to answer is, "What occurs during these dimension changes and do these changes affect sites that might be the location of the cold fusion effect and the behavior of contained tritium?"

We expect that if fusion reactions are to initiate at all, very high deuterium

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2. A detailed study of the pattern produced when tritium enters the cell from the environment has been made and may be published elsewhere.
3. "Hydrogen" will be used to denote all three isotopes of hydrogen. When hydrogen is referred to specifically, "protium" will be used.

concentrations are required regardless of the nuclear process. The D/Pd ratio of palladium at room temperature and under 1 atm deuterium pressure is limited to 0.66[17]. By applying a voltage to an electrolytic cell, the effective activity of deuterium can be significantly increased. However, this increase can only be retained if there are few routes available for the deuterium to leak out of the electrode. The question is, therefore, "how can the production of channels for gas release be prevented so that high local concentrations can be achieved"? The answer requires an understanding of the variables that affect this phenomenon. We have investigated the effect of electrode shape, purity and the rate of loading with both deuterium and hydrogen. Much additional work needs to be done to fully understand this important phenomenon.

Reduction in deuterium concentration can also result from its dilution by protium. A brief study was made to determine how much of the protium existing in the electrolyte is concentrated in a cathode during electrolysis.

II. EXPERIMENTAL

II. A. Absorption-Desorption Cycles Producing Excess Volume

Electrodes were prepared by arc-melting Johnson-Matthey powder (V8368501, 99.99% Pd), rolling the resulting button into a coin shape (2 mm thick x 15 mm diameter), and machining the diameter to give known dimensions. A few alloys containing carbon and lithium were also prepared by melting graphite powder or lithium metal with the palladium powder. Several 0.4- and 0.2-cm dia. rods (Johnson-Matthey) were also studied. All of these electrodes were spot welded to Pt leads and placed in electrolytic cells. Electrolysis was done using a current of 200 ma or 20 ma in a cell containing 0.1N LiOH or 0.1N LiOD as the electrolyte. The H/Pd or D/Pd ratio was measured (±0.001) by weighing the electrode at the time when the dimensions were determined (±0.0005 cm) using a micrometer. No detectable weight loss occurred during this 30 sec. measurement. Desorption was accomplished by allowing the electrode to sit in air at room temperature, at 104°C or at 175° C for various time intervals. Heating at 175° overnight in air removed all weighable hydrogen.

The excess volume fraction within the -phase is calculated using the equation:

Excess = [(Final Volume-Initial Volume)/Initial Volume] - [0.0172+0.14125 D/Pd], where the initial term in the equation is the volume of the electrode before hydrogen was added and the final term gives the volume fraction caused by lattice expansion. Only the first term was used after complete hydrogen removal.

II. B. Study of Tritium Loss from Pd used as a Cathode or Anode

Some coins that were prepared for the absorption-desorption study, and the 0.4- and 0.2- cm dia. rods were loaded with tritium by being electrolyzed in 0.1N LiOD containing $1.1-1.5x10^6$ d/min-ml of tritium and 98.8 mol % D_2O. After loading, the electrodes were placed in cells containing 40-45 ml of fresh 0.1N LiOD and electrolyzed as the cathode. The gas was recombined and collected in an I.V. bag.[4]. After most of the tritium had been removed by cathodic electrolysis, the electrode was placed in a new cell containing 40 ml of 0.1N LiOH and electrolyzed as the anode. This process removed the remaining tritium and placed it in the electrolyte where it was measured. Tritium was measured by taking aliquots of electrolyte or recombinate, mixing this with Opti-Fluor scintillator fluid and counting for 10 min. using a Packard Tri-Carb Liquid Scintillation Spectrometer, Model #3255[4]

In order to test the effectiveness of anodic electrolysis for tritium removal, a coin was loaded with tritium-doped protium solution and anodized in initially tritium-free 0.1N LiOH. Periodic aliquots were taken of the electrolyte. The gases were recombined and also measured.

II. C. Effect of Protium in an Electrolyte on the Measured D/Pd Ratio.

A coin containing some excess volume was electrolyzed in 0.1N LiOD (99.96 % D_2O) until it had achieved a steady D/Pd ratio of 0.664. Various amounts of H_2O or 0.1N LiOH were added to the electrolyte each day after the coin was weighed. The deuterium fraction in the coin was calculated from the weight change and compared to the calculated deuterium fraction in the electrolyte based on the amount of H_2O added.

III RESULTS

III. A. Error in Measurement of Deuterium Content by Weight Gain

A measurement of the D/Pd ratio using the weight increase has one serious error which is caused by the uptake of protium in preference to deuterium. Even when a relatively protium-free electrolyte is used, significant protium is transferred to the cathode. Consequently, the calculated D/Pd ratio obtained from weight gain will be increasingly less than the (D+H)/Pd ratio as the protium content of the electrolyte has an inevitable increases during use. Figure 1 shows the result of electrolyzing Pd in an electrolyte containing various mole fractions of deuterium. A total (H+D)/Pd ratio of 0.66, based on the value obtained when the purest D_2O was used, is assumed in each case. The high sensitivity to protium content in the near 100% D_2O region increases the uncertainty in the reported D/Pd ratio in this and in other studies. In addition, the deuterium may be sufficiently diluted by the presence of protium to prevent the Pons-Fleischmann Effect from occurring.

Heavy-water is known to easily absorb normal water from air and this study shows that such protium is further concentrated in the palladium during electrolysis.
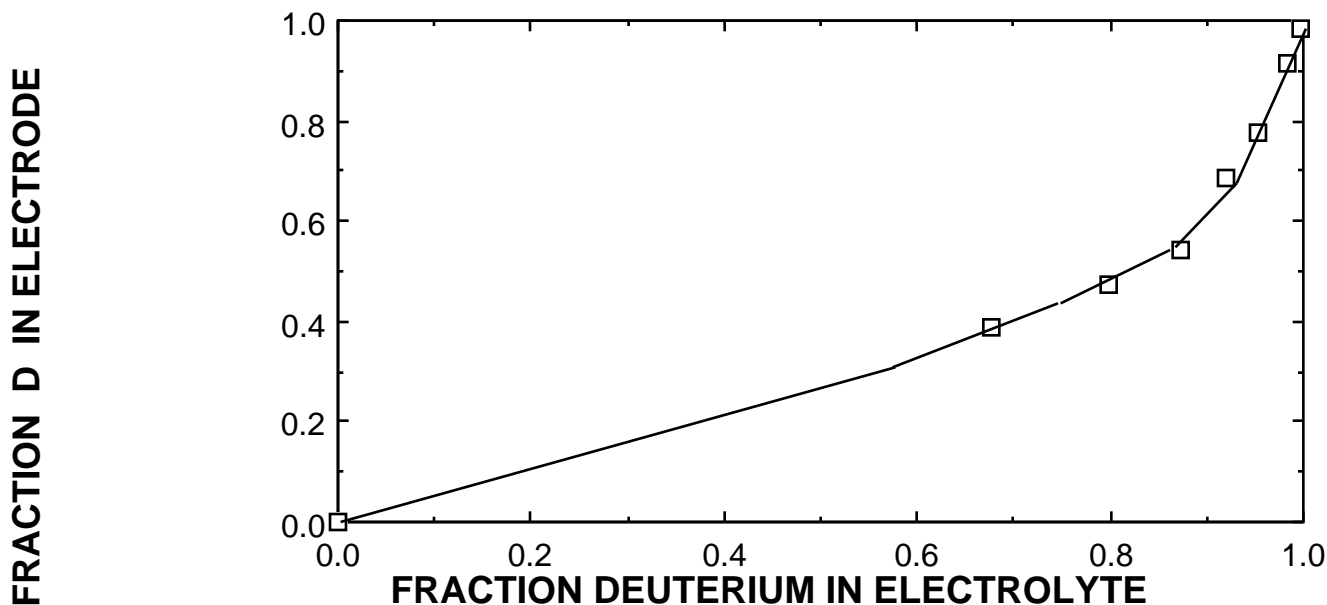

FIGURE 1. Fraction of deuterium in saturated Pd after electrolyzing

in a mixture of D_2O and H_2O (0.1 N LiOD,H).

III. B. Absorption-Desorption Cycles

Creation of excess volume depends in part on the rate of loading with hydrogen, the time during which high hydrogen activity is present, the shape of the electrode and its purity. Discs loaded at 20 ma and 200 ma containing various amounts of carbon or lithium, and rods loaded at 50 ma, 200 ma and 300 ma will be described.

III. B.1. Pure Palladium Disc Loaded at 200 ma

When hydrogen is first absorbed in certain discs, the volume increase is consistent with that calculated using the reported lattice parameters[18; 19; 20; 21].

Expected expansion is observed until the entire sample has converted to the   -phase, as shown in Fig. 2. However, as additional hydrogen is absorbed, the volume increases much more rapidly than expected. Consistent behavior is found between three discs that were electrolyzed at 200 ma.
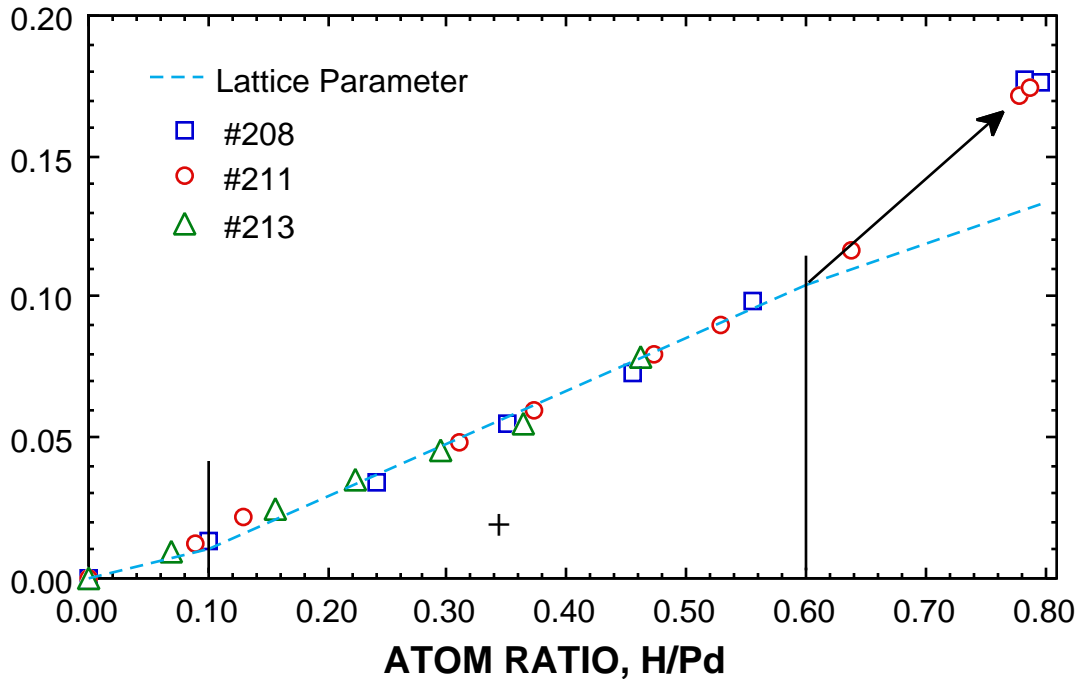
FIGURE 2. Comparison between volume expansion values, based on the physical dimensions and the lattice parameter, as a function of H/Pd atom ratio. Loading current is 200 ma.

