TITLE: EVOLUTION OF TRITIUM FROM DEUTERIDED PALLADIUM
SUBJECT TO HIGH ELECTRICAL CURRENTS

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EVOLUTION OF TRITIUM FROM DEUTERIDED PALLADIUM SUBJECT TO HIGH ELECTRICAL CURRENTS

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ABSTRACT

An increase in the tritium level was detected in deuterium when various configurations of palladium foil or powder and silicon wafers or powder were subject to a high pulsed current. The deuterium, at one atmosphere pressure, was circulated in a sealed loop containing the cell and an ionization chamber to measure the tritium increase as a function of time. Over 4800 hours of data, spanning 10 cells (including deuterium and hydrogen controls), were collected with this system. Average tritium production has varied from 0.02 to 0.2 nCi/h. Due to experimental constraints we have not been able to measure neutron output with these cells while simultaneously measuring the tritium increase. The question of tritium contamination in the palladium has been primarily resolved by the development of techniques that allow the palladium powder or foil to be reused. Various methods for increasing the tritium production, such as, increased current density, surface modifiers, and higher deuterium loading, will be discussed.

1. INTRODUCTION

The anomalous appearance of small amounts of tritium has been repeatedly observed in electrolytic and solid state gas loading experiments[1,2,3,4,5]. Some of these results were obtained with gas loaded discharge tubes operated at 25 kV, some with voltages as low as 50 V in electrolytic cells and some with only cyclic hydriding and dehydriding of metal. The only readily common features in all the experiments are the presence

of palladium (or other metal), deuterium and a disequilibrium condition for the deuterium. We will report on our tritium generation results from the Pd-Si-D cell when it is subjected to periodic unipolar current pulses. The primary advantages of this experiment are that it is reproducible, produces readily detectable tritium levels in a few hours or days and offers the possibility that it could be much more efficient. In our previous work, all tritium data was obtained in a batch mode, here we will, primarily, discuss our latest tritium results with a new, more sensitive, on-line tritium monitor.

Some have criticized[6] the detection of tritium because the signals are too low level, tritium is seemingly omnipresent and the palladium metal is subject to possible tritium contamination. We will briefly discuss the possible avenues for contamination and show that each is negligible in the experiments described. The magnitude of the signals discussed in this paper are multi-sigma and are often over a hundred times the tritium background in the supply gas. Furthermore, tritium may be the most sensitive and rapid indicator of anomalous nuclear behavior in deuterided metals. As such, it is well suited for rapid parametric investigations.

2. MATERIALS

The detailed analysis of our materials (Pd,Si,D2) has been described previously[1]. For this work we used, exclusively, either the Liquid Carbonic or Cryogenic Rare Gases deuterium that has less than 0.15 nCi/l of tritium. The major impurity in the deuterium is H_2 (0.6%). Major impurities in the Engelhard palladium are oxygen (980 ppm) Chlorine (80 ppm), Nitrogen (65 ppm) and Carbon (17 ppm), all other major impurities are (each) under 35 ppm by weight. A total of 159.3 g of palladium powder was used in our recent experiments described in this paper, of that amount, 38.5 g was used in various control experiments to test for tritium contamination. A total of 43.2 g of palladium foil (99.9%) from Johnson and Matthey was used in the foil cells; 0.44 g of this foil was checked for tritium contamination.

The 220 micron thick foils were always annealed at 850 C for 2 h at 10⁶ torr before use. These foils have been hydrided, dehydrided and annealed seven times and show neither a monotonic decrease nor increase in tritium production. Palladium powder can also be reused in experiments once it has been reoxidized at 623 K.

Tritium contamination in the palladium was tested

by three independent methods: dissolution and scintillation counting[7], hydriding and dehydriding and measurement[8] of ^{3}He. By these means we can assign an upper limit on tritium contamination of 0.005 nCi/g (i.e., no tritium detected within experimental error).

The silicon powder size distribution and morphology have been discussed previously[1], however, we are now using a monosized, sieved, intrinsic silicon with a particle size of 10 to 20 μm. Added to the silicon powder was 3% (wt) of either PVA or Dow XUS 40303 binder. These binders, ethanol solvents and silicon powder were tested for tritium contamination. No tritium could be detected over background. It has been found that the Dow binder contains a significant (300 ppm) amount of sulfur. The binder can be reduced during cell operation releasing the sulfur.

