

Reproducible tritium generation in electrochemical cells employing palladium cathodes with high deuterium loading

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Abstract

Reproducible tritium generation well above background has been observed in tightly closed D₂SO₄-containing cells in four out of four Pd wire cathodes of one type. Tritium analysis was performed before and after each experiment on the Pd, the electrolyte and the gas in the head space. No tritium generation was observed in four identical Pd cathodes in H₂SO₄ cells operated at the same time under the same conditions. A cyclic loading-unloading regime with low current densities, rather than the usual continuous constant current regime, was employed to attain D/Pd and H/Pd loadings of 1 ± 0.05 reproducibly. D/Pd loadings greater than 0.8 ± 0.05 appear to be necessary to generate tritium. The largest amount of tritium, generated in 7 days of continuous electrolysis, was 2.1×10^{11} tritium atoms, compared with a background of 4×10^9 tritium atoms. The concentration of tritium and its axial distribution in the Pd were determined and concentrations of up to 9×10^{10} atoms/g Pd were found compared with a maximum background of 5×10^8 atoms g⁻¹. The T/D ratio in the Pd is about 100 times larger than in the electrolyte or gas and indicates that tritium generation occurs in the Pd interior rather than at its surface. No tritium generation was observed in two other types of Pd electrodes in D₂SO₄, despite the attainment of D/Pd ratios near 1:1. Thus high D/Pd ratios appear to be a necessary but not sufficient condition for tritium generation in D₂SO₄ electrolysis.

INTRODUCTION

Since Fleischmann, Pons and Hawkins [1] published their original paper on “electrochemically induced nuclear fusion of deuterium” at ambient temperature and Jones et al. [2] reported on their “observations of cold nuclear fusion in condensed matter”, many groups have reported the occurrence of nuclear reactions in deuterium-loaded metals. In particular, a large number of groups have reported evidence for neutrons [3-10] and tritium [11-25]. While neutrons have generally been detected at only very low levels, tritium generation has been reported at levels 10^7 - 10^9 times higher. Unfortunately, these findings are not generally

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reproducible or predictable, which has made systematic investigations of these phenomena most difficult. Furthermore, doubts have been voiced [26,27] as to whether tritium found in Pd cathodes, employed in heavy water electrolysis, has been generated by “cold fusion” reactions or whether it was present in the palladium as a contaminant before any experiments were conducted. Such doubts, have not been confirmed in a study of the behavior of deliberately tritium-doped Pd [28] and in recent analyses of large numbers of as-manufactured Pd samples using two different methods [29,30].

The present study reports on the reproducible generation of tritium at levels well above background in Pd cathodes during heavy water electrolysis. Reproducibility of tritium generation has been achieved by developing a method for the reproducible achievement of D/Pd loading ratios near unity. A closed-cell design with internal gas recombination was employed, and the tritium contents of the electrolyte and the gas above the electrolyte were determined prior to and after an experiment. Pieces of Pd wire adjacent to that used as the electrode were analyzed before each experiment and the active electrode was analyzed after each experiment. A light water control cell was always run in electrical series with every D₂O cell under essentially identical conditions. This procedure always allows direct comparison of any tritium in the D₂O cell and the H₂O control cell.

EXPERIMENTAL

Cell design

In contrast with most cell designs used in cold fusion studies, the cell used in this study employed a fritted (porous) glass cylinder to separate the Pd cathode from the Pt anode compartment. A similar design has been used by a group at the Bhabha Atomic Research Centre, Bombay, India [31]. Such a design prevents direct contact of O₂ gas bubbles, formed at the anode, with the cathode and reduces the rate of diffusion of dissolved O₂ to the cathode. The influence of O₂ on the cathode through the gas head space is negligible owing to a gas recombination catalyst and excess D₂(H₂) in the head space. The cell is sealed sufficiently well to allow a vacuum ($< 10^{-3}$ Torr air) to be achieved using a mechanical pump and has provisions to measure the D/Pd (H/Pd) loading ratio continuously.

Figure 1 shows a schematic drawing of the cell. The Pd electrode (1 or 2 mm diameter wire) is placed at the center of the fritted glass tube which in turn is surrounded by a 0.1 mm thick Pt foil cylinder (anode) to provide uniform current distribution. The fritted glass tube has holes of mean diameter 200 μm . A Pd wire, charged to the $\alpha + \beta$ phase mixture, is used as a reference electrode in most experiments. The various parts are kept in position at the bottom of the cell with a Teflon holder, which has channels to equalize the electrolyte levels in the two compartments. The anodic and cathodic compartments are connected by an exterior loop so that the gases can recombine on a Pt catalyst placed above the anolyte. The electrolyte volume in the cell is approximately 38 cm³, whereas the total gas volume is approximately 300 cm³.

