

# Investigation of Fusion Reactions in Palladium and Titanium Tritide Using Galvanostatic, Coulometric, and Hydrogen Permeation Techniques

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We describe several electrochemical methods used to investigate the possibility of cold fusion phenomena in palladium and titanium tritide cathodes. We performed long-term (up to 77 days) electrolysis experiments with electrochemical cells of the University of Utah type at current densities as high as 1 A/cm<sup>2</sup>, while monitoring neutron and tritium levels. With some cells, we pulsed the current to determine if neutron bursts would result. In another cell, we used titanium tritide as the cathode to determine if D-T reactions yielding neutrons would occur. In no instance were levels of neutrons or tritium significantly above background except in the titanium tritide cell where isotopic exchange, occurring between the electrode and the electrolyte, resulted in significant tritium levels. We also combined x-ray photoelectron spectroscopy (XPS) and electrochemical hydrogen permeation experiments to determine the effectiveness of various Pd surface treatment procedures on the resultant electrochemical hydrogen absorption efficiency. Electroanalytical and thermal desorption/gas analysis techniques indicated the maximum loading of H in Pd was to a ratio of H:Pd = 0.8.

**KEY WORDS:** Hydrogen-permeation techniques; coulometric techniques; hydrogen: palladium ratio; hydrogen absorption efficiency.

## 1. INTRODUCTION

We describe the application of a variety of electrochemical methods and our results in applying them to investigate cold fusion phenomena in palladium and titanium tritide cathodes. Initially, we used galvanostatic techniques in an attempt to duplicate the University of Utah neutron fluxes.<sup>(1)</sup> We also utilized coulometric and Devanathan–Stachurski<sup>(2)</sup> electrochemical permeation techniques to analyze the loading of Pd with hydrogen. We determined the H content of Pd electrodes by quantitative coulometry during discharge of a loaded Pd electrode. Using the Devanathan–Stachurski method, we determined the effective hydrogen permeation flux of Pd foils as a function of surface treatment. This method allowed us to determine the fraction of H atoms (from the discharge of H<sub>2</sub>O) that entered the Pd lattice as a function of applied current density. The purpose of the coulometric and permeation experiments was to deter-

mine if there are surface treatments which allow full loading of a Pd electrode to a H:Pd ratio of 1.0.

## 2. EXPERIMENTAL

Our initial cells used galvanostatic techniques with no reference electrode in an attempt to duplicate the neutron fluxes observed in the University of Utah experiments.<sup>(1)</sup> In some cells, we used Pd/D reference electrodes to measure cold fusion cell potentials. The Pd/D reference electrodes were made by charging Pd with D in 0.1 M LiOD/D<sub>2</sub>O.<sup>(3)</sup> Potentials of the Pd/D reference electrodes, measured vs. a saturated calomel electrode (SCE) in 0.1 M LiOD/D<sub>2</sub>O, were -0.98 volts, in agreement with previous measurements.<sup>(4)</sup>

In cells with Pd cathodes, we used extruded Pd wire (99.99% from Engelhard) or rod (99.99% from Marz), initially as received and, in subsequent cells, after annealing at 1050°C in 10<sup>-6</sup> torr vacuum for 16 hours. We cleaned the Pd working electrodes using a 50 mA/cm<sup>2</sup> anodic/cathodic cycle for 100 sec followed by a second

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cycle for 30 sec, and performed the loading experiments in 0.1 M LiOD/D<sub>2</sub>O with Pt cage counter electrodes.

Anodic/cathodic cycling was not used on the titanium tritide cell to avoid damage to the electrode. This cathode was fabricated by depositing a thin film of titanium tritide on a copper substrate. For this cell, a Pd wire coil counter electrode was used.

Electrolytes were made using 99.9% isotopically pure D<sub>2</sub>O (Aldrich) or pyrolytically distilled H<sub>2</sub>O. The electrolytes were made in a glove box by dissolving >99.9% Li (Foote Mineral) of naturally occurring isotopic abundance directly in the D<sub>2</sub>O or H<sub>2</sub>O.