In this report, cells 39 and 40 were made of alternating layers of palladium foil and silicon wafers, while cells 41, 42 and 46 were constructed with palladium and silicon powder. A typical cell, made with powders, might contain 12 to 21 grams of palladium in eight layers and 6 to 8 grams of silicon distributed between seven layers. The palladium powder for cell 46 was pressed (11.2 MPa, 2000 psi) into disk form and then oxidized, in air, at 623 K for 2 hours (weight gain of 0.37%).

3. APPARATUS

Shown in Figure 1 is the stainless steel gas analysis loop containing a three liter ion gauge and a 310.9 cc calibration volume. The pressure gauges, ion gauge and sample and room temperatures are recorded on a computer log at 200 s intervals. In operation, a solid state cell would be attached to the loop and hydrided in situ with deuterium or hydrogen or a mixture of gas. The pressure drop during hydriding indicates the stochiometry of the PdD_x. The environmental chamber also enables us to heat (500 K) and cool (200 K) the sample allowing various levels of stochiometry.

The Femtotech ion gauge rejects pulse type radioactive events that effectively discriminate against radon and cosmic ray ionization. Prior to this study, the Femtotech background was usually between 1.8 and 2.2 nCi/l and had a low drift, initially (0.006 nCi/l-hr). It should be noted that the present instrument was calibrated with a gamma source so that the intrinsic drift rate of the loop would be as low as possible. Two micron filters are installed at the inlet of the ion gauge and at the outlet of the cell to
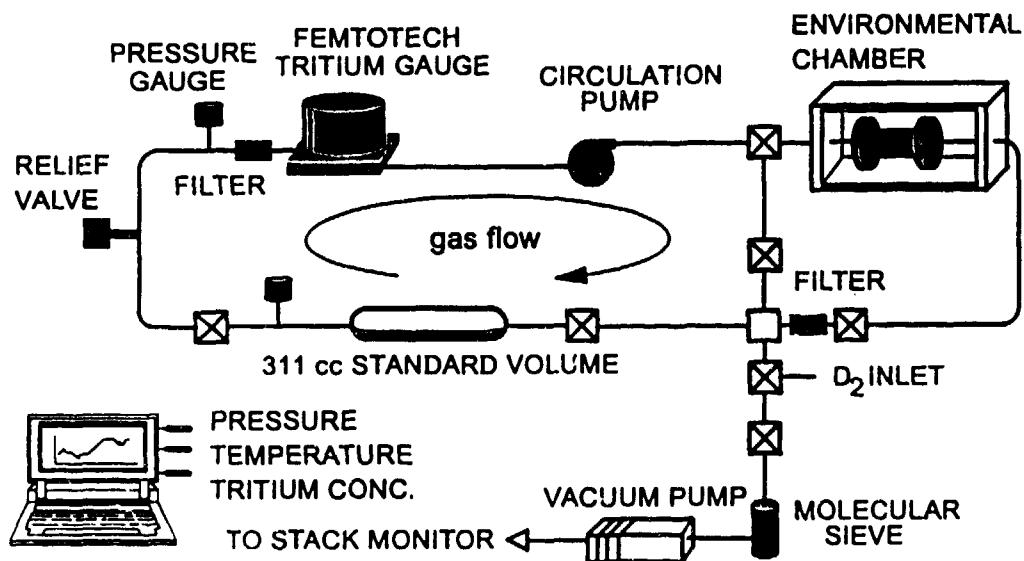
Figure 1. Tritium analysis system used in this study.

eliminate spurious responses due to particulates.

4. PROCEDURE

The procedure for hydriding a cell was to first fill the 3 l loop with deuterium gas at 600 to 1200 torr and measure the background tritium concentration, if possible. The gas would then be circulated around the loop for several days to determine if the apparent background rate is increasing. If the drift rate was less than 0.06 nCi/h then the loop was judged sufficiently clean to initiate a new powder-powder cell experiment. With the loop drift rate measured, fresh deuterium was introduced into the loop and the cell hydrided slowly with the deuterium flowing in the loop.

After the cell had been hydrided, the gas was circulated with the cell in place from 15 minutes to several days to again determine the background drift rate. Repetitive voltage pulses were then applied to the cell at 100 pps with a width of 200 us. Typically, the foil-wafer cells were run at 200 V and currents up to 25 A, while the powder-powder cells were run at 800 V at 1 A.

