

# Attempt to confirm the x-ray radiography results reported by S. Szpak et al.

Cite as: AIP Conference Proceedings 228, 551 (1991); <https://doi.org/10.1063/1.40674>  
Published Online: 29 May 2008

Zhong-Qun Tian, Steven C. Barrowes, and Haven E. Bergeson



View Online



Export Citation

Lock-in Amplifiers

Zurich Instruments

Watch the Video

# THE EFFECT OF HYDRIDING ON THE PHYSICAL STRUCTURE OF PALLADIUM AND ON THE RELEASE OF CONTAINED TRITIUM

by

Edmund Storms and Carol Talcott-Storms

*Nuclear Materials Technology, and Material Science and Technology Divisions  
Los Alamos National Laboratory, MS C348, Los Alamos, New Mexico 87545*

## ABSTRACT

When Pd gains or loses hydrogen or deuterium, the lattice expands or contracts causing a change in physical dimensions. Under certain conditions, there is an additional expansion that is largely irreversible. Repeated gain and loss of hydrogen causes this excess volume to steadily increase. After all dissolved hydrogen has been removed, the diameter of a rod is found to have increased and the length to have decreased. These changes suggest the creation of micropores and/or dislocations within the metal. Such changes in the environment within Pd metal can alter the local D/Pd ratio, affect the diffusion of impurities and, perhaps, affect the Fleischmann-Pons Effect.

Palladium cathodes that have been purposely contaminated with tritium show a rapid removal of the tritium with over 95% going into the evolved gas. This loss of tritium is first-order with a half-life that depends at least on cell current, amount of excess volume and electrode shape. The pattern of tritium release is consistent with the presence of micropores and is significantly different from that observed in active cold fusion cells. When used as an anode, over 99% of this dissolved tritium appears in the electrolyte thereby providing a method for its quantitative determination.

## INTRODUCTION

For the last year and one-half, we have been trying to produce tritium by the cold-fusion reaction in electrolytic cells using the trial and error technique. We were searching for the magic combination of special conditions that would give positive

results on a regular basis. The few positive results<sup>1,2</sup> convinced us, at least, that the phenomenon is real and that tritium can be produced under these unusual conditions. The many negative results showed that the probability of having all the necessary conditions present at the same time is very small, making this approach very unproductive. Therefore, we decided to adopt a different method, one which studied the phenomena that might prevent the fusion reactions. We made one basic assumption in order to evaluate which reactions might be important. This assumption is

**For the fusion reactions to occur, the local concentration of deuterium must exceed a critical value.**

Four phenomena that affect the deuterium concentration have been identified.

1. H/D ratio in electrolyte
2. Current density
3. Surface poisons
4. Concentration of micropores

The first three items are relatively well known and will be discussed only briefly. The fourth item is the major subject of this presentation.

**ITEM 1:** Everyone in this field knows by now that heavy-water easily picks up normal water from the air. It may not be as fully appreciated that this protium in the electrolyte is further concentrated in the palladium. Figure 1 shows how the fraction of deuterium in the electrode is reduced as protium is added to the electrolyte. This effect is most significant in the region near pure D<sub>2</sub>O where it has an enrichment factor of 4. Consequently, while the lattice may be fully loaded with H+D, the D concentration may be reduced below the critical value for fusion to occur if minor amounts of protium were present in the electrolyte.

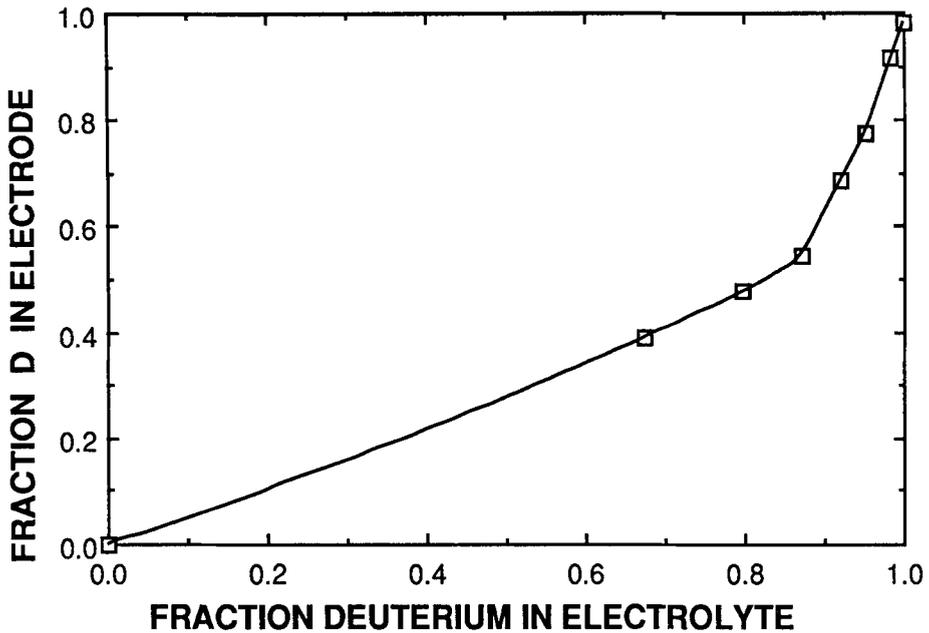


Fig. 1. Measured fraction of deuterium in saturated Pd after electrolyzing in a mixture of  $D_2O$  and  $H_2O$  (0.1 N LiOD,H).