Fig. 3 shows two cycles, one using protium and the other using deuterium, that were kept below ʹ-min (minimum composition of the ʹ-phase). No significant difference between desorption and absorption is seen until the composition exceeds ʹ-min during the third absorption cycle. An excess volume of 7% resulted, 5% of which was retained after complete removal of deuterium. In these cases (#208, #211, #213), the ʹ– ʺ transition alone was not able to produce excess volume.
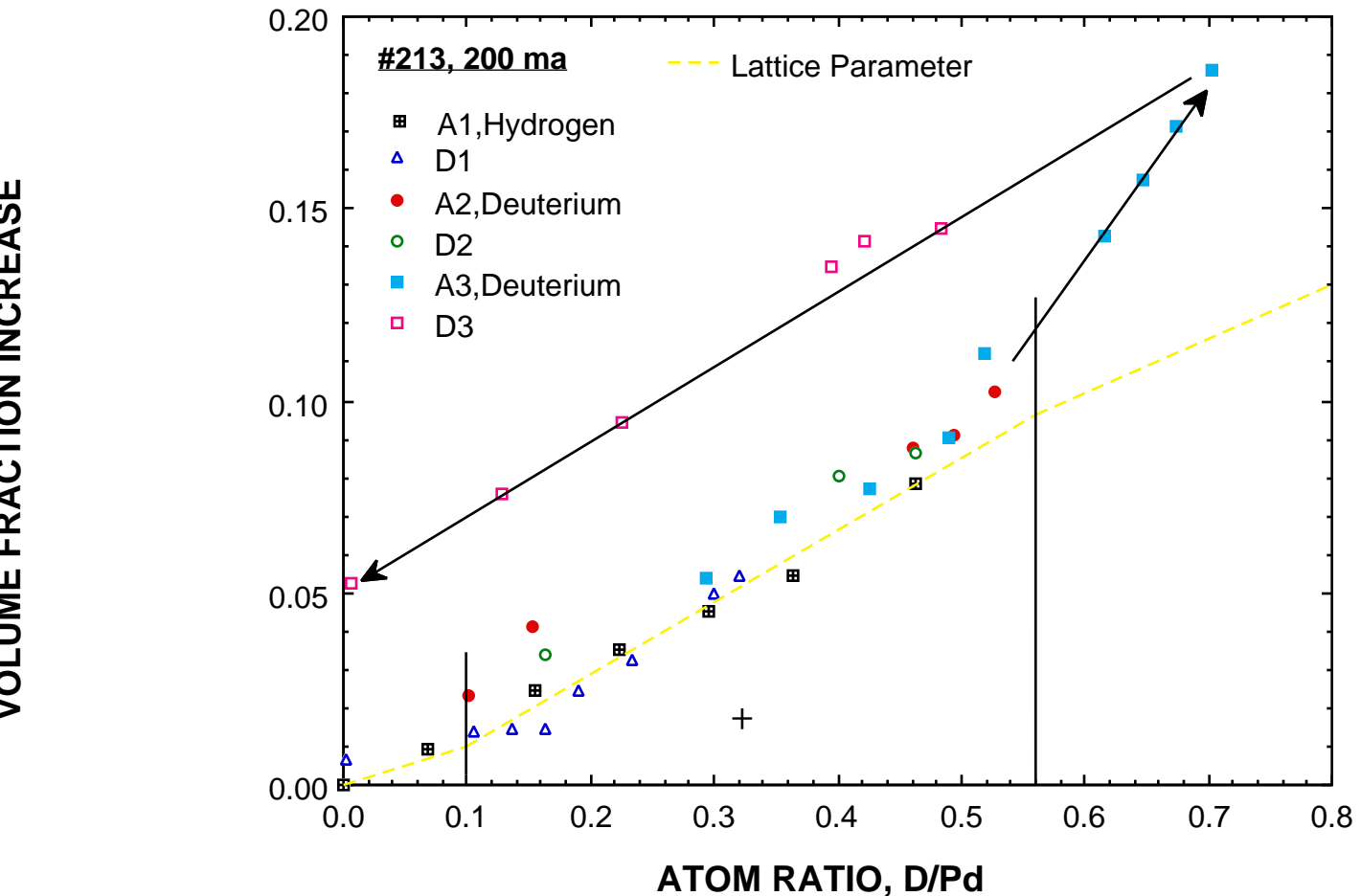

FIGURE 3. Volume change produced by absorption-desorption cycles within the ʹ + ʺ - phase region The first cycle of #213 involved hydrogen while the remaining two cycles used deuterium. Note that the phase boundary for the ʺ - phase (ʺ-min) falls at a lower D/Pd ratio when deuterium is used compared to the value when protium is in the lattice.

Fig. 4 shows the result of four cycles done entirely within the -phase region. This coin contained 10% excess volume, owing to a previous cycle, and a composition of H/Pd=0.788 when this study started. Subsequent cycles caused the volume to change by an amount consistent with the expected lattice parameter change although a slight hysteresis occurred during desorption. No additional excess volume was produced as long as the – phase did not form.
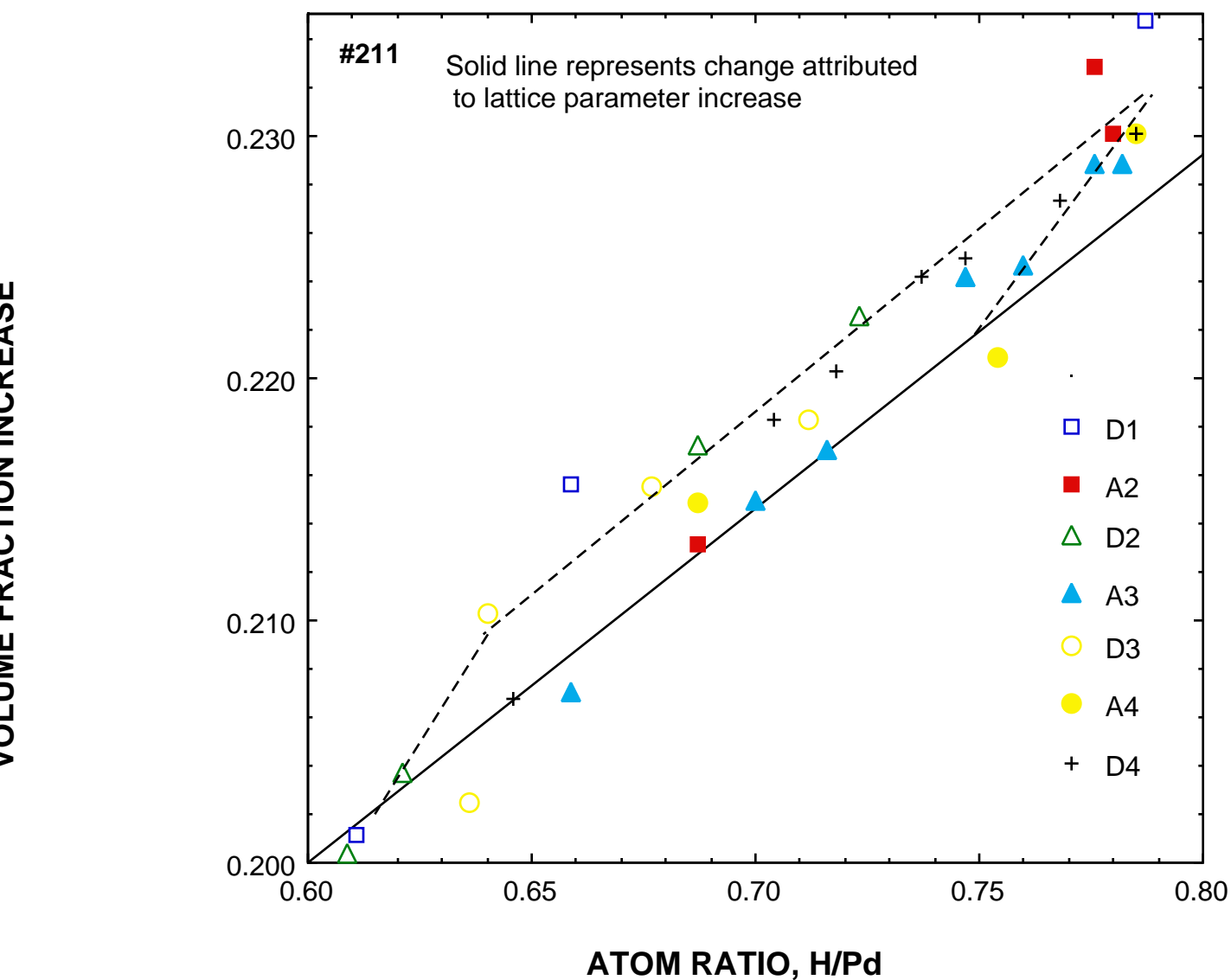

FIGURE 4. Volume change produced by absorption-desorption cycles within the - phase region. Loading current is 200 ma.

Figure 5 shows an example of two cycles of absorption and desorption where the

– transition occurred. The volume fraction within the – two-phase region during

desorption is very close to the volume expansion during the following adsorption.

Thus, even after the first cycle, the permanent volume excess does not happen unless

the composition of palladium has exceeded -min. This pattern was consistent during

at least 5 cycles. Each cycle is independent of the preceding cycle in its effect on the

production of excess volume within the range of this study.

These results show that neither the volume change associated with the –

transition nor with the increased hydrogen activity in the -phase is, by itself, sufficient

to produce excess volume in these discs. However, a combination of these two sources

of stress produces nearly the same amount of excess volume each time it occurs.
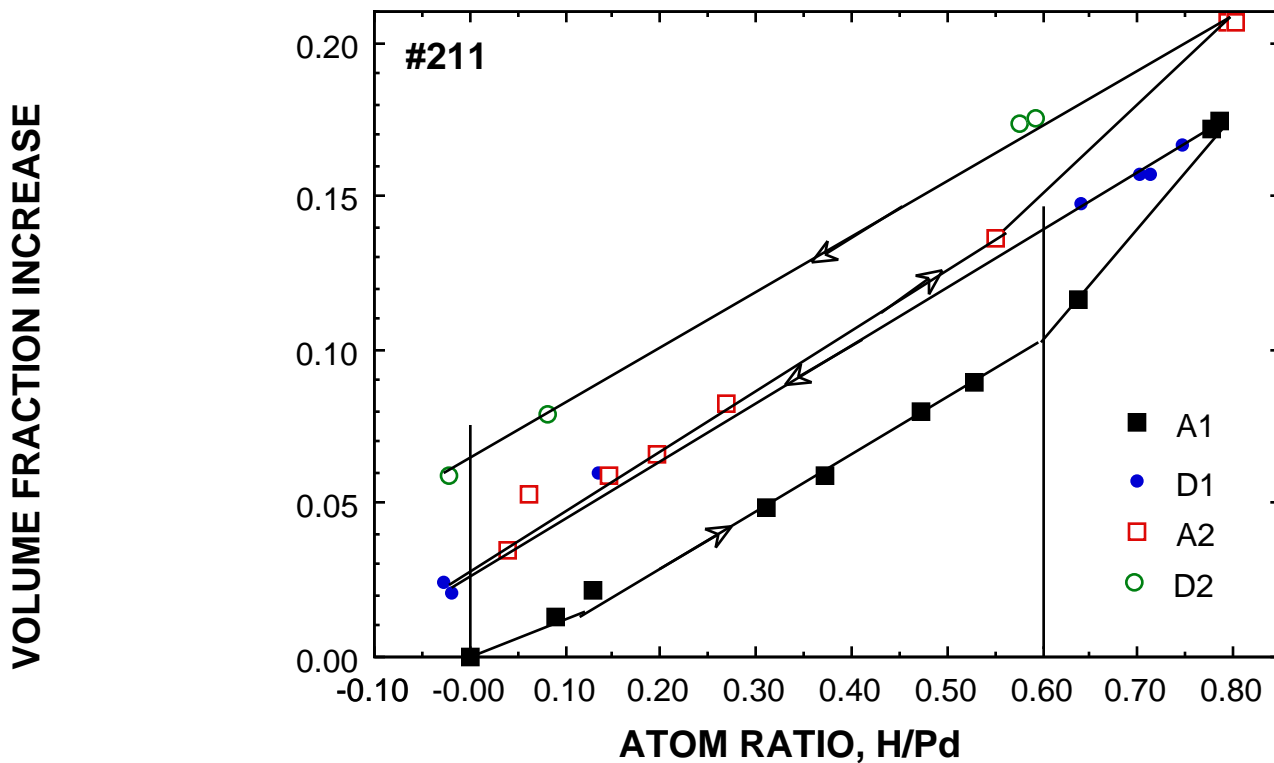
FIGURE 5. Effect of multiple cycles into the -phase region. Loading current is
200 ma.