The neutron detectors were based on the capture of neutrons in a tube filled with <sup>3</sup>He gas. Detectors for both the palladium and titanium tritide experiments were of similar design. The detector for the titanium tritide experiment is detailed here. The neutron detector is based on a Los Alamos SNAP-II design produced commercially as Directional Fast Neutron Detector Model RD-23. The electronic control unit and readout was a Smart Radiation Monitor-200 (Eberline Instrument Corp.). The detector consists of two gas proportional counter tubes (2.5 cm in diameter, 20.3 cm long, filled with 4 atm <sup>3</sup>He) imbedded in a polyethylene cylinder (12.7 cm in diameter, 25.4 cm long). Neutrons are detected via the <sup>3</sup>He(n,p)<sup>3</sup>H nuclear reaction in which a thermal energy neutron interacts with a <sup>3</sup>He nucleus to produce a proton and a triton. Each such interaction produces an electrical pulse in the tubes that is amplified, pulse height analyzed, and counted. If fast neutrons are emitted from the test cell, located adjacent to the neutron detector, some will be slowed to thermal energies by collisions in the polyethylene cylinder. Some fraction of the thermal neutrons will reach the detector tubes and be counted. The polyethylene cylinder is surrounded by a sheet of cadmium (0.8 mm thick) that shields the detector from externally produced thermal neutrons. A polyethylene annulus 5.8 cm thick around most of the cylinder shields against external background fast neutrons. In this experimental arrangement, additional polyethylene slabs 6 cm thick surrounded the test cell and neutron detector for additional shielding.

The neutron counter was calibrated by placing a californium-252 spontaneous fission source (average neutron energy 2.3 MeV) emitting  $7.0 \times 10^4$  ( $\pm 4\%$ ) neutrons per second at the location of the test cell. The counter has essentially the same response ( $\pm 10\%$ ) to the neutrons from Cf-252 as to the 2.45 and 14 MeV neutrons from deuterium fusion. The observed counting rate with the source in place of 910 count/sec indicated an efficiency of 1.3% (counts per 100 neutrons emitted from

the cell). This compares to an estimated efficiency of the Fleischmann-Pons neutron detectors of 0.01%.<sup>(1)</sup>

The two neutron detectors used to monitor the palladium experiments used 11 <sup>3</sup>He tubes inserted into a polyethylene moderator of dimensions 38 × 24 × 7.6 cm. The efficiency of each of these detectors for the experimental geometry was about 4%.

We also performed periodic sampling and analysis of the electrolyte in the cells, with appropriate blanks, to determine tritium concentrations by liquid scintillation counting.

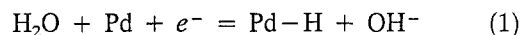
For the coulometric experiments to determine H:Pd ratios, after loading the Pd working electrode with H by cathodic polarization in 0.1 M LiOH/H<sub>2</sub>O electrolyte we potentiostatically controlled the potential in the anodic regime such that it was sufficiently anodic to quantitatively oxidize all the H desorbing from the Pd but not so anodic as to promote the occurrence of competing reactions (such as H<sub>2</sub>O oxidation). For the permeation experiments, a 75- $\mu$ m thick Pd foil was mounted between two electrochemical cells. One half of the cell was used as the charging side to galvanically discharge H<sub>2</sub>O, again in 0.1 M LiOH/H<sub>2</sub>O electrolyte. The potential in the other half of the cell, controlled vs. an SCE, was set to oxidize the permeating H to determine permeation rates.

### 3. RESULTS AND DISCUSSION

#### 3.1. Hydrogen-Permeation Techniques

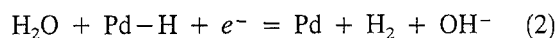
Adsorption, recombinative desorption, absorption, and solid-state diffusion of hydrogen in palladium occur in the following sequence:

(1) adsorption:

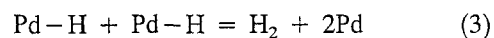


where Pd-H represents the hydrogen in a chemisorbed surface state,

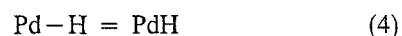
(2) surface recombination and desorption: this may occur by two possible sequences. One is electrochemical:



and the other is chemical recombination after surface diffusion:



(3) absorption:



where PdH represents hydrogen absorbed in the metal lattice at octahedral lattice sites, and

(4) diffusion:

$$dC(x,t)/dt = D\{d^2C/dx^2\} \quad (5)$$

where  $D$  is the diffusion coefficient of  $H$  in the metal lattice,  $C$  is the hydrogen concentration in the metal lattice,  $x$  is the distance into the metal lattice, and  $t$  is the time.