**ITEM 2:** The higher the charging current, the greater the number of atoms of D that are available to diffuse into the palladium electrode. However, each atom has a choice to either diffuse into the metal, thereby increasing the D concentration, or to combine with another D atom and leave the surface as  $D_2$  gas. As will be seen later in the presentation, as the current is increased a greater fraction of the available deuterium leaves the surface as gas. Therefore, there is a practical upper limit to the benefits produced by increasing the current.

**ITEM 3:** Special impurities on the surface can change the proportion of available atoms that enter the metal. This is a very complex problem that I will not discuss here.

**ITEM 4:** The unexpected production of micropores in palladium, when it is charged with hydrogen, is the major subject of this talk. As these pores form, the achievable D/Pd ratio is reduced to a limiting value of 0.66-0.67<sup>3</sup>. The channels allow deuterium to leak out and efforts to achieve a high deuterium concentration are

frustrated, similar to trying to fill a leaky bucket. This work also shows that the leaking deuterium, as well as any tritium that it might contain, appear in the gas, with very little in the electrolyte.

## EXPERIMENTAL

The experimental work will be divided into two parts: a study of excess volume and a study of tritium release from a contaminated electrode. These two parts are related because the tritium can be used as a tracer to determine the path of hydrogen release caused by the excess volume. In addition, this work shows the behavior of a contaminated palladium cathode.

Coin shaped discs and rods of various diameters were charged with deuterium in 0.1N LiOD followed by discharge in air or by heating to 104° or 175° C for various times. The D/Pd ratio was obtained from the weight change and the volume was calculated from the measured physical dimensions. The excess volume is that above the expected volume, calculated from the known lattice parameter<sup>4</sup>.

These samples, as well as others that had not been previously loaded, were completely cleaned of absorbed deuterium and electrolyzed at various currents in electrolytes containing tritium. After the metal had been fully loaded, the electrode was transferred to a fresh cell containing tritium-free 0.1N LiOD and cathodic electrolysis was continued. Periodic tritium measurements were made of the electrolyte and the recombine. In addition, one cell was studied by anodic electrolysis.

More details of the experimental methods can be found in a complete paper that will be published soon.

## RESULTS, Part 1

Three discs were studied by charging at 200 ma or 20 ma. As deuterium or hydrogen is added to palladium, the metal expands as the hydride is formed. In the former case, the volume, based on physical measurements, was found to follow normal expansion until the  $\alpha$ -phase had completely converted to the  $\beta$ -phase. This behavior can be seen in Fig. 2. Once the composition of

the  $\beta$ -phase was increased, the volume increased above the normal value calculated from the lattice parameter.

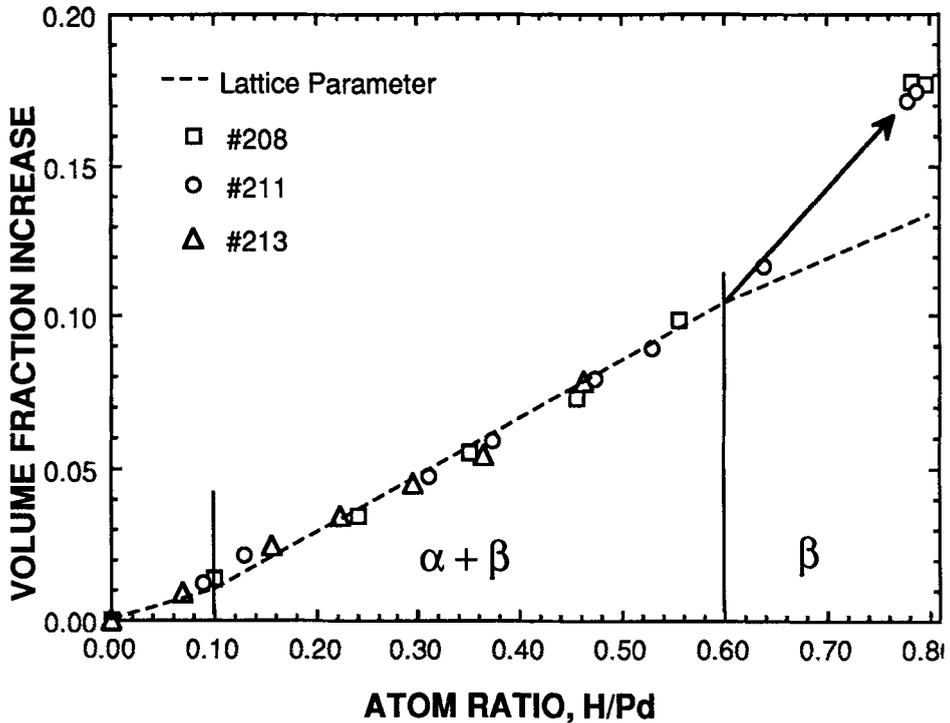


Fig. 2. Comparison between the volume expansion calculated using the physical dimensions and the lattice parameter increase. Volume fraction increase is calculated by the relationship [final volume-initial volume]/initial volume. Loading current is 200 ma.