To dehydride the samples, the environmental chamber temperature was increased to 473 K. This caused the majority of deuterium to be released from the palladium. A final dehydride could be accomplished by closing off the cell evacuating the loop and then opening the hot cell to vacuum. The last 6-10% of the deuterium could be recovered by this method.
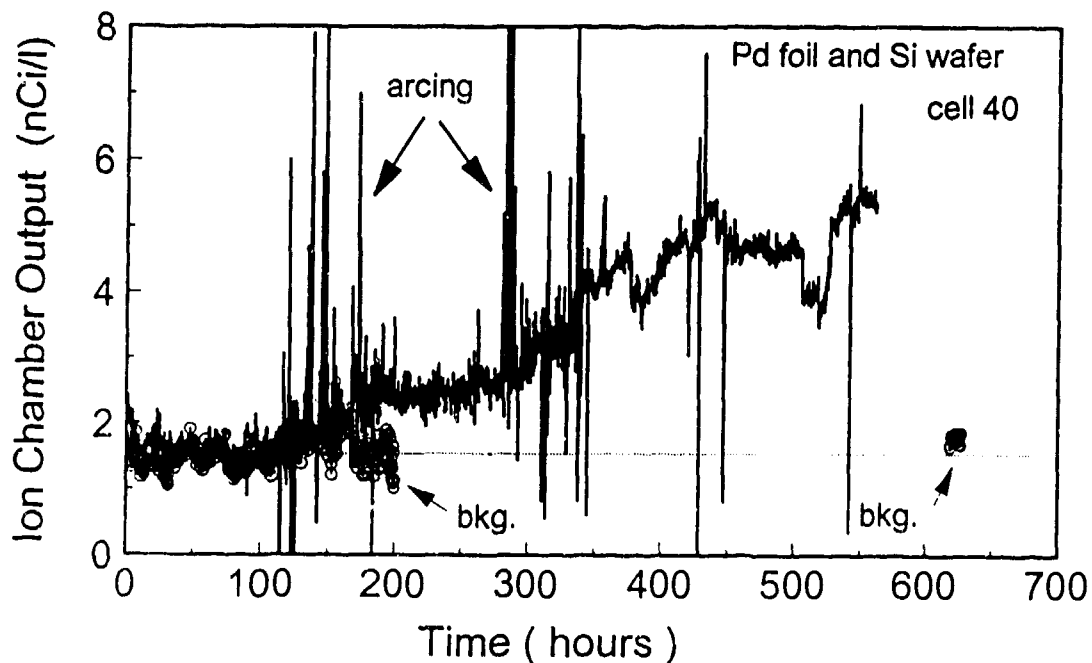
Figure 2. Comparison of background and foreground
results with palladium foil.

5. RESULTS

Shown in Figure 2 is the time evolution of tritium
from the first palladium foil cell (40) to be run in
the system after the Femtotech was connected to the
computer. Figure 2 shows the background (open circles)
level (prior to run 40) and the foreground level, with
cell 40 but without current excitation, for nearly 110
h. The curves are nearly identical. After 110 h the
cell was pulsed at 170 V at 5 A. The onset of the
pulsing is indicated by the large current spikes due to
ionized gas that entered the ion chamber. During this
time the tritium output increased until about 200 hours
when the voltage was turned off. The pulsing was halted
because it was unclear what effect the large ion pulses
were having on the background tritium level. However,
at 200 hours there is a clearly different tritium level
for the background and for the cell. The background run
only extends contiguously from 0 to 200 hours because
it was taken prior to the running of Cell 40 and it was
unknown how long experiment 40 would continue. From 200
to 290 hours the current was off and the tritium level
remained relatively constant. At 290 hours the voltage
pulsing (400 V at 12.5 A) was again resumed resulting
in large current spikes. After about 350 hours the cell
stopped arcing however, the tritium level continued to

increase. The Femtotech was recalibrated at 375 hours resulting in a sudden drop in the reading. After 450 hours the current was discontinued. Finally at 560 hours the cell was dehydrided. Immediately after the dehydride, the old deuterium was pumped out and replaced with fresh gas. The background tritium level with the fresh gas is seen to be within 6% of the initial value. The total amount of tritium in this cell was then determined to be about 10.2 nCi or 0.043 nCi/h. Prior to this, the loop drift rate was less than 0.006 nCi/h. Therefore, the generation rate with the cell was about a factor of 7 greater than without the cell.