For the Devanathan-Stachurski permeation measurements, we charged a 75- $\mu\text{m}$  Pd membrane from one surface and determined the hydrogen flux exiting at the opposite surface. The hydrogen concentration in the chemisorbed state ( $\text{Pd}-\text{H}$ ) on the exit surface was maintained at zero by electrochemically oxidizing hydrogen that had diffused to and desorbed at the exit surface. At steady state, the electrochemical current measured at the exit surface is proportional to the hydrogen permeation flux:

$$i = nFd\{dC/dx\} \quad (6)$$

which, for the boundary conditions of our experiment, reduces to

$$i = nFDC/l \quad (7)$$

Here,  $i$  is the permeation current density,  $n$  is the number of electrons transferred in the  $H$  oxidation reaction,  $F$  is Faraday's constant, and  $l$  is the membrane thickness. For known  $D$  and  $l$ ,  $C$  is calculated from steady-state values of  $i$ . In the case of palladium, a two-phase composite sample is formed in the experiment described previously when absorbed hydrogen saturates the  $\alpha$  phase and forms the  $\beta$  phase starting at the charging surface (see Fig. 1). The  $\alpha$  phase will still exist at the exit surface since the  $H$  concentration is maintained at zero. In this situation,  $C$  at the charging surface and the Pd:H ratio cannot be determined unambiguously solely from the measurement of  $i$ . Nonetheless, the measured permeation flux given by

$$i = nFD_{\alpha}\{dC_{\alpha}/dx\} \quad (8)$$

can be measured at the exit surface and relates directly to the quantity of hydrogen absorbed. The following boundary condition must be satisfied at the  $\alpha/\beta$  interface:

$$nFD_{\alpha}\{dC_{\alpha}/dx\} = nFD_{\beta}\{dC_{\beta}/dx\} \quad (9)$$

In Fig. 2, permeation fluxes are plotted against charging current densities for five palladium cathodes that received a variety of surface pre-treatment procedures. Flame washing using a propane torch, palladizing

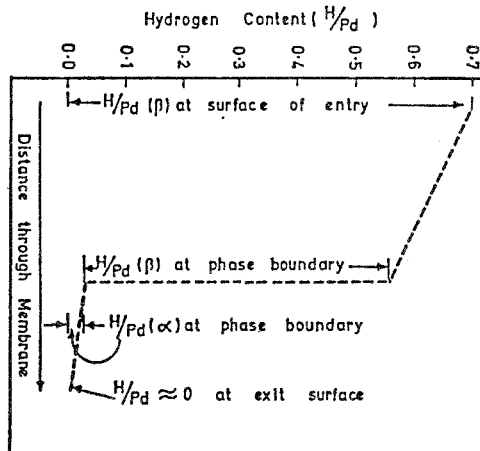


Fig. 1. Representation of the concentration gradient through a Pd membrane containing an  $\alpha$ ,  $\beta$ -phase boundary, during steady-state hydrogen permeation with a pressure of 1 atm  $\text{H}_2$  at the input surface, and very low concentrations of hydrogen at the exit surface at 25°C (from Ref. 5).

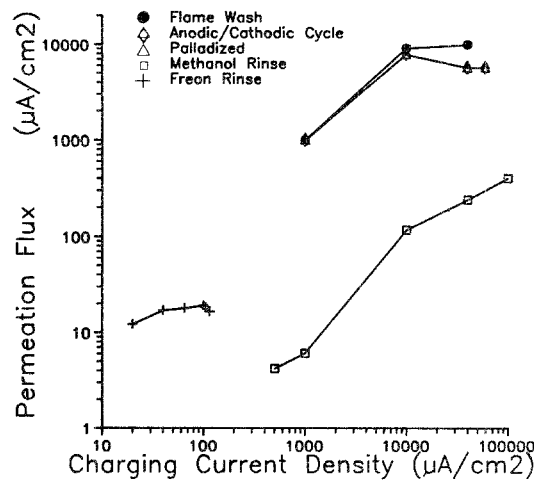


Fig. 2. Devanathan-Stachurski permeation results for 75- $\mu\text{m}$  Pd foils that received different surface pretreatment procedures. Electrolyte: 0.1 M LiOH in  $\text{H}_2\text{O}$ .

from a  $\text{PdCl}_2$  solution, and anodic/cathodic cycling in 0.1 M LiOD/ $\text{D}_2\text{O}$  are all effective means of enhancing hydrogen absorption into the lattice. In contrast, rinsing the palladium with organic solvents, methanol and freon in the present case, results in poor hydrogen absorption. The data of Fig. 2 is replotted in the form of absorption efficiency in Fig. 3. Even in the case of the best surface preparation procedures, absorption efficiencies decrease