If the deuterium content was kept below the  $\beta$ -phase region, absorption-desorption cycles could be done without creating significant excess volume, shown in Fig. 3. Once again, when the composition was caused to exceed  $\beta$ -min, excess volume occurred and this remained after all hydrogen had been removed.

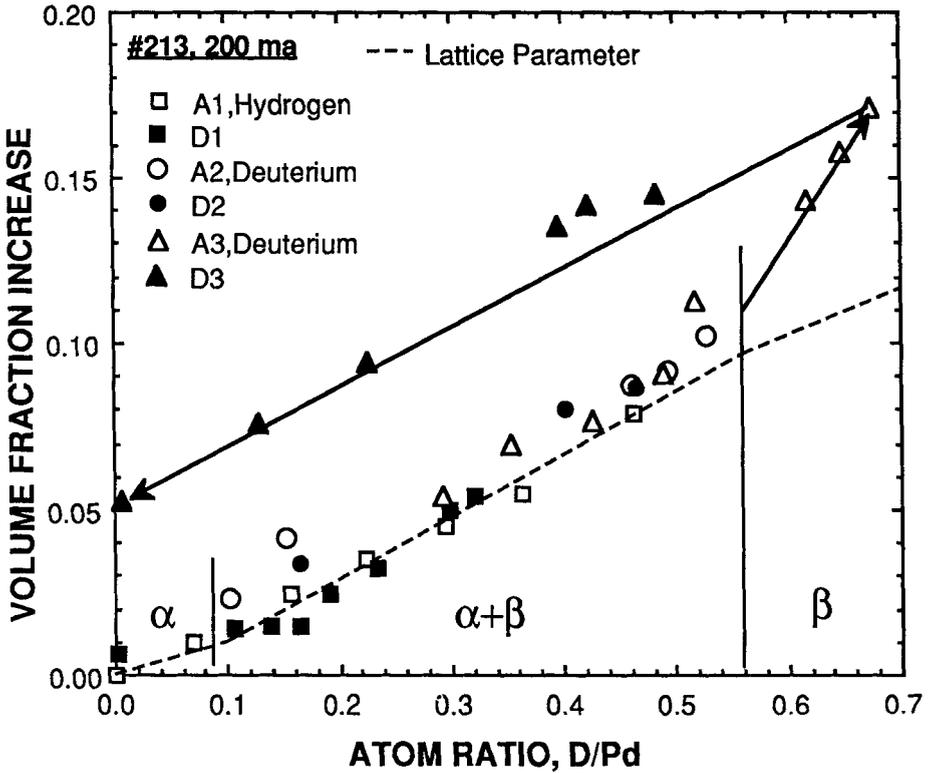


Fig. 3. Volume fraction vs D/Pd. The first cycle involved hydrogen while the remaining two cycles used deuterium. Note that the phase boundary for the  $\beta$ -phase ( $\beta$ -min) falls at a lower D/Pd ratio when deuterium is used compared to the value when protium is in the lattice, as expected. A=absorption, D=desorption

Absorption-desorption cycles done entirely within the  $\beta$ -phase also did not produce additional excess volume although a small amount of hysteresis can be seen in Fig. 4. Because this disc already contained excess volume, the formation of additional volume is based on a comparison to the slope of the volume calculated from the lattice parameter.

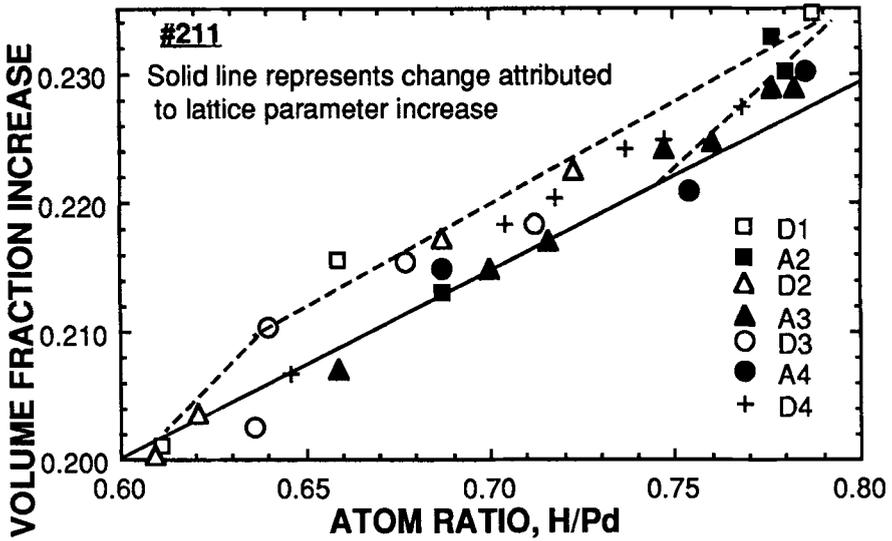


Fig. 4. Volume change produced by absorption-desorption cycles within the  $\beta$ -phase region. Loading current is 200 ma.