A summary of the next series of experiments is shown in Figure 3. Cell 41 was run immediately after cell 40 and was a control cell consisting of 20 g of palladium powder and 10 g of silicon powder pressed into disks and placed in a cell to be deuterided but not pulsed. The first 24 h after cell 41 was hydrided showed no increase in tritium output, therefore as a worst case it was decided to heat the cell to determine if the tritium level would increase. The curve is marked where the heating began and an immediate rise in tritium level was noted. This was not unexpected because the stainless cell chambers had been previously used with active tritium producing cells. After 210 h cell 41 was completely dehydrided resulting in a total increase of 7.2 nCi or 0.034 nCi/h or slightly less than the foil cell. However the foil cell was run near room temperature (308 K) rather than 423 K. After cell 41 was removed and the old deuterium pumped out, fresh deuterium was introduced into the loop at 600 torr and circulated in the loop (no cell) at room temperature for 210 h. The drift rate with this gas was 0.006 nCi/h.

Next, cell 42 was prepared as a standard 9 layer Pd-Si cell and was hydrided with fresh gas. The gas was circulated through the loop and the cell for 15 minutes to let the Femtotech stabilize and then the current was applied resulting in an almost immediate rise in the tritium level as shown in Figure 3. The temperature of the cell did not rise enough (5 K) to notice any significant dehydriding of the palladium. The pulsing conditions were initially 1000 V, 0.1 A (chosen to mitigate the possibility of breakdown of the cell). As the experiment continued, the voltage and current were increased slowly (to 1200 V). After 210 h the voltage was discontinued and the cell dehydrided by raising the temperature to 200 C. The excess tritium in the cell and the average rate of generation was 25.1 nCi and 0.11 nCi/h respectively for tritium gas (DT).
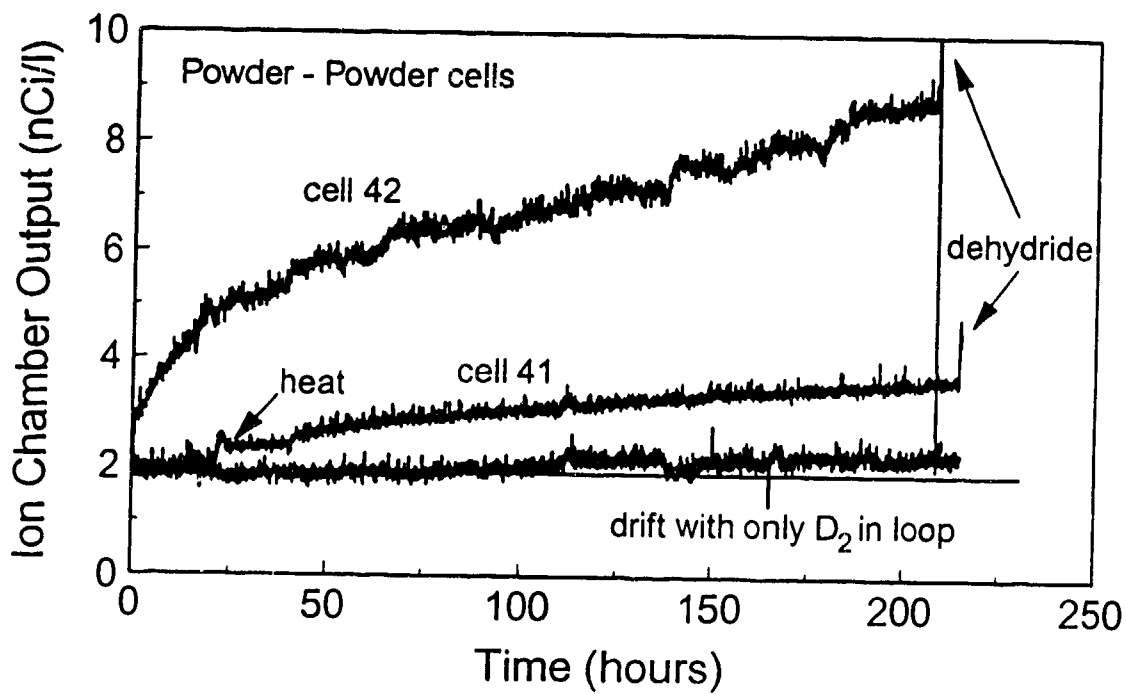
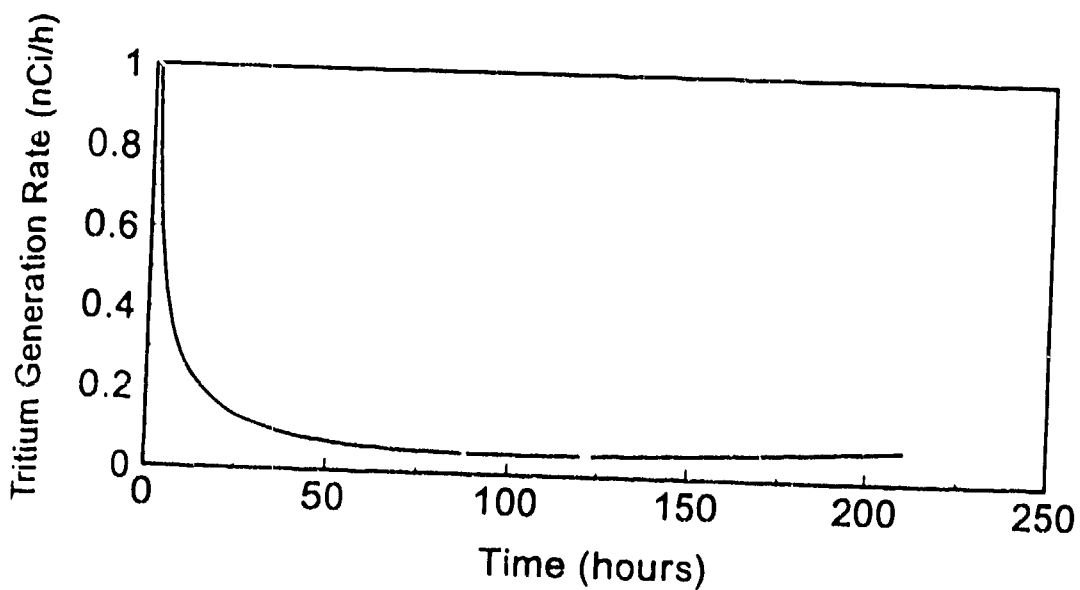Figure 3. Comparison of background, hot control cell and active powder cell.