Permanent volume expansion is associated with an increase in thickness and a decrease in diameter of the coin shaped electrode. As can be seen in Fig. 6, absorption of hydrogen causes both the thickness and the diameter to increase. However, when all hydrogen has been removed before the next absorption cycle, an increased thickness and a decreased diameter remains. Indeed, this coin had acquired a pillow shape after 5 cycles. Part of this shape is probably caused by a lower, nonuniform composition at the edges. Nevertheless, carried to the limit, palladium seems to be trying to form a sphere.
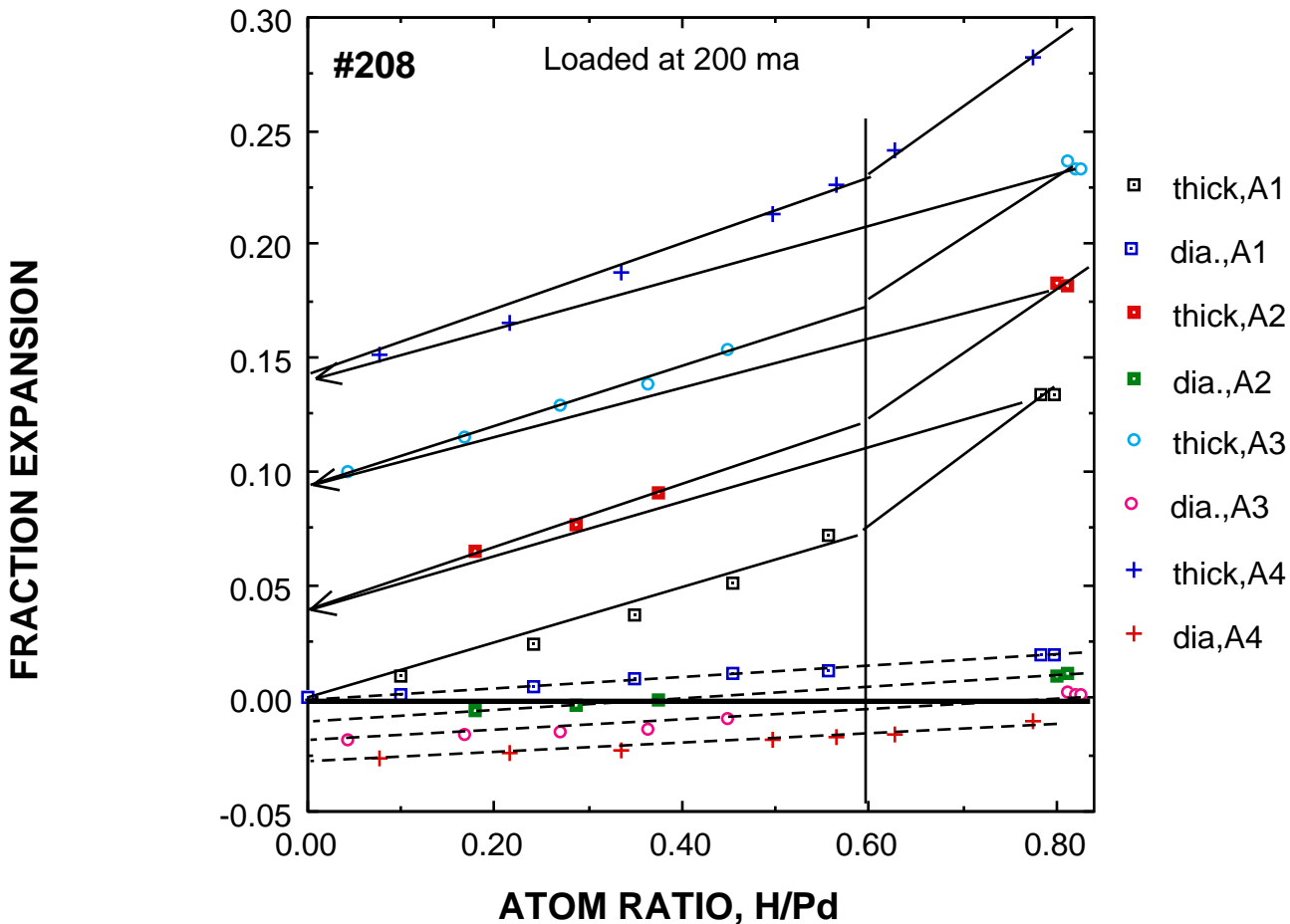
FIGURE 6. Comparison between expansion of the thickness and the diameter during four absorption-desorption cycles as a function of H/Pd ratio. The lower data sets describe the behavior of diameter. Only data for the absorption part of the cycles are shown.

III.B.2. Pure Palladium Disc Loaded at 20 ma

When two discs were loaded at 20 ma, excess expansion was produced immediately, as can be seen in Fig. 7. Apparently, if the loading is sufficiently slow, excess expansion occurs when -phase starts to convert to -phase. Further addition of deuterium to the -phase added little additional excess volume.

From this behavior, we conclude that the rate of charging affects the growth of excess volume in addition to the need to create sufficient stress within the metal.
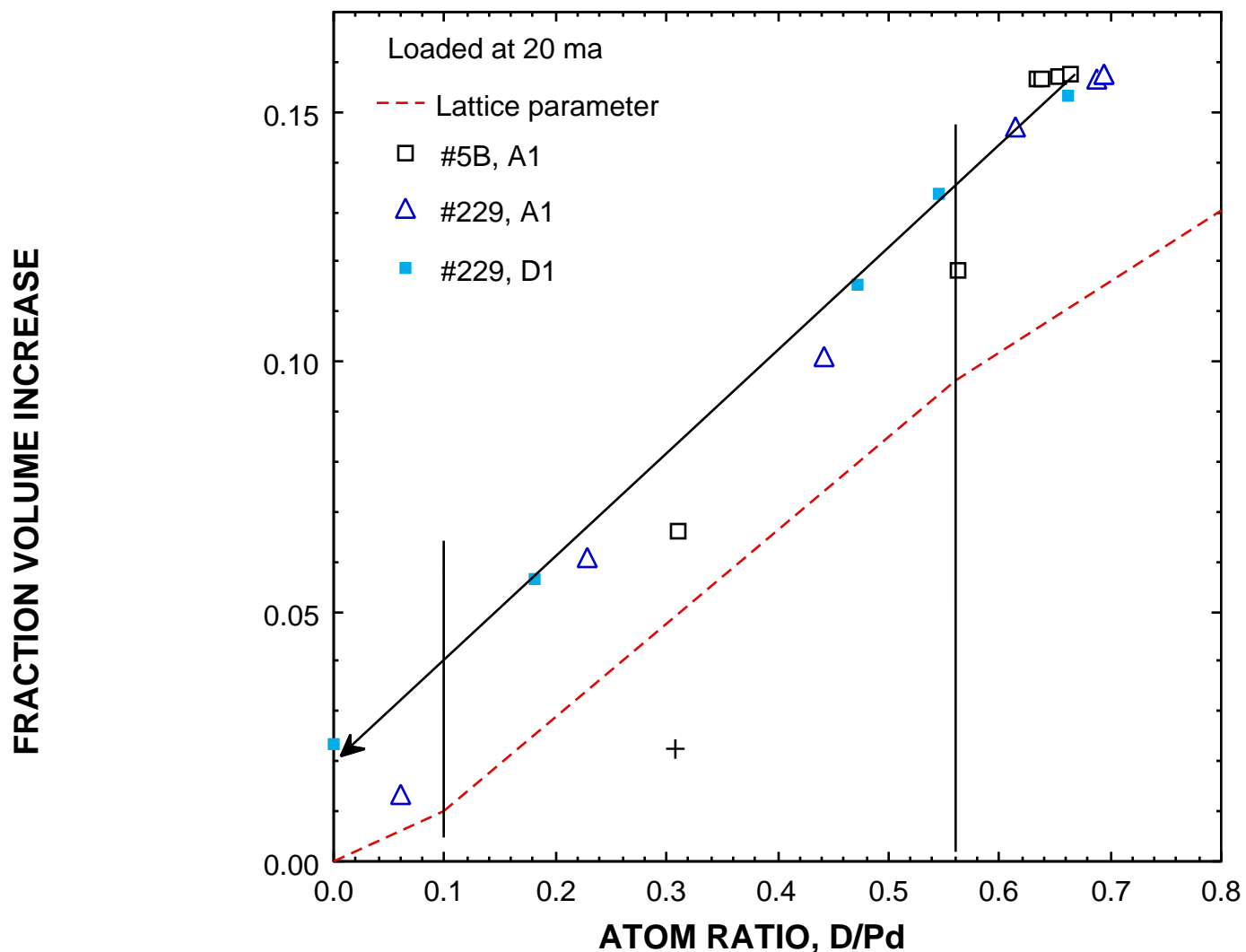
FIGURE 7. Volume fraction vs D/Pd ratio for several absorption-desorption cycles. Loading current is 20 ma

III.B.3. Pure Palladium Rod

Two pieces of a rod (0.4 cm dia., Johnson Matthey) were electrolyzed in 0.1N LiOD at 200 ma using separate cells. The measured volume is compared to that calculated from the lattice expansion in Fig. 8. Rod #1 was studied as delivered while rod #2 was heated at 175° overnight in air before it was electrolyzed.