Repeated cycles of loading and unloading each cause a similar increase in excess volume up to at least 5 cycles. Two cycles are shown in Fig. 5.

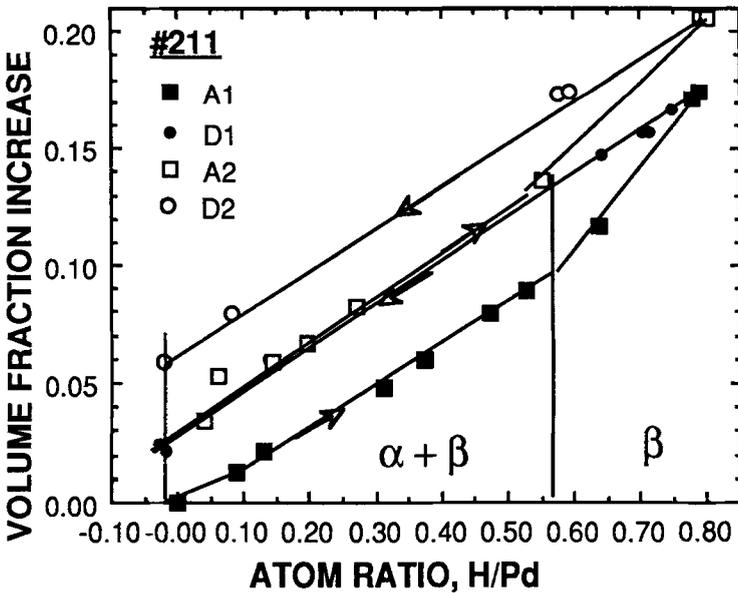


Fig. 5. Volume fraction vs H/Pd ratio for several absorption-desorption cycles. Loading current is 200 ma.

In contrast to the behavior when the charging current is 200 ma, a charging current of 20 ma produced excess volume as soon as the  $\beta$ -phase started to form. Two disc-shaped electrodes are compared in Fig. 6.

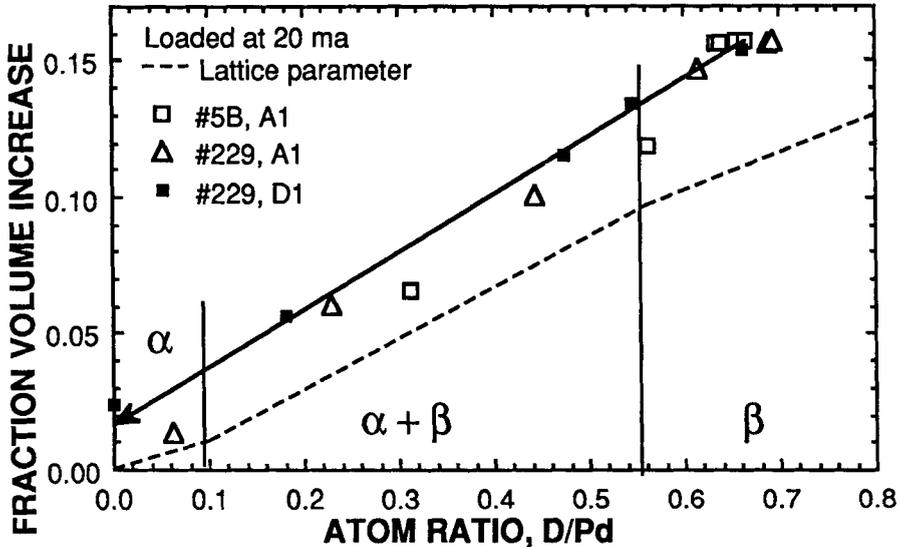


Fig. 6. Volume fraction vs D/Pd ratio for several absorption-desorption cycles. Loading current is 20 ma

The residual excess volume, i.e. that remaining after all hydrogen has been removed, is associated with a decrease in the diameter and an increase in thickness. Figure 7 shows how the diameter and thickness changes during 3.5 cycles. The disc shape seems to be trying to become a sphere<sup>5</sup>.

Two 4-mm dia. rods, cut from the same stock, were loaded at 200 ma. As can be seen in Fig. 8, the first rod (#230) produced no excess volume during 1.5 cycles. However, the second rod, that was loaded in a tritium containing cell, had 3% excess volume after the first loading. Apparently, this material was on the edge of being able to resist deformation so that minor differences in physical structure were sufficient to make a difference.