Figure 4. Tritium generation rate from cell 42.

Figure 4 shows the tritium generation rate for cell 42 as a function of time. Two features are evident, the initial rate of tritium evolution can be as much as 10 times the average rate and the rate at

long times increased slightly perhaps due to the increased pulsing current. The nonlinear slope is directly observable in Figure 3. The slope for the control cell, by comparison, appears to be approaching an asymptote typical of a source of tritium diffusing out of the wall of the vessel.

After cell 42, it was found that the loop was severely contaminated with TDO and the drift rate with hyarogen or deuterium in the loop was nearly the same as with cell 42. Repeated flushes and heating of the system were required to clean up the loop. If we attribute all the post run tritium to cell 42 we find that the cell produced a total of 173.8 nCi (1.08 nCi/h). Ultimately, the drift rate of the system could be reduced only to about 0.03 nCi/h, much higher than the 0.006 nCi/h drift rate found prior to cell 42.

The experimental run with cell 46 clearly illustrates the problems that the tritiated water generated in these cells can cause in the loop. Shown in figure 5 is a comparison of cell 42 and cell 46 that is identical in construction to 42 except that the palladium (in cell 46) had been oxidized as previously explained. Cell 46 was hydrided at 258 K to retain any water vapor that might be generated during the exothermic hydride process. After about 5 hours the liquid nitrogen dewar ran empty and the temperature rose releasing the water vapor resulting in a quenching of the ion gauge and an apparent decrease in output. The ion gauge reading recovers after about 10 hours and at the time indicated in the figure the pulser was started, resulting in a further increase in the tritium level.

At 140 hours the current was raised abruptly to 1 A. The generation rate of tritium increased after this change. After 210 h the experiment was terminated and the cell was dehydrided resulting in 21 nCi detected in the gas. The cell was then dehydrided and was disconnected from the loop, this caused the gas flow to greatly increase due to the removal of the palladium and silicon powder plug. The increased flow caused the ion chamber output to swing negative and then positive. The chamber output eventually stabilized at 29 nCi/l or a total of 81 nCi.