Rod #1 (#230) shows no evidence of excess volume expansion after 1.5 cycles. This behavior is in sharp contrast to the coin shaped electrodes. However, repeated cycling causes a steady reduction in length, as shown in Fig. 9. Because of this effect, measurement of length is not a good method for determining the D/Pd ratio. The effect of this additional cycling on the the volume could not be accurately determined
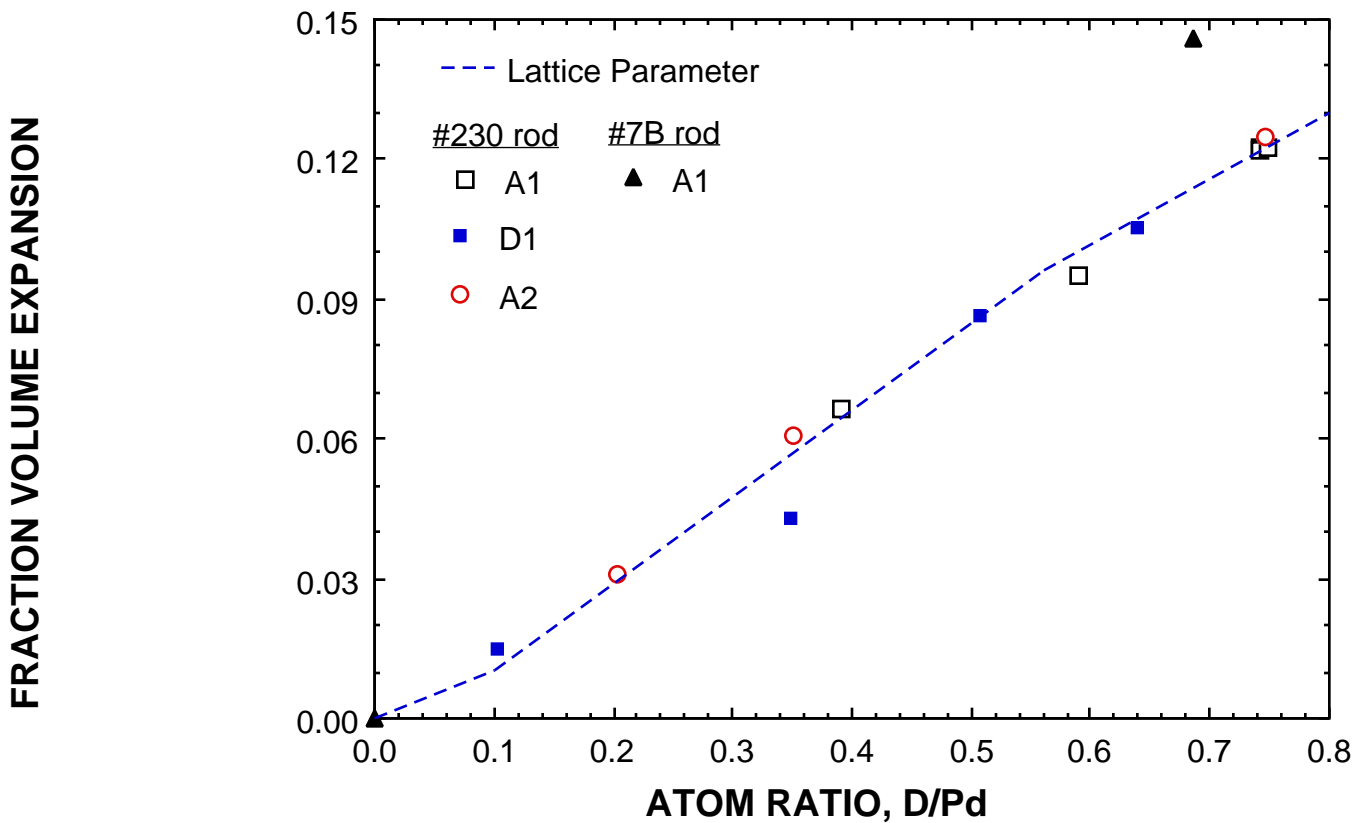

FIGURE 8. Volume expansion produced in Pd rods by the uptake of deuterium. Loading current is 200 ma.
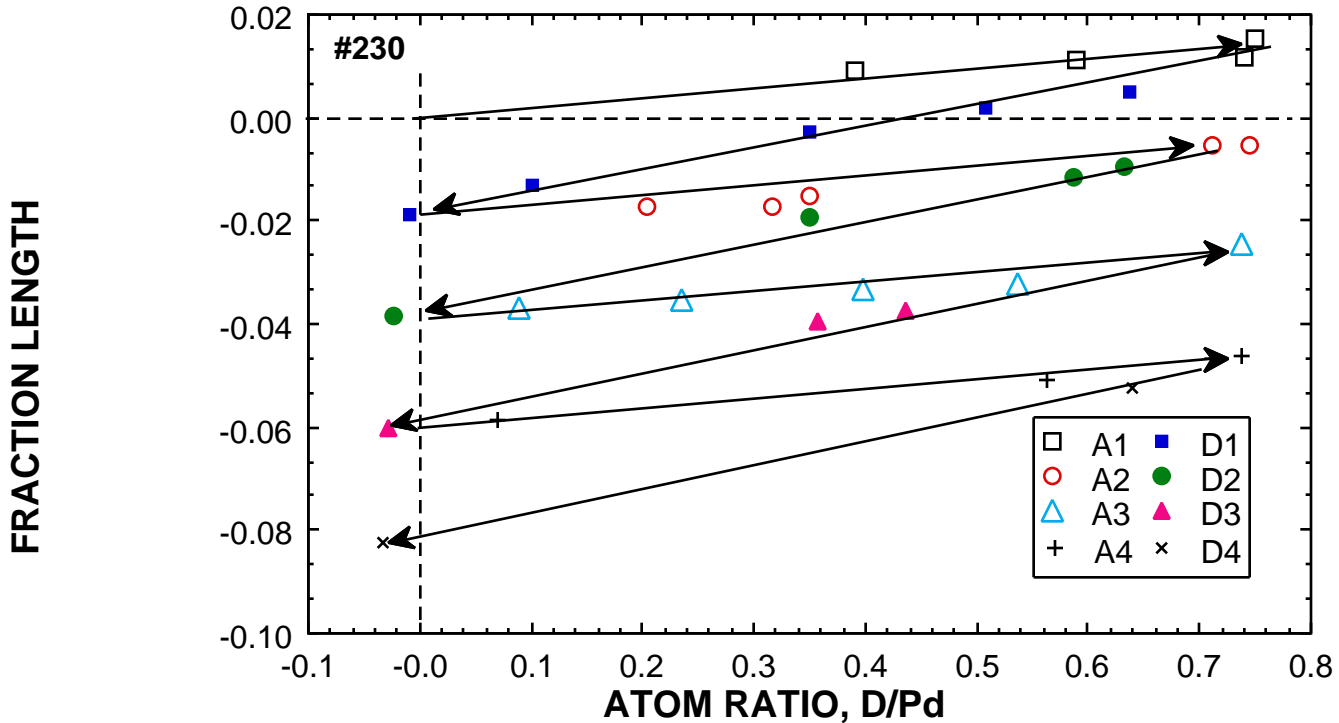
FIGURE 9. Fractional change in length of a rod as a function of D/Pd ratio during several absorption-desorption cycles. The loading current was 200 ma. A=absorption, D=desorption

because the rod gradually acquired an elliptical cross-section. A volume excess of between 1 and 2% seemed to have occurred after 4 cycles. After all deuterium had been removed by heating at 175° C, weight-loss was observed after each cycle. Although some coins lost a small amount of weight after cycling, the amount lost by this rod is exceptionally large (0.0020 ±0.0001g =0.06%). Scratches parallel to the axis gradually formed on the surface at intervals of a few tenths of a millimeter. This sample shows that it is possible to load an electrode with deuterium without producing initial excess volume.

Rod #2 (#7B) was electrolyzed in tritiated water at 200 ma. The one data point, taken after complete loading, shows (Fig, 8) a significant excess volume. This volume increase cannot be attributed to the presence of the very small amount of tritium (10^{-12} moles). Apparently, two electrodes cut from the same Pd rod can behave in different ways.

A third piece of this rod and a 6.3-mm dia. rod were electrolyzed initially at 50 ma in 0.1N LiOD. The D/Pd ratios measured after 24 hrs at the indicated currents are compared in Fig. 10. As long as the excess volume is below a critical value, an increased current results in an increased D/Pd ratio. However, when the excess volume fraction for the 4 mm rod increased from 0.022 to 0.034, there was a drop in the D/Pd ratio. It is apparent from this behavior that excess volume can grow after the electrode has completely converted to the -phase if a sufficiently high hydrogen activity is produced. When the critical value has been exceeded, electrolysis can not increase the deuterium content above that which is in equilibrium with gas a 1 atm. Thus, an electrode may suddenly lose deuterium for no apparent reason.
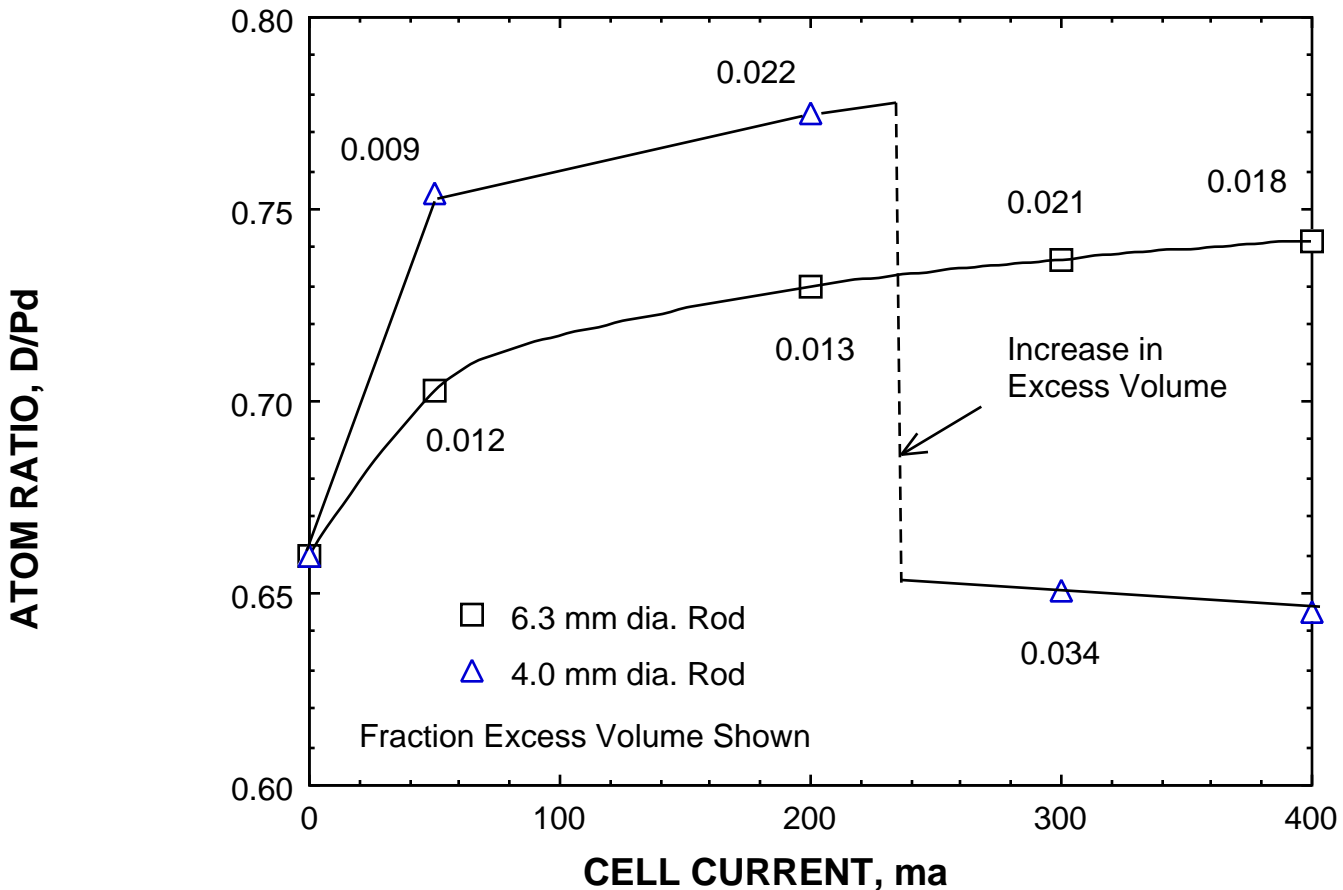

FIGURE 10. Deuterium content produced in a Pd cathode by the indicated cell current. Values for the fraction excess volume are indicated next to each point.