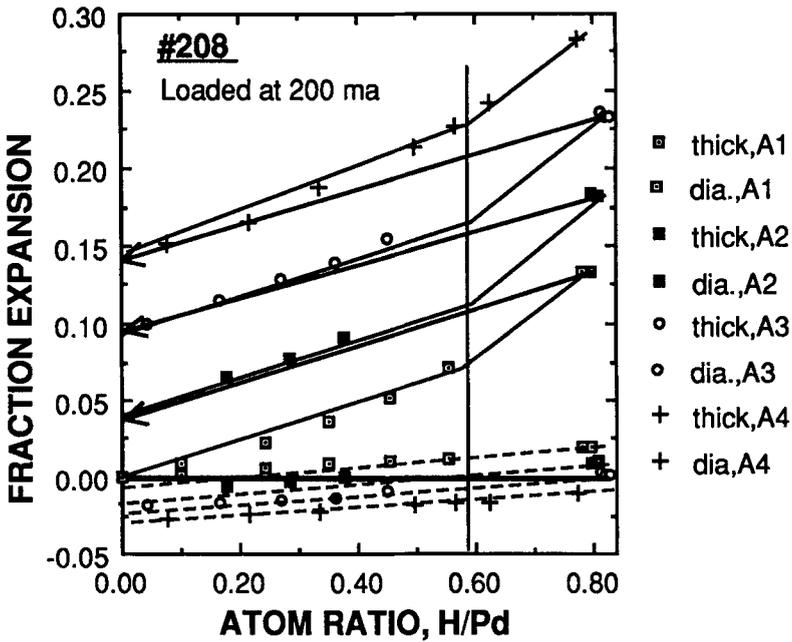


FIG. 7. Comparison between the expansion of the thickness and the diameter during four absorption-desorption cycles as a function of H/Pd ratio. The lower data sets describe the behavior of the diameter. Only data for the absorption part of the cycles are shown.

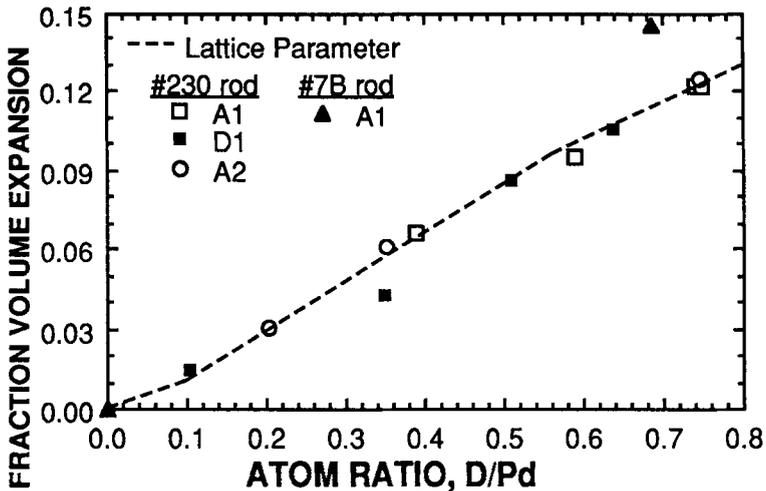


FIG. 8. Volume expansion produced in Pd rods (4-mm dia.) by the uptake of deuterium. Loading current is 200 ma.

When excess volume was present in rods after hydrogen was removal, an increase in diameter and a decrease length was measured. The length decrease is plotted in Fig. 9. This behavior shows that the use of sample length to determine the D/Pd ratio is not an accurate method. The length will decrease below the expected value should excess volume form while the sample is being loaded. In addition, inadvertent loading-unloading cycles may produce an accumulative error.

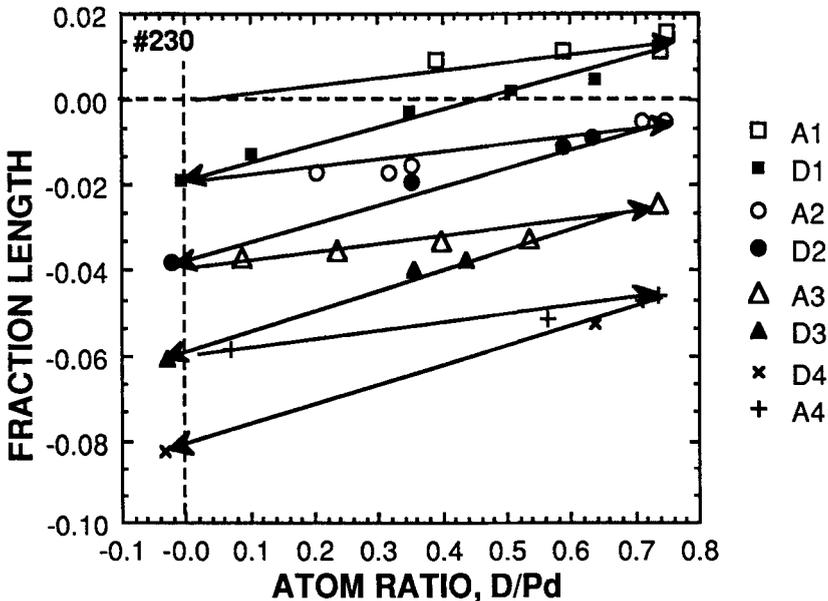
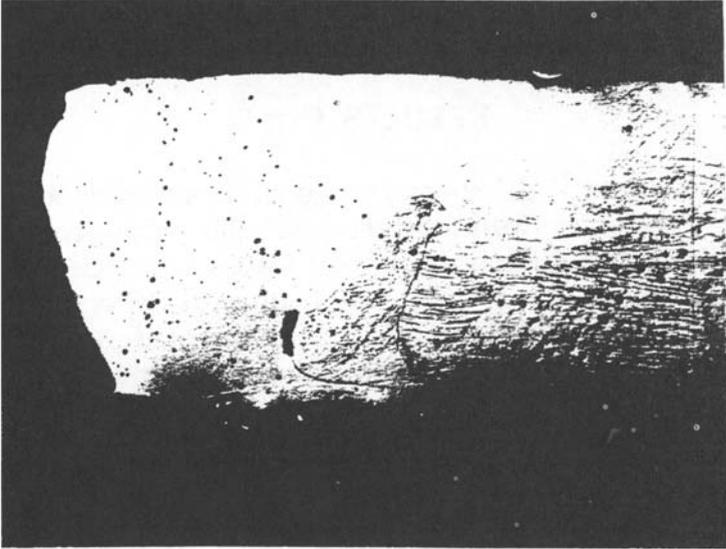