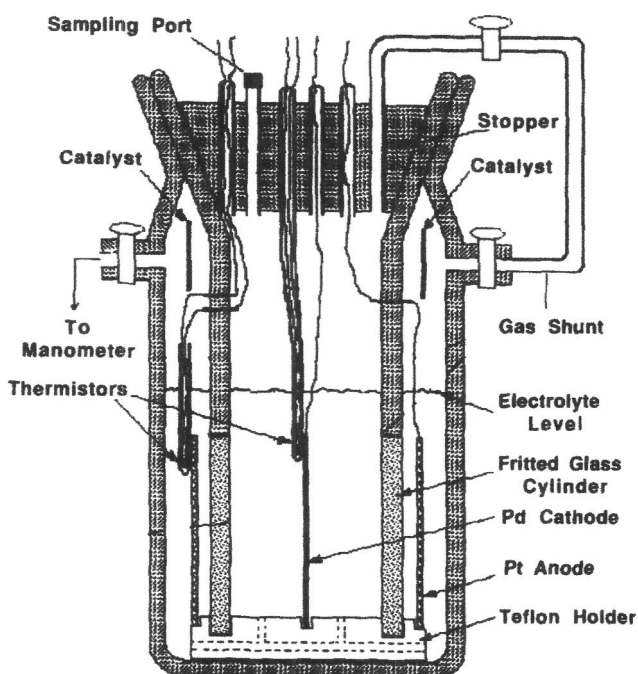


Figure 1. Schematic drawing of electrolytic cell.

A simple water-filled manometer, comprising two burets which are connected at their lower ends with flexible tubing, serves to determine volume changes in the gas volume above the electrolyte which are proportional to the loading ratio. This technique, developed in the 1950s [32], was improved and successfully applied in recent D_2 loading studies of Pd [33]. The use of H_2O in the manometer results in the transfer of a small amount of H_2O to the 0.5 M D_2SO_4 electrolyte. The rate of H_2O transfer to the 0.5 M D_2SO_4 was determined experimentally as 2.8×10^{-3} mol per day, equivalent to a contamination of the D_2SO_4 by H_2O amounting to 0.13% per day.

Materials and reagents

To avoid problems of glass dissolution and plating of glass components on the Pd cathode, as encountered in LiOD solutions [13], our experiments were carried out in 0.5 M H_2SO_4 for the light water control cells and 0.5 M D_2SO_4 for the heavy water cells. The heavy water (99.9% isotopic purity) was purchased from Cambridge Isotopes Laboratories Ltd. The 0.5 M D_2SO_4 solution was made by diluting conc. D_2SO_4 (98%, balance mostly D_2O , Aldrich Chemical Co. Inc.) with D_2O ; the 0.5 M H_2SO_4 solution was made by diluting conc. H_2SO_4 (96%, Baker Analyzed Reagent) with deionized H_2O . In one experiment, Li_2SO_4 (solid 99.99%) (Aldrich Chemical Co. Inc.) was added to the acids.

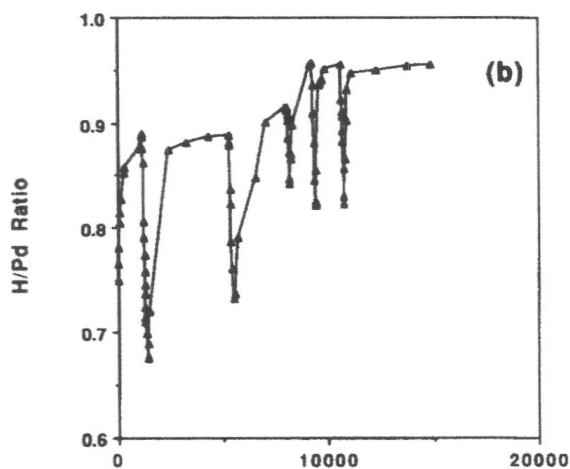
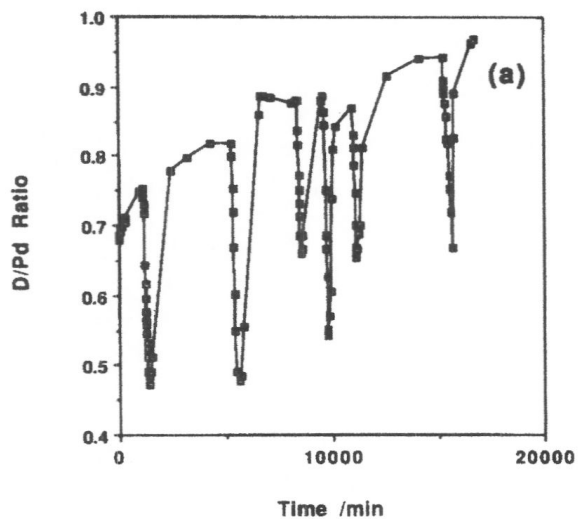


Figure 2. (a) D/Pd and (b) H/Pd loading ratios as a function of time: 0-1109 min, 30/10 mA charge (C); to 1377 min, 30/20/10 mA discharge (D); to 5253 min, 10 mA (C); to 5619 min, 30/10 mA (D); to 8359 min, 10 mA (C); to 8545 min, 30 mA (D); to 9588 min, 10 mA (C); to 9788 min, 30/20 mA (D); to 10 968 min, 20 mA (C); to 11 126 min, 30 mA (D); to 15 266 min, 10 mA (C); to 15 709 min, 30/10 mA (D); to 16 737 min, 20/10 mA (C).