It should be noted that the powder used in cell 46 was reused from a hydrogen control cell (43). Because cell 43 was run after cell 42 and the contamination from 42 was not fully appreciated, the drift rate on the hydrogen control was unacceptably high (0.095 nCi/h) but the reused powder from cell 46 still exceeded this value if only the TD is taken (0.136 nCi/h) and very much exceeded the value if all the
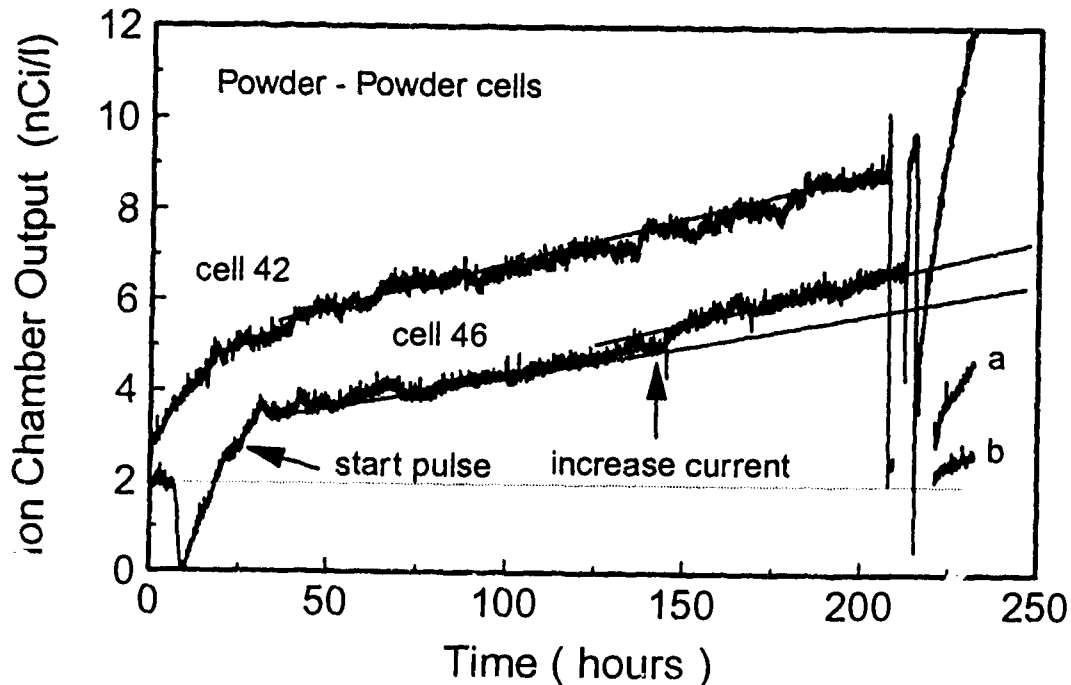
Figure 5. Tritium generation from cell 46 and 42.

tritium (TD+TDO) detected is taken into account (0.47 nCi/h).

Also shown in Figure 5 is the background and drift rate in the loop with just hydrogen immediately after cell 46. A section of this curve is labeled "a". As can be seen, the background is elevated from the nominal value of 2 to about 2.8 nCi/1 and the drift rate of the loop is much higher than any of the backgrounds without cells. After 2 hot flushes of hydrogen the drift rate and background are as shown in segment "b". It is seen that the drift rate has decreased and the initial background is nearly equal to the "normal" value of 2 nCi/1. This is very strong evidence that cell 46 put tritium into the system. It was eventually found that 7 or more flushes were required to return the loop to a low drift state with dry hydrogen. However, with wet (0.1% H_2O) hydrogen four or more additional flushes are necessary before the source of tritium seemed to be exhausted.

6. DISCUSSION

Tritium has been detected in these Pd-Si systems when excited by unipolar pulses. There are four plausible sources for the excess tritium. The tritium could be contamination in the palladium, silicon or

binder, the tritium could be hiding in the loop, the tritium could be coming out of the cell container and finally the tritium could be generated in the palladium.