III.B.4. Pd-C Alloy Disc Loaded at 200 ma

Presence of carbon changes the expansion behavior. Figure 11 compares the thickness expansion ([final thickness-initial thickness]/initial thickness]) for pure Pd and two different concentrations of carbon. The amount of expansion at -min is reduced as the carbon content is increased. Expansion at deuterium contents above -min is clearly reduced for a carbon content of 1 atomic %, The presence of 2.8 atomic % C so reduces the solubility limit for deuterium that the effect on expansion is not easy to discern.

We conclude that carbon has a higher solubility in the – phase than in the – phase and that its presence reduces the lattice parameter of the -phase because dissolved carbon reduces the thickness expansion compared to the absence of carbon. Carbon also reduces the amount of deuterium that can be dissolved in the lattice.
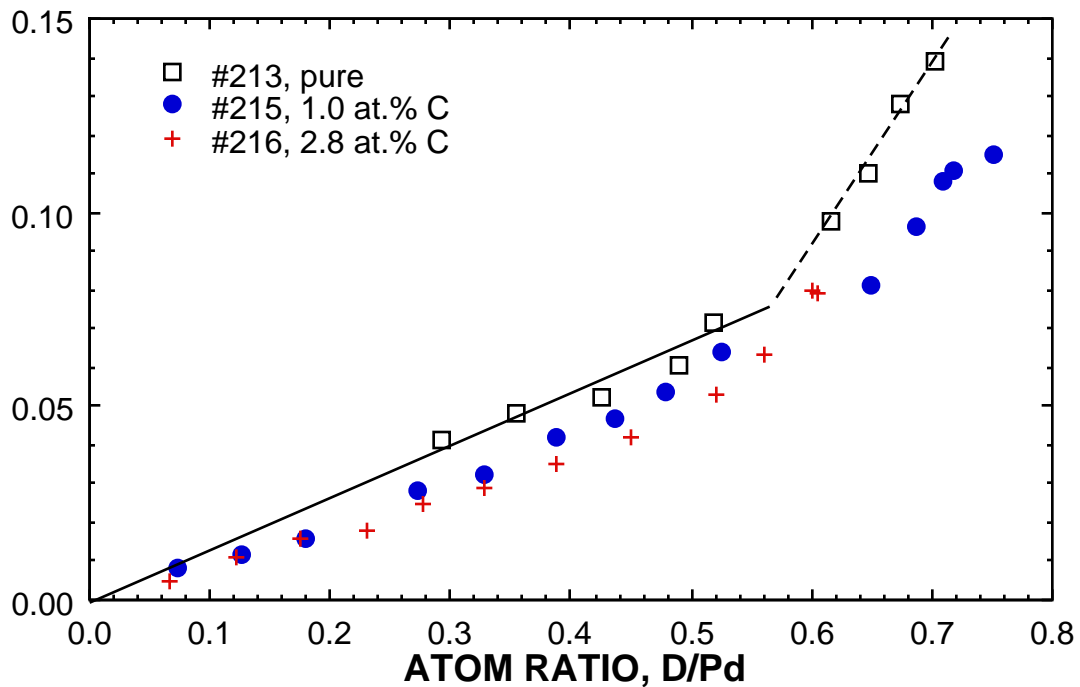

FIGURE 11. Effect of carbon on the thickness expansion as a function of deuterium content.

III.B.5. Pd-Li Alloy Disc Loaded at 200 ma

The addition of lithium to palladium also has a marked effect on the thickness expansion as can be seen in Fig. 12. A small amount (Li/Pd=0.012) causes the expansion to be linear with no break at   -min. In addition, the amount of expansion is greater than that measured for pure palladium. As the lithium content is increased, the expansion behavior approaches that for pure palladium. The sample at Li/Pd=0.051 is an exception to this pattern.

We propose that lithium, at certain compositions, so weakens the lattice that excess volume can be produced as the   -phase converts to the   -phase without the need to add deuterium to the   -phase. This effect is observed at Li/Pd= 0.012, 0.023 and 0.051 but not at 0.025 and 0.045. The failure of the latter two samples to follow the general pattern can not be explained at this time.
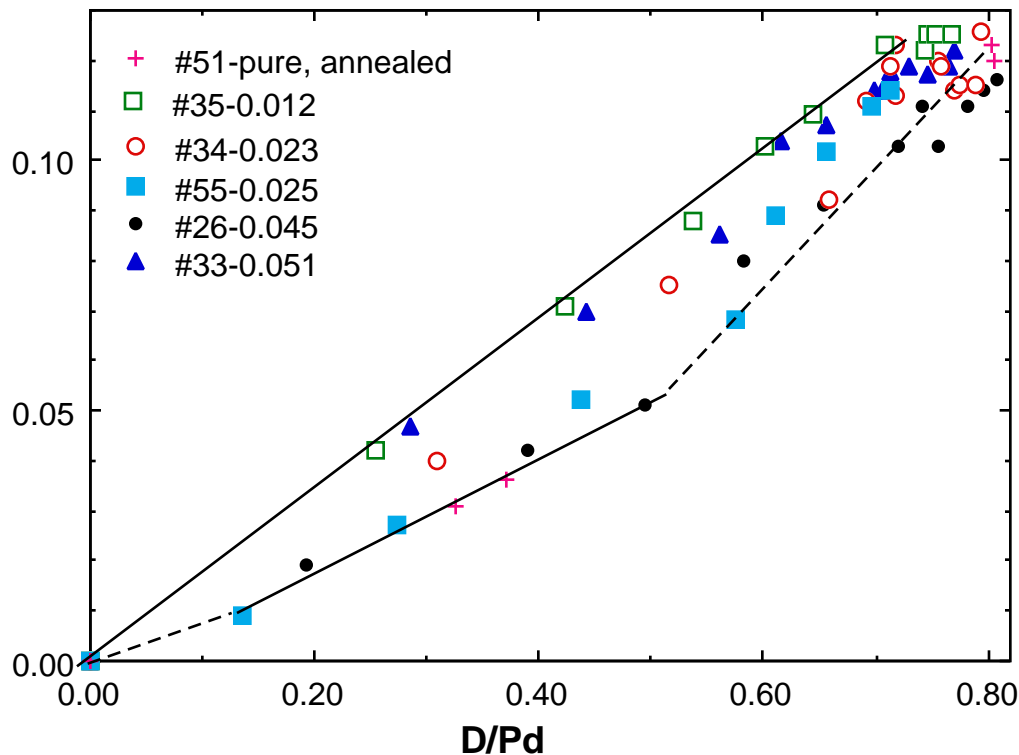

FIGURE 12. Effect of lithium on the thickness expansion as a function of deuterium content. The Li/Pd ratio is listed. Lines are drawn through the data for cells #35 and #26.

III.B.6. Rate of Desorption Study

A coin shaped electrode containing 4% excess volume was allowed to lose deuterium while sitting in air at room temperature. Two regions of behavior are apparent in Fig. 13. During the initial region, the sample has a composition that is completely within the -phase. After about 4 hours, the loss rate changes at a composition where -phase is expected to form. Once some -phase is present, the loss rate is significantly reduced. The reverse behavior has been observed during charging. Although all samples studied in this way showed similar behavior, the slopes in the two regions had a variety of values.

We propose that desorption and absorption is limited partly by diffusion and partly by surface conditions. The diffusion rate through the – phase is much greater than through the – phase.
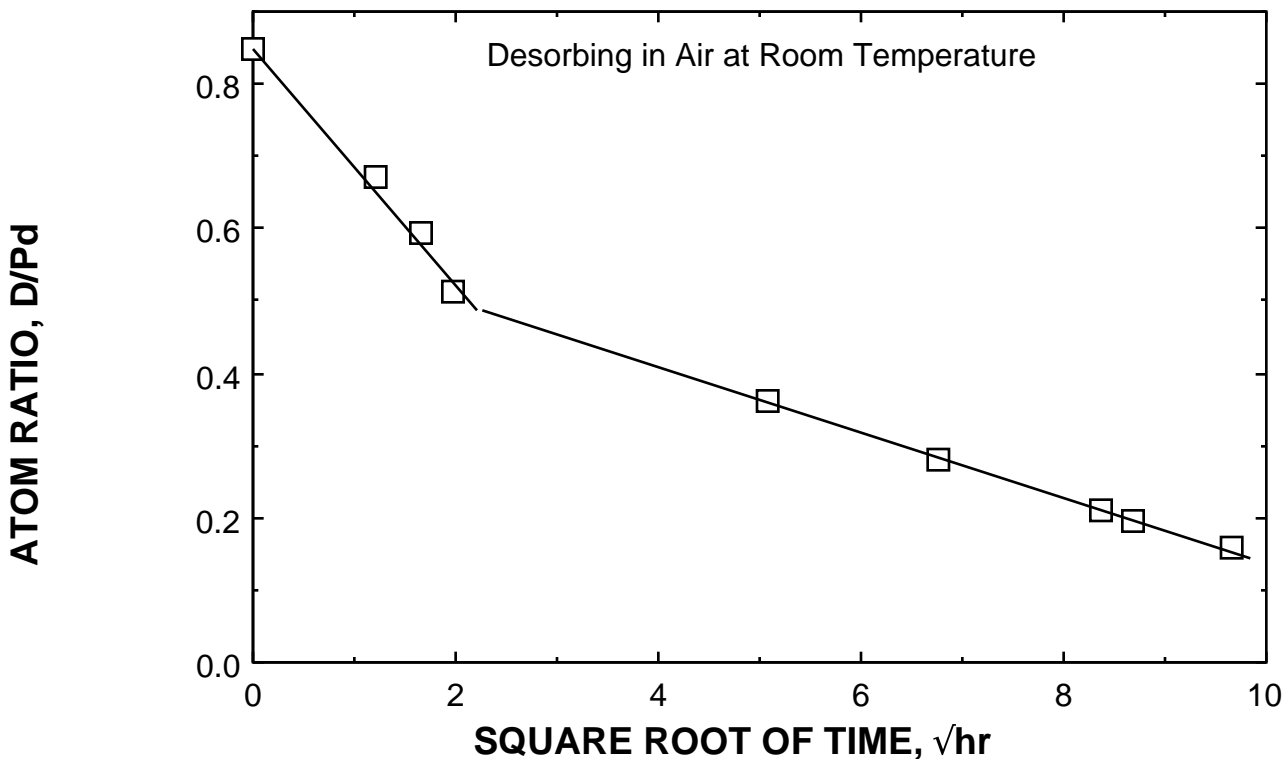

FIGURE 13. D ⁄ Pd ratio as a function of square root of time time for a coin shaped Pd electrode (4% excess volume) losing deuterium at room temperature in air.