The H₂O and 0.5 M H₂SO₄ contained no measurable tritium within the accuracy of the liquid scintillation counting [29,30] i.e. 1 dpm ml⁻¹ (decompositions per minute per milliliter) or 9.28 × 10⁶ tritium atoms ml⁻¹. The D₂O and 0.5 M D₂SO₄ had typical tritium contents of 10 dpm ml⁻¹. Occasionally, however, bottles with D₂O from the same supplier had tritium contents of up to 300 dpm ml⁻¹. These were rejected, with the exception of one experiment where the results of the analysis were completed only after the experiment had started.

Deuterium gas was purchased from Air Products & Chemicals Inc. and Al-phagaz-Liquid Air Corporation. Both suppliers use heavy water electrolysis to produce D₂ gas, and both purchased the heavy water from the same source (Ontario Hydro, Canada). According to our analysis [34] the gas purchased from Alphagaz had a low tritium count of 110 dpm/l⁻¹ of D₂ gas (0.05 nCi l⁻¹). The gas supplied by Air Products had a count of 0.13-0.14 nCi l⁻¹. Similar results were obtained by T.N. Claytor at Los Alamos National Laboratory.

Cathodes were of three different types or origins: (a) 1 mm diameter cold-drawn Pd wire (99.99% purity) from Aesar-Johnson Matthey; (b) 2 mm diameter cold-drawn Pd wire (99.9% purity) from Hoover & Strong; (c) 2 mm wide \times 0.5 mm thick cold-rolled Pd + 5% Li alloy ribbon prepared at the University of Utah [35]. All electrodes were approximately 3 cm long. Analysis for tritium contamination of 90 pieces (later increased to more than 130 pieces) of as-supplied Pd [30] from Johnson Matthey and Hoover & Strong showed no tritium contamination within the accuracy of the analytical technique, i.e. 5×10^8 T atoms/g Pd or approximately 1 T atom/ 10^{13} Pd atoms.

Anodes were cylinders of 2.8 cm diameter and 3 cm length, made from 0.1 mm thick Pt foil (99.98% purity) from Johnson Matthey. The Pt was provided with a Pt black layer by plating from PtCl_2 solution employing well-known procedures.

A 1 cm wide \times 8.5 cm long piece of fuel cell grade Pt catalyst on Ag-plated Ni screen (type ESN by E-TEK Inc.) was used as a recombination catalyst. It was positioned in the gas head space of the anode compartment approximately 3 cm above the electrolyte level.

Instrumental set-up

All experiments were performed using an identical light water control cell run in electrical series to the heavy water cell. The two cells were contained in two separate water baths of type EX-510D (NESLAB Institute Inc.) which controlled the temperature at $27 \pm 0.02^\circ\text{C}$. The laboratory was air-conditioned, with room temperature in the first week of May at $26.9 \pm 0.9^\circ\text{C}$ and in the first week of June at $28 \pm 1^\circ\text{C}$. Humidity levels were 35-40% r.h. The barometric pressure was read every few hours on a mercury barometer and had typical values from 634 to 646 Torr over a 4 week period.

The catholyte and anolyte temperatures were measured continuously using two thermistors (Thermometrics Inc., type SP60 BT 103 M1). They were enclosed in glass beads of diameter 0.14 mm and had a sensitivity of $\pm 0.02^\circ\text{C}$. The glass bead of the catholyte thermistor was cemented to the Pd cathode using thermally conductive epoxy (Thermalloy Inc., Thermalbond no. 4952). The anolyte thermistor was positioned close to the exterior of the Pt anode. The thermistors were calibrated in a water bath against a standard thermometer with a precision of $\pm 0.02^\circ\text{C}$. The measured thermistor resistances were converted to temperature using an Omegabench™ software program from Omega Engineering Inc. in conjunction with a Macintosh IIX computer.

Constant cell currents were applied with a precision constant current source (Keithley, model 228A). The potentials of the cell and cathode versus the reference electrode (where applicable) were read with multimeters (Keithley, model 179) and recorded on a hybrid § recorder (Yokogawa, model HR 230). Temperatures and potentials were stored in the computer.

§ This should probably be “hybrid.”