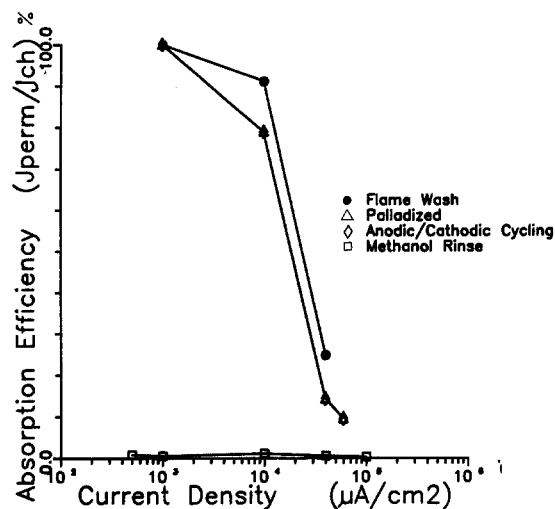


Fig. 3. Efficiency of absorption of H into lattice of 75- $\mu\text{m}$  Pd foils as a function of charging current density. Electrolyte: 0.1 M LiOH in  $\text{H}_2\text{O}$ .

tremendously at high charging current densities as most of the cathodic current contributes to hydrogen evolution (Eq. 2).

Surface studies of Pd foils cleaned under various procedures indicate a correlation between surface carbon content and electrochemical hydrogen absorption efficiency (Table I). Absorption efficiency is affected by contamination since sites suitable for H absorption are blocked by carbon. As-received surfaces and those cleaned in methanol have large carbon (1s) x-ray photoelectron spectroscopy (XPS) peaks and are poor hydrogen absorbers. Surfaces that were palladized, anodically/cathodically cycled, flame washed, or heat treated have small XPS peaks for carbon. Even for the best surface pre-

paration procedures, high charging current densities promote additional surface contamination and contribute to decreased absorption efficiencies.

### 3.2. Coulometry and Thermal Desorption

We determined absorbed hydrogen contents and H:Pd ratios of cathodically-charged Pd by three methods: (1) galvanostatic discharging and simultaneous monitoring of the potential of the Pd electrode, (2) potentiostatic discharging and coulometric determination of the quantity of desorbed hydrogen, and (3) thermal desorption and measurement of the volume of liberated hydrogen gas. For the latter, Pd foils were immersed in liquid nitrogen to prevent liberation of hydrogen during transfer to the vacuum chamber. In all three experiments, an H:Pd ratio, using flame wash and anodic/cathodic cycling surface preparation, of 0.8 was obtained indicating that ratios greater than one cannot be attained using these surface-preparation procedures when charging is performed at room temperature.

### 3.3 Cells of the University of Utah Type

Results for long-term electrolyses of cells patterned after those of Fleischmann and Pons<sup>(1)</sup> are summarized in Table II. In the two-electrode cells, cell voltages are primarily determined by applied current density, electrolyte resistivity, and cell geometry, i.e., configuration of the electrodes. For cell 2, the potential is reported vs. a Pd/D reference electrode, but still includes contributions from the uncompensated resistance in the cell. The cells were not immersed in thermostatted constant temperature baths; cell temperatures were therefore primarily a function of applied current density and resultant cell

Table I. X-Ray Photoelectron Spectroscopy Results on Pd Foil Cathodes

Cathode preparation	XPS signal (arbitrary units)					Hydrogen absorption efficiency at 10 mA/cm <sup>2</sup>
	Pd	O	C	S	Cl	
As received	16	19	62	1	1	—
Cleaned in methanol	22	22	47	7	1	1%
Palladized	48	34	17	0	0	79%
Anodic/cathodic cycling	50	32	17	0	0	79%
Flame washed	40	57	3	0	0	91%
600°C, air, 1 min	35	52	13	0	0	—
900°C, air, 1 min	35	52	11	0	0	—
600°C, vacuum, 30 min	49	31	14	5	0	—

Table II. Summary of Long-Term Electrochemical Fusion Cells<sup>a</sup>

Cell	Cathode	Electrolyte	Current density (mA/cm <sup>2</sup> )	Potential (volts)	Duration (days)	Tritium <sup>d</sup> content (counts/min)
1	Pd wire, extruded, 15 × 0.05 cm	0.5 M LiOD	40–80	3–5	36	48.1
2 <sup>b</sup>	Pd wire, extruded, 46 × 0.05 cm	0.1 M LiOD	40–110	0.5–1	33	47.6
3 <sup>c</sup>	Pd wire, extruded, annealed, 10 × 0.05 cm	0.1 M LiOD	65–990	4–18	61	49.1
4 <sup>c</sup>	Pd rod, extruded, annealed, 4.6 × 0.32 cm	0.1 M LiOD	65–350	5–16	77	47.9
5 <sup>c</sup>	Pd rod, extruded, annealed, 4.6 × 0.32 cm	0.1 M LiOH	65–350	4–14	77	16.9
6	Ti tritide, thin film on Cu substrate, 6 cm <sup>2</sup>	0.1 M LiOD	50–300	4–9	5	>10 <sup>6</sup>

<sup>a</sup> Additional cells were operated under various conditions for shorter times, but are not detailed here.