Fig. 9. Fractional change in length of a rod as a function of D/Pd ratio during several absorption-desorption cycles. The loading current was 200 ma. A=absorption, D=desorption

Although not all of the excess volume is thought to involve channels or cracks, there is evidence that some of the void space does provide paths for loss of deuterium from the lattice. Fig. 10 shows a photomicrograph of a disc that contains 11% excess volume. Lines of holes are seen that, under high magnification, are found to have an elliptical shape with the minor diameter between 2  $\mu\text{m}$  and 5  $\mu\text{m}$  and an aspect ratio near 2. These are proposed to be cylindrical shaped tubes that have been cut at an angle. Larger void space (bubbles) as well as undefined changes in physical structure have also been seen. The observed void

space does not appear to account for all of the excess volume.



**Fig. 10.** Photomicrograph cross-section of a disc containing 11 % excess volume. Magnification x28.

### **DISCUSSION, Part 1**

The formation of excess volume is proposed to result from stress release. This release occurs most easily in a disc compared to a rod. If stress is developed slowly, the stress associated with the  $\alpha$ - $\beta$  transition is sufficient to produce void space. A more rapid creation of stress is not relieved when  $\alpha$ -phase is converted to  $\beta$ -phase but requires the addition of hydrogen to the  $\beta$ -phase. The excess volume is associated with a reduction in the largest dimension and an increase in the smaller dimension. Each loading-unloading cycle adds approximately the same amount of excess volume. Micropores or channels form within the electrode along with additional void space. Volume excess as high as 25% has been seen in this study after repeated loading-unloading cycles.

The question that must now be answered is, "What effect does this excess volume have on the loss of deuterium from the

electrode?" This can be studied using tritium as a tracer for deuterium. The behavior of contaminated electrodes will also be discussed in this part.

## RESULTS, Part 2

Contaminated palladium, when electrolyzed as the cathode, deposits most of the tritium in the gas. The tritium concentration in the gas starts high and drops as it leaves the electrode. Fig. 11 shows the accumulated amount of tritium in the respective locations. All samples show this basic behavior with only minor differences in the relative proportion between gas and liquid.

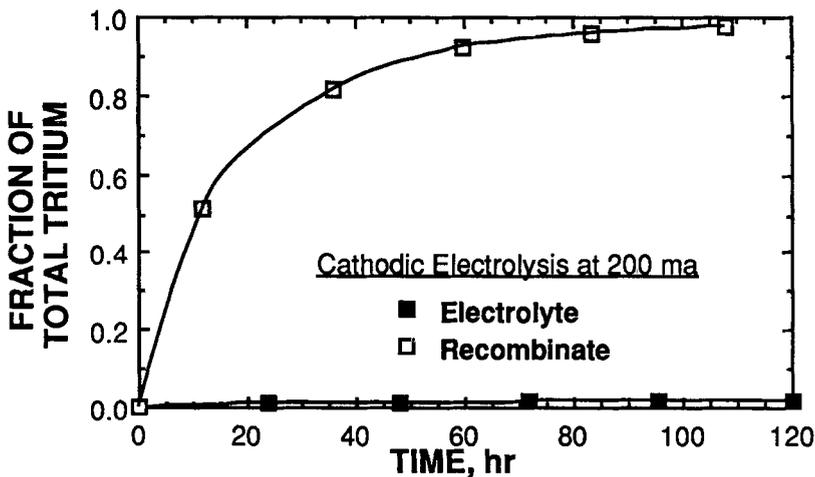


Fig. 11. Fraction of tritium released from contaminated palladium in the gas and in the electrolyte as a function of time. This cell (#2B) was electrolyzed at 200 ma.

This loss of tritium is first-order in all cases with a rate constant that depends on the excess volume, loading rate and electrode shape. Other variables may be important but were not investigated in this work. Figure 12 compares the log total tritium concentration divided by tritium concentration at various times for two typical electrodes. All samples had  $R^2$  values above 0.997.