Since no tritium could be detected in any of the materials the possibility that the loop or the cell body is contaminated has to be considered. The cell bodies were heated to 473 K in deuterium with all constituent parts except for the powder. No excess tritium could be detected in this test.

The next most likely source of excess tritium is from hideout in the loop itself. The loop has been previously exposed to tritium for calibration purposes and other cells have generated copious amounts of tritium that may have diffused into various parts of the system. In one test, (during the cleanup after cell 42) the Femtotech was valved off from the rest of the loop and showed no drift (< 0.02 nCi/h) but when the valves were open the tritium level immediately jumped and the drift rate increased to 0.12 nCi/h. The loop was heated to 423 K for this test to promote cleanup.

Another possibility is that the ionization gauge may be directly affected by some agent originating in the cell such as water vapor, CO_2 or carbon deposits caused by the arcing. It is unlikely that the carbon deposits could have migrated to the ion chamber to cause enhanced leakage since the background after cell 40 was very close to the initial value. It is also very unlikely that there would have been enough of a change in the composition of the gas to change the ionization efficiency by any significant amount since additions of CO_2 (1 to 5 torr out of 1200 torr) are undetectable by the ion chamber. The fact that the chamber did not drift with the valves closed yet the system was drifting indicates that contamination of the ion chamber itself is not the primary factor. Furthermore, it is apparent that the ion chamber can be quenched by the presence of water, but we have no evidence that leakage current due to adsorbed water on the probe insulator will give anything other than a negative reading.

From what has been discussed above it should be apparent that the loop contains various reservoirs for TDO hideout and storage. We believe the storage is of TDO rather than TD based on our extensive experience with similar systems that have been exposed to high levels of gaseous tritium. These systems can be cleaned up quickly and without the problems we have experienced here.

The TDO is released slowly over a period of days as the material exchanges with normal water or is

deadsorbed from the surfaces of the loop. Many flushes of hydrogen or deuterium are required to remove the water and to return the loop drift rate to a low level.

Cell 41 and 42 should be viewed as cells that were run with a relatively clean system containing very little adsorbed TDO. The drift rate as seen in Figure 3 was low initially and after cell 41 but very high after cell 42. We attribute this to the formation of TDO in cell 42 and also in cell 46 due to the oxide layer on the powder. Foil cells have no oxide and did not exhibit this effect.

Since the TDO was not present in the loop initially, it must have come from the powder. The TDO had to be generated in the cell because the powder has no detectable tritium. It is not clear at this point if this implies a faster reaction at the surface (near the oxygen), but clearly the TDO was generated in the first 24 to 50 hours of operation. After that, the apparent rate of tritium generation is influenced by the exchange and deadsorption rate of the TDO.

7. CONCLUSIONS

A reproducible method of tritium generation has been demonstrated. The tritium output scales with the current applied to the cells. The tritium yield is found to depend strongly on the type of palladium metal used (powder or foil). Various tests for tritium contamination confirm that there is no chance of initial tritium contamination in the powder, foil, or other materials used in this study.

Annealing of the palladium seems to be necessary to reactivate foils after a deep dehydride. Lower values of stochiometry or lower gas pressures are less efficient for the generation of tritium. In the experiments conducted to date, tritium production is not enhanced by increasing the concentration of hydrogen in the deuterium gas.

On the basis of an analysis of all our experiments and those of others[9] it appears that the tritium is produced during the dehydriding of palladium deuteride with a surface impurity layer. The layer in the case of the powder and the foil may be an oxide or a monolayer of adsorbed CO. Other impurity layers such as metals may be much more effective. The main effect of the current is to dehydride the palladium by heating. Only a small area near the surface is important to this process. The foil is less productive than the powder because of smaller surface area and the fact that the surface barrier is largely absent. In the powder cells,

the rapid decline in tritium production at the start of
the experiment may be due to the depletion of the
favored oxygen sites at the interface. The only
purpose of the silicon is to provide a non ohmic heat
source near the palladium surface. Arcing is less
efficient than cyclic heating because the arcing
essentially melts the palladium resulting in a complete
dehydride, the material then would have to be
reannealed to become active. However, partial
dehydriding within the two phase region perserves the
activity of the material.

If our conclusions are correct, it should be
possible to construct much more efficient cells with
less material. More robust partially permeable surface
modifiers are available and microfabrication of the
palladium would allow rapid hydride-dehydride cycles.

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