<sup>b</sup> This cell was operated in a three electrode configuration, with a Pd/D reference electrode.

<sup>c</sup> In addition to continuous operation at the current densities noted, cells 3, 4, and 5 were also pulsed between the low and high current densities to determine if neutron bursts occur.

<sup>d</sup> Compared with background levels of 18.5 counts/min for 0.1 M LiOH/H<sub>2</sub>O and 50.9 counts/min for 0.1 M LiOD/D<sub>2</sub>O.

voltage and ranged between 30–77°C. Tritium concentrations of the electrolytes were identical to baseline values, with the exception of the electrolyte in the cell containing the titanium tritide cathode where isotopic exchange between cathode and electrolyte produced high concentrations in the electrolyte.

In Fig. 4, an example of representative output of two neutron detectors used for Pd electrolysis cells is shown. Neutron counts are identical for the detector located near operating electrolysis cells and the background detector, located some distance away from the cells but in the same laboratory. Based on the efficiency of the detectors, we estimate an upper limit on the fusion rate in our cathodes of  $10^{-22}$ – $10^{-23}$  d(d,n)<sup>3</sup>He fusions/d/sec.

During the titanium tritide experiment, the neutron count rate did not significantly deviate from the background rate of  $71 \pm 4$  counts/hour, equivalent to the emission of about 1.5 neutrons/sec from a source located at the test cell. A small diurnal variation in the neutron count rate of 4% and gradual changes in the average rate

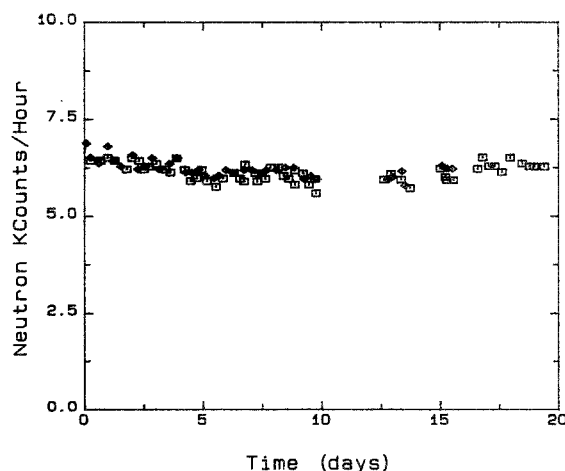


Fig. 4. Neutron counts/hour for detectors located near operating electrolysis cells (diamonds) and 3 meters away from operating cells (background detector, squares). Neutron counter efficiency ca. 4%.

of about 5% per week were observed and are believed to be due to the variation in the background due to cosmic ray. These variations are commonly observed in the monitoring of background neutrons and were also observed in a neutron counter located in an adjacent building.

#### 4. SUMMARY

We operated long-term electrolysis cells patterned after the University of Utah cells consisting principally of a Pd cathode and a Pt anode in 0.1 M LiOD/D<sub>2</sub>O electrolyte. We used extruded Pd wire, both as-received and after annealing at 1050°C in 10<sup>-6</sup> torr vacuum for 16 hours, and further treated Pd electrodes by anodic/cathodic potential cycling. In one cell, we used a reference electrode fabricated by electrochemical formation of palladium deuteride in the  $\alpha$ - $\beta$  phase transition region. We observed no evidence of neutron generation above background (sensitivity of 10<sup>-22</sup>-10<sup>-23</sup> d(d,n)<sup>3</sup>He fusions/d/sec) in any of the cells. Periodic sampling and analysis of the electrolyte in the cells also failed to show tritium above background levels. In another cell, we used a titanium tritide foil as the electrode to determine if deuterium-tritium fusion reactions could be made to occur in a metal lattice. We operated this cell for 5 days at current densities ranging from 50-200 mA/cm<sup>2</sup> and found no evidence for neutron generation. Tritium analyses of the electrolyte showed enrichment with operating time indicating isotopic exchange of deuterium for tritium in the lattice. Using hydrogen permeation techniques, we showed that surface treatments such as

palladizing, anodic/cathodic cleaning cycles, and flame washing are superior to ultrasonic cleaning in methanol in increasing the effective charging flux of Pd foils. Further, x-ray photoelectron spectroscopy of these samples confirmed that these three surface treatments yield surfaces with less carbon contamination. Electrochemical and thermal desorption techniques used to determine H:Pd loading ratios showed that, even using the most effective surface treatment procedures, the H:Pd ratio was about 0.8.

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