III.B.7. Metallographic, Neutron Diffraction and X-ray Examination

Metallographic examination of a pure sample that had 11 % residual volume expansion after desorption showed no cracks when examined at 1000x. However, lines of pits were observed through out the piece as can be seen in Fig. 14. At high magnification without etch, an elliptical shape (2-5μm x 4-10μm) is seen with the long axis parallel to the face of the disc. These are thought to be openings to tubes that run throughout the electrode. While other sets of tubes might run in other directions, the cut may have been made at too shallow an angle for their cross-sections to be revealed. Although the pits did not appear to correspond to the present grain boundaries of the -phase, they might have been on grain boundaries when the piece was entirely -phase. We do not yet know whether these micropores can account for all of the excess volume.

PHOTOGRAPH NOT AVAILABLE

FIGURE 14. Photomicrograph of palladium that has 11% excess volume.
Magnification is x28

Examination by transmission electron microscopy (TEM) showed a high concentration of dislocations. Neutron diffraction examination of a sample that had 22% volume expansion after all hydrogen had been removed showed no significant lattice parameter difference (±0.0002 Å) compared to pure palladium.

III.C. Study of Tritium Loss from Pd Cathodes

Five discs[22] and three rods were studied. The purposes were (1) to determine how fast tritium is removed from a cathode containing tritium and deuterium using a heavy-water electrolyte; and (2) to determine the effect of the excess volume on this pro-perty. The weight, area, pretreatment and final D/Pd ratio after tritium loading are listed in Table I.

One electrode (#2B) had been cycled until a residual excess volume of 20 % had been achieved. Coin #5B was not previously electrolyzed. All of the coins were cleaned by sand blasting using Al_2O_3 in high pressure argon. The rods were not previously electrolyzed and were cleaned with trichloroethylene or acetone.

TABLE I
Weight, area, D/Pd ratio, pretreatment of Pd discs
before electrolysis in tritiated D_2O of indicated concentration.
Fraction of available tritium that was taken up by electrode is shown.

Number	Weight,g	Area, cm^2	Bulk D/Pd$^{(1)}$	Pretreatment	Tritium Concentration, d/min-ml$^{(2)}$	Fraction T
2B	5.22	5.78	>0.69	Coin #213	1.5×10^6F	0.41
4B	5.22	5.78	>0.68	Coin #213	1.4×10^6G$^{(3)}$	0.48
5B	5.05	5.45	>0.64	Unused coin	1.4×10^6H	0.30
6B	5.22	5.78	>0.65	Coin #213	1.4×10^6H	0.29
7B	3.50	3.18	>0.68	4 mm Ø rod	1.4×10^6H	0.15
8B	0.95	1.65	>0.71	2 mm Ø rod	1.4×10^6H	0.19
9B	2.53	2.38	>0.71	4 mm Ø rod	1.3×10^6I	0.32
10B	6.28	6.75	>0.72	Coin #229	1.3×10^6I	0.32

(1) Values are lower limits because of the unavoidable presence of H_2O in the loading cell (98.8 mol % D_2O).

(2) Letter indicates batch of loading solution used.

(3) Solution contained 88 mol % D_2O.

These electrodes were placed in sealed cells such that all tritium leaving the cell had to pass through a recombiner where it was collected as water. Of the 1.6 ml col-

lected each day when the unloading current was 200 ma, 1 ml was used to measure the tritium content. When the unloading current was 100 ma, 0.5 ml was used to measure the tritium content. Thus, the tritium measured each day was an average of that released during a 24 hour period. On the other hand, the electrolyte accumulated tritium during the entire duration of the study. Corrections were made for the amount lost when 1 ml was removed for daily measurement. No electrolyte was added to the cell during this time.

The data can be analyzed in several different ways. A determination will be made of the relative concentration and content of tritium in the electrolyte and the gas, the rate of tritium removal, and the efficiency of tritium uptake by palladium when competing with deuterium. The main object of this work is to show the general characteristics of several phenomena using relative values. Because this is not intended to be a quantitative study, high precision is not needed.

As can be seen in Fig. 15, the tritium content of the gas starts high and drops as electrolysis proceeds. There is very little change in the tritium content of the electrolyte during this time. This behavior was characteristic of all electrodes studied and would be expected if a contaminated Pd electrode were used in a cold fusion cell.
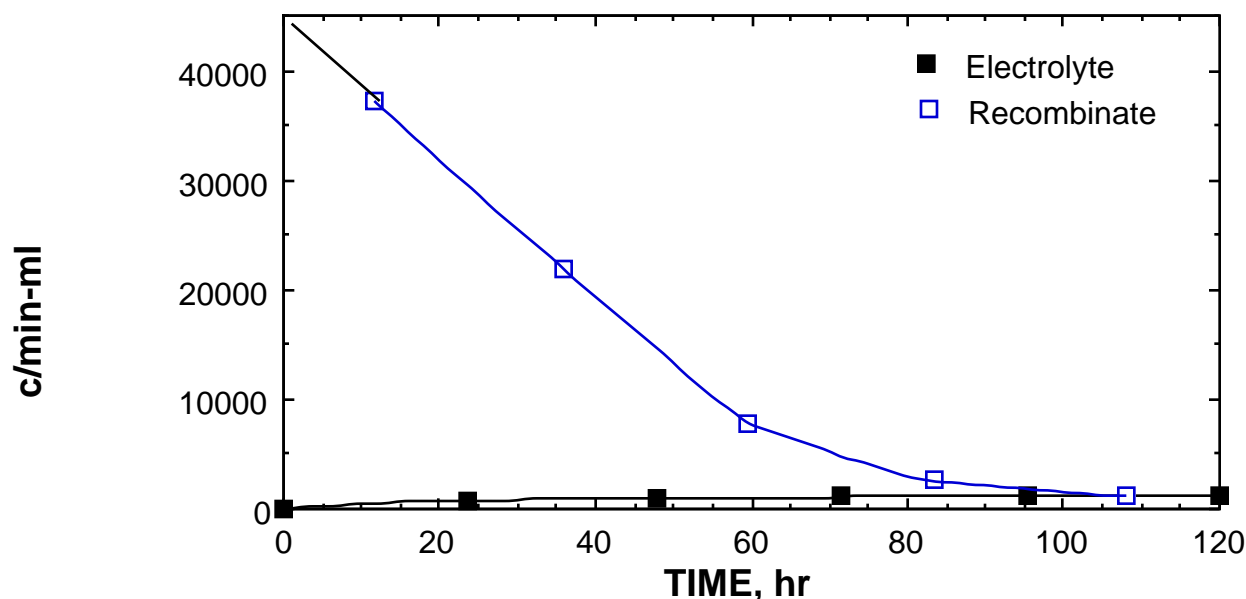

FIGURE 15. Tritium concentration in recombinate and electrolyte as a function of time. Cell electrolyzed at 200 ma with contaminated palladium (Cell #2B) as the cathode in 0.1 N LiOD.

The total quantity of tritium released into the gas and into the electrolyte is shown as a function of time in Fig. 16. This sample had 97.2% of the total tritium in the gas and 1.8% in the liquid after 120 hrs of electrolysis. When this electrode was discharged at 100 ma instead of 200 ma, 95.2% of the tritium appeared in the gas and 3.6% was found in the electrolyte. Similar minor differences occurred between all the samples. The remaining tritium was not released during these times.
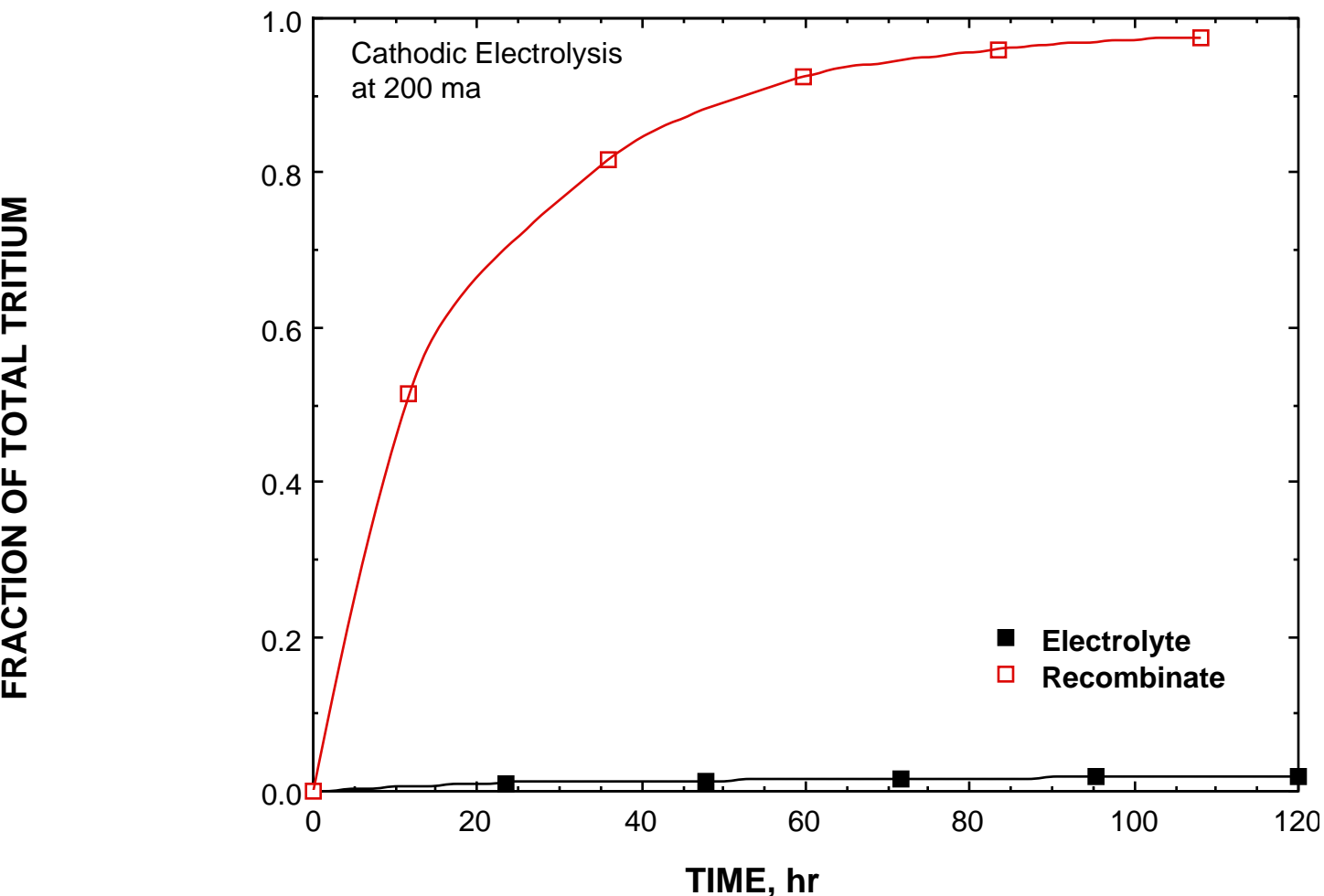

FIGURE 16. Fraction of tritium released from contaminated palladium in the gas and in the electrolyte as a function of time. This cell (#2B) was electrolyzed at 200 ma.