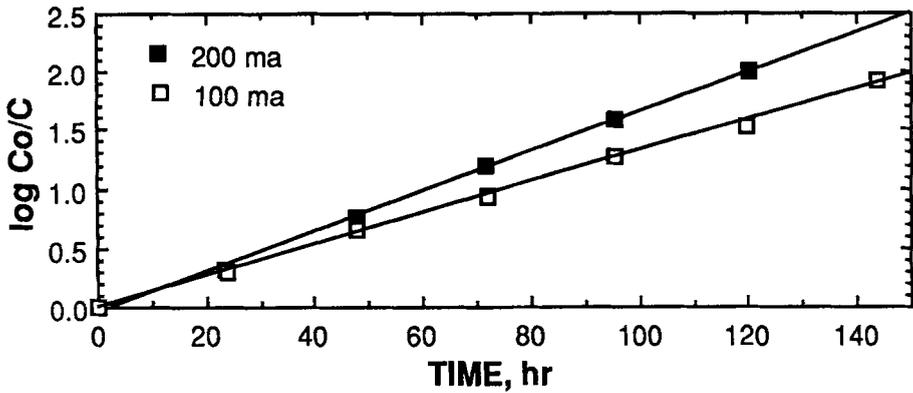


Fig. 17. Time variation of log (initial tritium concentration in the electrode divided by the tritium concentration after the indicated time). The palladium electrode was electrolyzed as the cathode at the indicated currents.

The rate constant increases as the cell current is increased but a limiting value is approached. This can be seen in Fig. 18 for a disc shape, normalized to 20% excess volume. Above 300 ma (52 ma/cm<sup>2</sup>), we propose that any additional current increase produces mostly gas that leaves from the surface without diffusing into the palladium. The study suggest that an increase in charging current has a greater effect when the concentration of channels is lower.

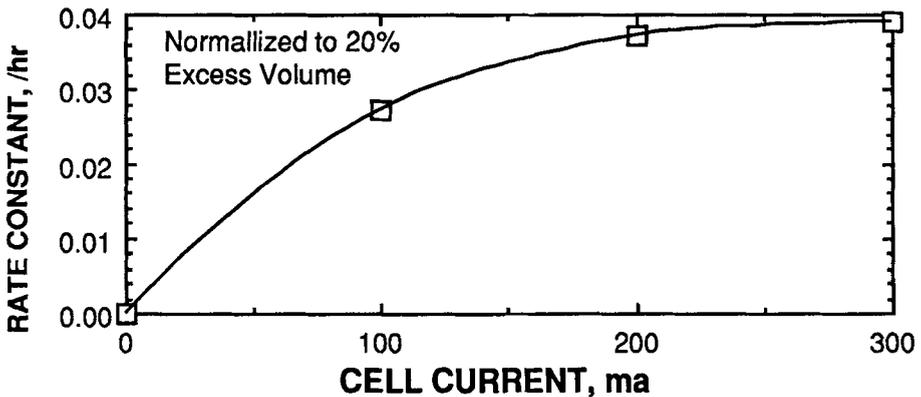


Fig. 18. Rate constant for hydrogen removal vs cathodic cell current adjusted to 20% excess volume. Area = 5.78 cm<sup>2</sup>

One disc was loaded with tritium and electrolyzed as the anode. Essentially all of the tritium ( $\approx 99.4\%$ ) appears in the electrolyte. Figure 19 shows the tritium content of the electrolyte in terms of the amount of tritium contained in the electrode as a function of square root of time. When the fraction reaches 1.0, all of the contained tritium would have been transferred to the electrolyte. A break in slope is observed at a composition that other studies suggest corresponds to the first formation of  $\alpha$ -phase. This behavior indicates that the loss of tritium (hydrogen), under this condition, is diffusion controlled. The diffusion rate apparently increases once some  $\alpha$ -phase forms.

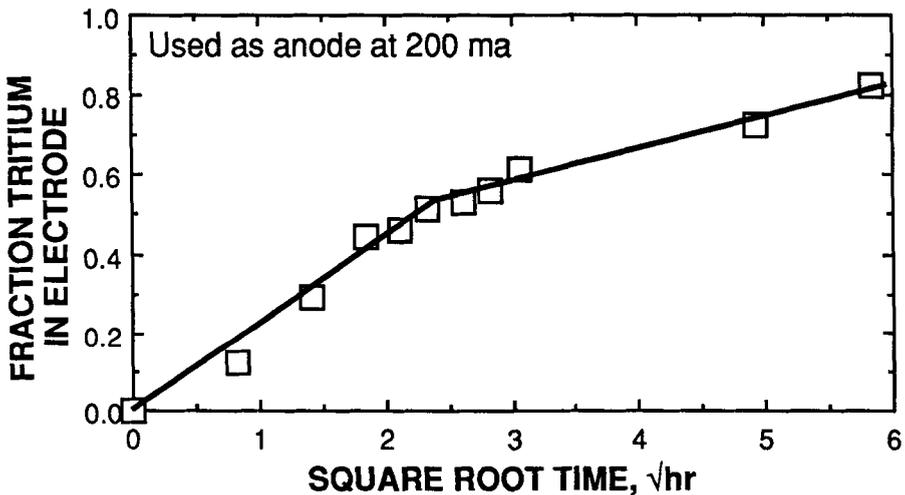


Fig. 19. Fraction of tritium contained in the electrode that appeared in the electrolyte vs square root of time.