Loss of tritium is a first-order reaction. The log of total tritium concentration divided by the tritium remaining when plotted as a function of time produces a straight

line from which the rate constant can be calculated. Figure 17 compares the behavior of
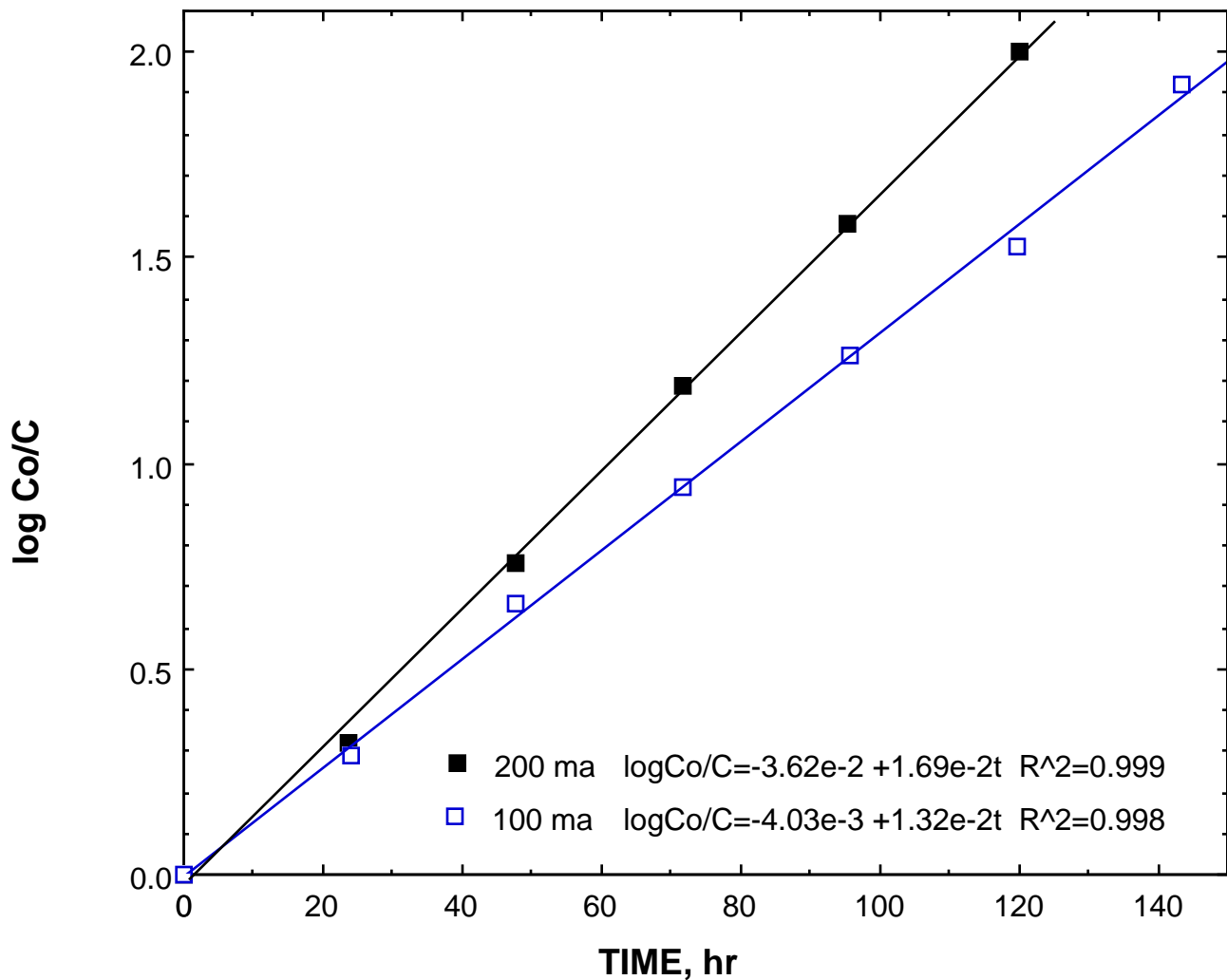
FIGURE 17. Time variation of log (initial tritium concentration in the electrode divided by the tritium concentration after the indicated time) as a function of time.   Palladium electrodes were charged with a mixture of deuterium and tritium at the indicated currents and then electrolyzed as cathodes in 0.1N LiOD electrolyte at the indicated currents.

two electrodes as described in Table I. Tritium is swept out of the electrode at a linear rate that can be expressed as a half-life as listed in Table II. The process of adding tritium to an electrode will be called "loading" and its removal will be called "unloading".

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TABLE II

Rate constant and half-life for tritium removal at the indicated

loading and unloading currents. The excess volume in the

electrode before and during unloading is indicated

| Sample | k,hr^{-1} | Half-life, hr | Current, ma | | Excess Volume, % | |
			Load	Unload	Initial	Final
2B(disc)	0.0388	17.9	200	200	20	24
4B(disc)	0.0298	23.2	200	100	24	26
5B(disc)	0.0398	17.4	20	200	0	5
6B(disc)	0.0422	16.4	200	200	24	32
7B(rod)	0.0294	23.5	200	200	0	4
8B(rod)	0.0556	12.5	200	200	0	6
9B(rod)	0.0340	20.4	100	200	0	5
10B(disc)	0.0355	19.5	200	300	4.5	11

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Because each loading cycle increases the excess volume, a coin (#6B) that was run previously as #4B was loaded and unloaded at 200 ma in order to determine if this additional volume had any effect on the loss rate. Apparently, an increase in excess volume from 24% to 32% reduced the half-life from 17.9 hr to 16.4 hr. This indicates that an increase of   0.0004 in the rate constant is caused by each 1% increase in excess volume when the coin is charged at 200 ma. Although this value is very uncertain, being based on only two points, it is needed later to make minor corrections for changes in excess volume during other studies.

Three coins were studied to determine the effect of unloading current on the rate constant. Electrode #2B had   24% excess volume when loaded. This disc was loaded with tritium using 200 ma and was unloaded using the same current. Electrode #4B was a repeat of run #2B but was unloaded at 100 ma. Electrode #10B contained 11%

excess volume when loaded and was unloaded at 300 ma. These three measurements were adjusted to an excess volume of 20% using the approximate factor determined above. The data, plotted in Fig. 18, show that when the unloading current is increased, thereby increasing hydrogen flux within the electrode, the loss rate of tritium is increased and approaches a constant value.

We conclude that, as the cell current is increased, an increased quantity of hydrogen that is formed on the surface leaves directly as gas rather than diffusing into the metal where it would displace hydrogen into the micropore network. Such behavior suggests that at high charging currents the deuterium content will not increase significantly as the charging current is increased further.
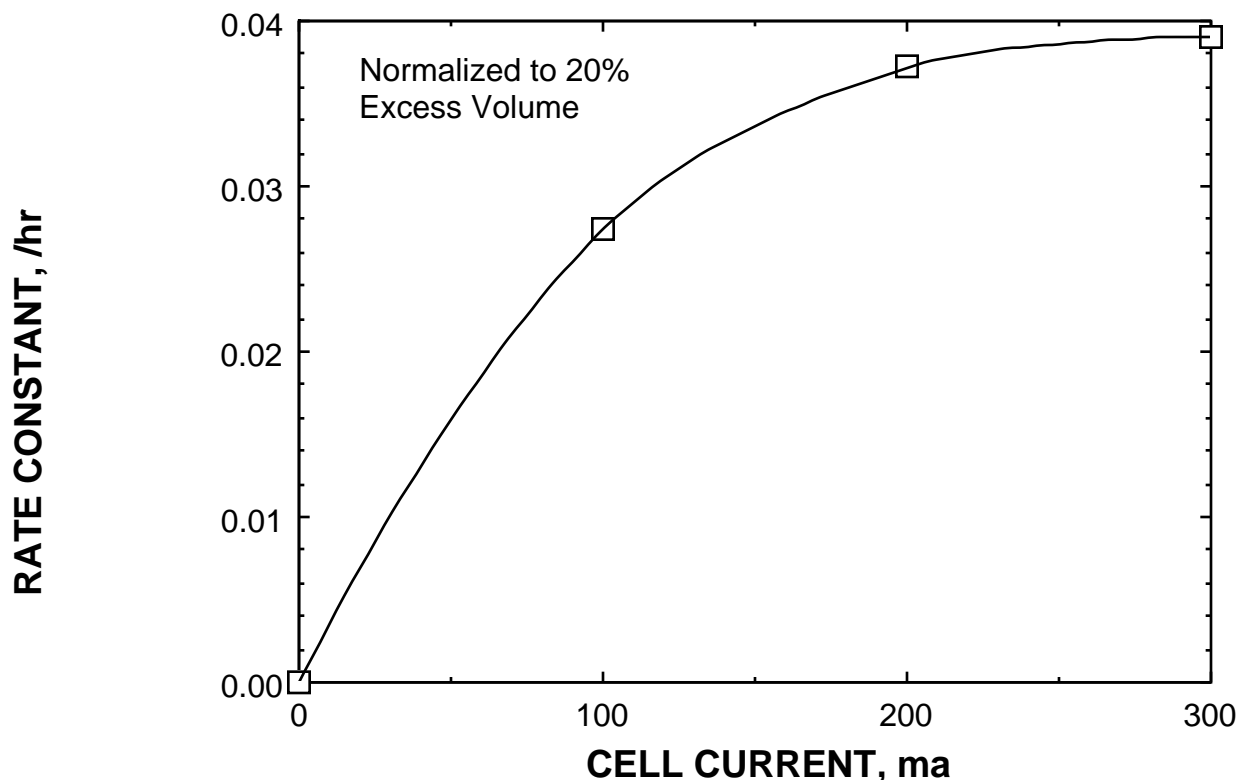
FIGURE 18. Rate constant for hydrogen removal vs cathodic cell current adjusted to 20% excess volume.

Electrode #5B, containing no initial excess volume (an unused coin), was loaded using 20 ma charging current to minimize micropore growth and was unloaded using 200 ma. In spite of the slow loading rate, this coin contained 5% excess volume when

loaded. This small volume produced an unexpectedly small half-life of 17.4 hr.
Apparently, not all excess volume is equally effective in promoting hydrogen loss.

Several rods were studied to determine whether the shape and size of the electrode
were important. A 0.4 cm dia. rod that contained 4% excess volume when loaded had a
half-life of 23.5 hr. A second rod, containing 5% excess volume, gave a half-life of 20.4
hr, in good agreement with the first sample. However, both samples had a larger half-
life compared to a disc of the same excess volume. On the other hand, a 0.2 cm dia. rod,
when loaded and unloaded at 200 ma, had 6% excess volume and a half-life of 12.5 hr,
about half of the value obtained for a rod of twice the diameter. The loss rate of
dissolved hydrogen appears to be proportional to the length of those channels that can
reach the surface. The smaller the diameter the shorter is the distance to the surface
from the interior.

During loading, there is a preferential uptake of deuterium compared to tritium.
Table I lists this quantity as "Fraction T" which is calculated from the equation [T/D
ratio in the electrode divided by T/D ratio in the loading electrolyte]. The variety of
values suggests that the surface condition has an effect.   If the value for #4B is
eliminated, because the electrolyte contained only 88% D_2O, the most likely enrichment
factor is near 0.3 for the reaction that absorbs hydrogen. Thus, tritium has a tendency
to remain in the electrolyte rather than enter palladium.   On the other hand, when gas
is produced during electrolysis, the value is 0.55±0.02[4]. In this case, tritium also has a
tendency to remain in the electrolyte. Although these values have interesting
theoretical implications, the general conclusion is that tritium is easily displaced by
deuterium or protium when it is dissolved in palladium.