## DISCUSSION, Part 2

Tritium present in a cathode appears in the gas. This behavior suggests that there is a flux of hydrogen that passes through the electrode even when the electrode has become saturated with hydrogen. This flux sweeps tritium (hydrogen) to channels where gas forms on the channel surface. This gas moves to the surface of the electrode where it leaves as bubbles. The greater the number of channels that are present, the easier this hydrogen can leave, and the lower is the achievable hydrogen content. This behavior can be seen in Figure 20 where two rods are compared after being

charged for 24 hrs at each current. The rod having the lowest excess volume achieved the highest D/Pd ratio. However, sometime after a ratio of 0.77 had been reached in this rod, the excess volume increased with a corresponding reduction in the ratio to 0.65. Apparently, this increase in excess volume allowed a sufficient loss

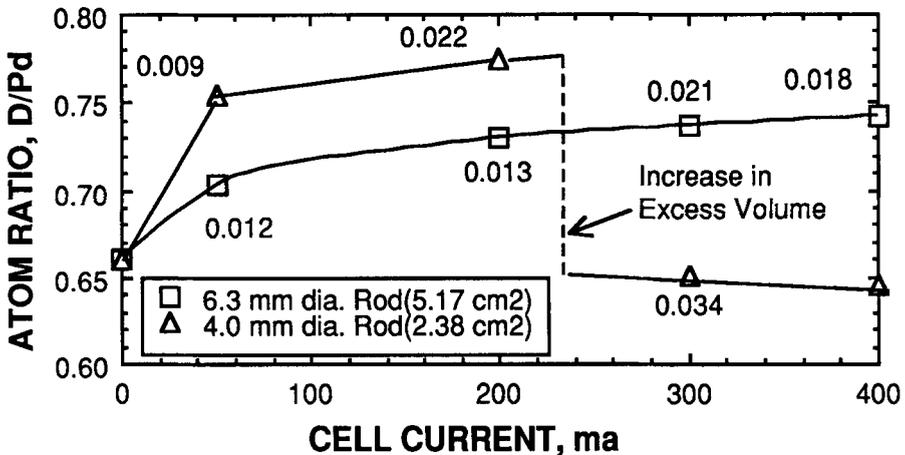


Fig. 20. Effect of excess volume produced by increased cell current on the average D/Pd ratio. The excess volume is indicated for each point.

rate for deuterium, so that an increase in charging current could not increase the composition. This behavior further indicates that some of the excess volume communicates with the surface. When this communication occurs, the average D/Pd ratio falls and no amount of cell current can significantly increase the value. This effect can happen at a relatively low excess volume which depends on the size and shape of the electrode.

## GENERAL DISCUSSION

The ability to achieve high, bulk deuterium compositions in palladium electrodes depends, in part, on the absence of excess volume. Production of this volume has a complex relationship to electrode history, shape, purity, and other, still undefined, factors. This study has shown that this phenomenon needs to be considered when trying to achieve high deuterium compositions.

Electrodes that are contaminated with tritium will deposit the tritium in the gas when used as a cathode. This behavior

means that tritium found in the electrolyte and attributed to cold fusion can not be blamed on tritium contamination of the electrode. Even the presence of spot contamination, caused presumably by islands of a stable hydride, would not cause this tritium to enter the electrolyte. If this stable hydride releases tritium, it will have to pass through the palladium lattice in which it will be subjected to all the chemical factors that affect dissolved tritium. Only if these islands are located on the surface would an exchange with the electrolyte be conceivable. If this were the location, exchange with the electrolyte would be expected to occur immediately after the electrode was placed in the cell, not after many hours of electrolysis. Dissolved and spot tritium can be easily detected by electrolyzing the electrode as an anode. In this mode, all of the tritium will eventually appear in the electrolyte.

### ACKNOWLEDGEMENT

The authors are grateful to the following for their valuable help: Don Ott (M-1) for NMR analysis to determine the D/H ratio, Joe Bubernak (CLS-1) for taking tritium samples, Tom Zocco (MST-5) for TEM examination, and Robert Reiswig (MST-6) for metallographic examination. Financial support was provided by the U.S. Department of Energy, and steady encouragement was given by B. Matthews (NMT-1) and J. Anderson (MST-3).

### REFERENCES

1. E. Storms and C. Talcott, "Electrolytic Tritium Production", *Fusion Tech.* **17**, 680 (1990).
2. E. Storms and C. Talcott, "A Study of Electrolytic Tritium Production", *The First Annual Conference on Cold Fusion*, Salt Lake City, Utah, 28 Mar. 1990.
3. E. Wicke and G. H. Nernst, "Zustandsdiagramm und thermodynamisches Verhalten der Systeme Pd/H<sub>2</sub> und Pd/D<sub>2</sub> bei normalen Temperaturen: H/D-Trenneffekte", *Ber. Bunsen Ges. Phys. Chem.* **68**, 224 (1964).
4. J.E. Schirber and B. Morosin, "Lattice Constants of Beta-Pd-H<sub>x</sub> and Beta-PdD<sub>x</sub> with x Near 1.0", *Phys. Rev. B* **12**, 117 (1975).
5. W. Krause and L. Kahlenberg, "On Palladium-Hydrogen", *Trans. Electrochem. Soc.* **68**, 449 (1935).