III.D. Study of Tritium Loss from a Pd Anode

A Pd coin was loaded with tritium from a 0.1N LiOH electrolyte. After being
charged to a composition of H/Pd=0.787, the electrode was placed in a cell containing
0.1N LiOH and electrolyzed at 200 ma as the anode using Pt as the cathode. The
evolved gas was recombined and collected. Periodic tritium measurements were made
of the electrolyte and the recombinate was measured after 24 hours when sufficient

volume had accumulated. The tritium/protium ratio in the electrolyte was used to calculate the amount of tritium that would be expected to appear in the electrolyte if tritium and protium were absorbed into electrode without preference. This quantity was divided into the measured quantity of tritium at various times. After 56 hrs, 74% of the hydrogen was gone from the electrode. If the remaining hydrogen had the same T/H ratio as that which had been removed, the final distribution ratio is 0.15. This compares with a similar ratio for deuterium and tritium of 0.3 as described in III.C. Of the total tritium contained in the electrode, 0.6% appeared in the evolved gas.   The absence of tritium in the gas shows that the micropores are not effective in removing gas when the internal pressure has been reduced below the saturation limit.

Removal of tritium by anodic electrolysis is a diffusion controlled process similar to the behavior when palladium is allowed to desorb in air.   Figure 19 shows how the fraction of tritium in the electrode that appears in the electrolyte changes with square root of time. A similar coin, when allowed to desorb in air at room temperature, shows a similar change in loss rate after about 4 hrs as can be seen in Fig. 13. This composition corresponds roughly to the initial formation of some β -phase along with the α -phase. The implication of these two studies is that hydrogen, along with the small amount of tritium, diffuses to the surface where it is converted to H_2O when the electrode is used as an anode in water and it is converted to H_2 when the electrode is in air. In each case, the rate determining step is diffusion through pure β -phase at first and then through a mixture of α – and β -phase. This study shows that tritium can be removed from Pd and determined quantitatively by anodizing in a cell and measuring the tritium content of the electrolyte.
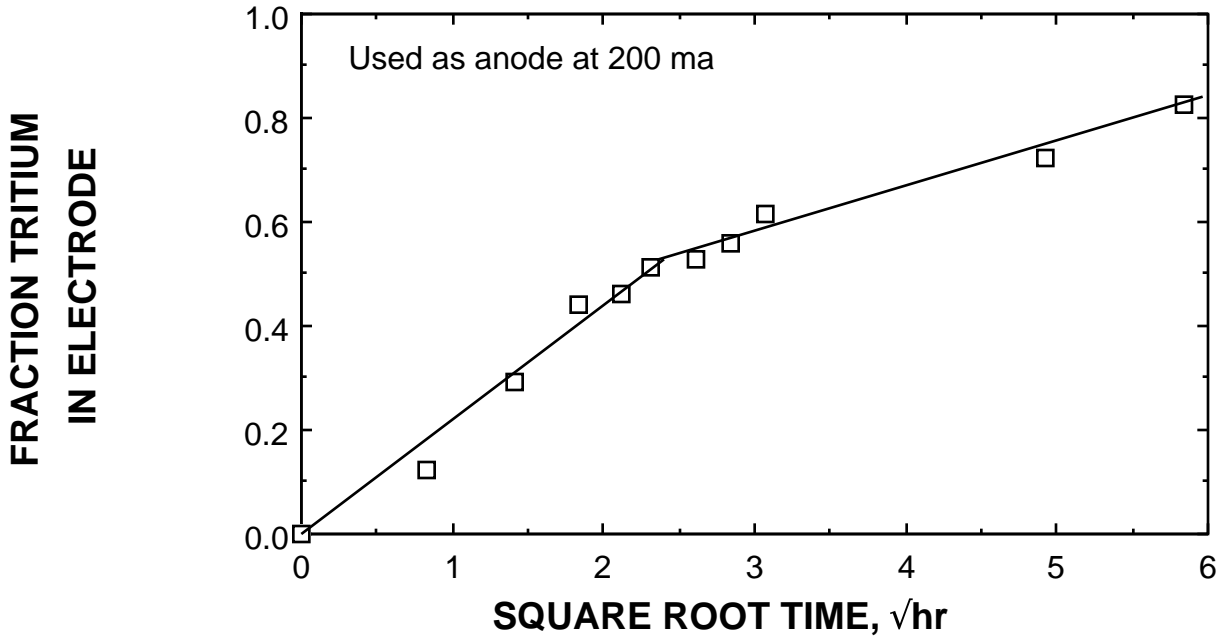
FIGURE 19. Fraction of tritium contained in the electrode that appears in the electrolyte vs square root of time. The palladium was electrolyzed as the anode at 200 ma.

IV. DISCUSSION

We propose that the volume expansion associated with -to -phase conversion and further addition of hydrogen creates internal stress that can produce cylindrical shaped capillaries as well as other void space within palladium. When these channels succeed in reaching the surface, the rapid loss of hydrogen determines the maximum composition of the hydride that can be reached in an electrolytic cell. Formation of these channels is dependent on the shape and purity of the electrode as well as on the charging rate for hydrogen. Clearly, other subtle factors involving the metallurgy of palladium play an important role because different effects are seen within the same batch of material.

Stress associated with - to -phase conversion by itself is sufficient to produce excess volume if loading is sufficiently slow or if certain impurities, such as lithium, are present (Figs. 7 and 12). If stress is not relieved upon phase conversion, void space may occur when additional stress is produced as hydrogen is added to the -phase (Figs. 3

and 4). Although, this stress by itself is not sufficient to cause the void space to grow larger (Fig. 5), a sample that does not form excess volume during charging to an initial composition limit might slowly grow excess volume as additional hydrogen is forced into the lattice by a higher charging current (Fig. 10). Once formed, this excess volume does not change significantly when hydrogen is removed (Figs. 4 and 6). Each subsequent addition of hydrogen adds to the excess volume by a similar amount, at least within the extent of this study. Electrodes have been observed to produce quantities of excess volume between 0% and 6% after full saturation is reached during the first loading and up to 32% excess after repeated cycling.

There is no indication in the data that all of the void space is owing to the capillaries or that all of the capillaries communicate with the surface. Indeed, the relatively small half-life coupled with the small excess volume shown by #5B suggests that loading under certain conditions may increase the efficiency of the resulting capillaries to remove hydrogen. The relative behavior between the two rods of different diameters (#7B and #8B) suggests that the length of the capillaries is important; a small diameter rod having a faster loss rate than a large diameter rod for nearly the same amount of excess volume.

The shape of the electrode is important in determining how internal stress is relieved. If a coin shaped electrode is used, the internal pressure can be relieved most easily by void formation parallel to the faces. Consequently, this electrode can be viewed as a coin shaped container filled with gas at high pressure. As the pressure builds up, the thickness would expand and the diameter would contact. If the material were flexible, it would eventually form a sphere. Indeed, after many cycles, the discs were found to have a pillow shape with a reduction in diameter. On the other hand, a cylindrical shaped container will hold higher internal pressures before the strength of the material is exceeded. The smaller the diameter, the higher the pressure that one would expect to be contained. Apparently, one 4 mm dia. rod used in this study was sufficiently strong to resist the internal pressure (Fig. 8). Of course, the behavior of any shape will depend on the strength of the palladium which is determined by its purity and the absence of sites for void formation. Thus, the metallurgy of the electrode is important. The best shape would be a small sphere of pure palladium.

The loss of tritium mainly to the gas during cathodic electrolysis indicates that there is a continuous flow of hydrogen within an electrode containing excess volume even when it has become fully saturated. To the extent that channels form, hydrogen rapidly leaves the metal when the internal activity exceeds a pressure of 1 atm. In other words, in the presence of an increasing concentration of channels, electrolytic action is expected to be increasingly ineffective in raising the composition above $PdD_{0.66}$ or $PdH_{0.70}$ [4]. Such fixed points of gas evolution on the surface are consistent with the optical observations of bubble evolution[23].

The flux of hydrogen through the metal sweeps any dissolved tritium into the gas whether it is present owing to contamination or because of a proposed cold fusion reaction. Tritium resulting from contamination is expected to appear in the gas as soon as the D/Pd ratio has reached a value that gives a pressure in excess of one atmosphere. Tritium that appears in the electrolyte of an open, but sealed cell[5], barring surface contamination, is proposed to result from production at a surface. Only here can tritium exchange with deuterium in the electrolyte. Tritium that appears mainly in the gas after many days of electrolysis can not be caused by contamination of the electrode or by pickup from the environment. Other studies show that environmental tritium always appears mainly in the electrolyte[4].

How does this behavior relate to the cold fusion reaction? It is generally agreed that if nuclear reactions involving deuterium are to occur, a high, local concentration of deuterium in the metal would be necessary regardless of the nuclear model. If the reaction involves "n" deuterium atoms, the nuclear reaction rate is expected to be proportional to the deuterium concentration raised to the "n" power. Thus, the reaction rate might be a steep function of deuterium concentration after the concentration had reached the critical value needed for a reaction to initiate. If micropores formed within

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4. These values are the respective hydride compositions that are in equilibrium with hydrogen at 0.66 atm, the pressure at Los Alamos, and 300K. Both values should be increased by 0.01 to correspond to 1 standard atmosphere.
5. An open cell is one that allows the gas to leave without recombination. A closed cell is one in which the recombinate is returned to the electrolyte. A sealed cell is one that collects the recombinate external to the cell without contact with the environment.

the electrode, the ability to form such high, local concentrations of deuterium would be reduced as the gas quickly diffused out. Part of the deuterium loss might be offset by using higher charging rates but there is a limit to this approach. Indeed, heat production has been found to increase as the current density is increased[24; 25] and tritium production has been associated with sudden increases in charging current[2; 1]. If this analysis is correct, those electrodes that formed a minimum of micropores and were charged at a sufficiently high rate might achieve a high deuterium concentration on the surface. The deuterium concentration could be increased further by a suitable poison, in order to discourage D-D recombination; and the use of protium-free electrolyte, in order to avoid protium dilution. These conditions are expected to apply to all proposed nuclear reactions involving deuterium, whether heat or tritium is produced.

At LANL[4], we have produced tritium after about 4 days and very little appears in the gas. This behavior indicates that the tritium is not caused by contamination of the electrode (contamination is released mainly into the gas). Other environmental sources have been explored in detail and the results may be published elsewhere.. Workers at Texas A & M University[2; 3] have produced tritium after the cells were electrolyzed for many days. In their case, the tritium appeared mainly in the gas although the recombinate was later added to the electrolyte. We suggest that contaminated palladium was not involved (contamination is released immediately) and that tritium was produced below the surface in contact with the electrolyte. Thus, a tritium atom could either diffuse through the unavoidable impurity layer created during the long electrolysis and exchange with hydrogen in the electrolyte, or it could diffuse through the metal until it reached a micropore where it could combine with a deuterium atom to make DT gas. Apparently, the latter route was the most likely. Wolf[14; 15], also at Texas A & M, found tritium in electrolytic cells which he claims is caused by palladium contamination. The tritium in his cells does not behave like that found in this study for samples of palladium that are known to be contaminated. Consequently, doubt now exists about his claim.

This work has revealed a major phenomenon involving the creation of micropores. We expect this phenomenon to have a major impact on understanding the proposed

cold fusion reaction and to deserve additional study. In addition, the behavior of tritium with respect to cathodic and anodic electrolysis has been revealed so that cells showing the presence of this isotope can be properly interpreted.

ACKNOWLEDGEMENT

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