Experimental procedure

Before each experiment, the tritium contents of the electrolyte, pieces of Pd from the same wire spool from which electrodes were cut and the D₂ fill gas were determined. In addition, the D₂O in each new bottle for the preparation of 0.5 M D₂SO₄ and the deionized H₂O for the preparation of 0.5 M H₂SO₄ were analyzed for tritium. A Beckman LS 5000 TD liquid scintillation counter was employed for these analyses. For analysis of the liquids, 1 ml of liquid was added to 10 ml of scintillation cocktail (Beckman pseudocumene-xylene). For analysis of tritium in Pd, the Pd was acid digested and a distillation-gas recombination procedure in a closed system was used to capture all escaping tritium in liquid form [30]. Further details of the procedures have been published elsewhere [29,30].

Since an accurate value of the tritium contamination level was not supplied by the manufacturers, a tritium analysis procedure for D₂ gas was developed [34]. The recombination reaction of D₂ with O₂ gas on a Pt catalyst surface was used to obtain aliquots of heavy water for analysis. A gas-tight vessel was connected to a gas buret to measure the volume of D₂ gas recombined. An evacuated vessel containing a 12 cm² piece of catalyst was filled with D₂ gas. Oxygen was injected with a syringe through a septum and the D₂ displacement was measured. The recombined heavy water was rinsed out with distilled H₂O and analyzed for tritium.

No tritium analysis was performed on the fuel cell catalyst, epoxy and glassware. Any tritium contamination of these materials should show up to the same extent in the D₂O cells and the H₂O control cells and thus be recognized. No evidence for tritium contamination was found.

Pt leads of diameter 0.25 mm were spot-welded to Pd electrodes. The electrodes were rinsed in ethanol and deionized H₂O. The Pd wires were then palladized in PdCl₂ solutions in H₂O or D₂O using a cathodic current density of 15 mA cm⁻² for 2 min. Finally, the electrodes were preloaded with H₂ gas or D₂ gas, employing a vacuum system described elsewhere [36]. The H/Pd or D/Pd loading ratio was determined by weighing before and after gas loading. Teflon tubing was then slipped over the Pt leads and the electrodes were quickly introduced into the electrolytic cell. Gas preloading resulted in typical loading ratios of 0.45 to 0.75, and these values remained unchanged when exposure to laboratory air was limited to the manipulations mentioned above.

The electrolytic cells and manometer legs communicating with the cells were evacuated and then refilled with D₂ and H₂ gas at ambient pressure [33]. This assured proper and immediate functioning of the internal gas recombination catalyst by preventing the formation of oxygen chemisorption layers [37]. The vacuum was applied for 15-30 min and the pressure monitored with a mercury manometer to assure that the remaining pressure was due to water vapor (26.7 Torr at 27°C). The leak rate of air into the evacuated cell was established initially on one cell. Within 24 h, the mercury manometer reading remained stable when the ground glass joints were greased (Dow-Corning silicone high vacuum grease) and a vacuum rubber hose was used to connect the water manometer to the cell. During experiments, leak checks were performed periodically by pressurizing the cells slightly. This was done by adjusting the position of the

movable buret of the manometer and establishing that the level of the water column did not change with time, once an electrode was essentially fully loaded.

When starting the electrolysis, essentially no D₂ (H₂) gas was generated on the Pd. The O₂ gas generated on the Pt anode recombined with the prefilled D₂ (H₂) to form water. The amount of D₂ (H₂) consumed by reaction with the O₂ is precisely equivalent to the number of D (H) atoms absorbed by the Pd. Hence the decrease in the gas volume in the cell is a precise measure for the D/Pd (H/Pd) loading ratio. The gas volume stops changing when full loading is attained. Gas volume determinations were always performed with the manometer levels equalized so as to maintain ambient pressure in the cell [32,33]. The volume changes determined at a particular pressure and temperature were reduced to standard pressure and temperature, and the amount of D₂ absorbed by the Pd was determined from the universal gas equation. On the basis of the errors in measuring volume, pressure and temperature, we estimate that the overall error in our loading ratio determinations is $\pm 5\%$.

After completing an experiment, which generally lasted for about a week, the electrolyte, Pd electrode and gas were analyzed for tritium and compared with the amounts of tritium present before the experiment. The Pd electrodes were cut into several pieces, of which four were analyzed individually.

RESULTS AND DISCUSSION

D/Pd and H/Pd loading ratio

To achieve D/Pd or H/Pd loading ratios approximately equal to unity reproducibly, it was found necessary to load and partially unload the Pd repeatedly with low current densities. The precise procedure and detailed loading results obtained for a number of electrodes have been described elsewhere [38]. Typical results of D and H loading measurements on Pd wires of diameter 2 mm and length ca. 3 cm (Hoover & Strong) are shown in Fig. 2. Both wires had been preloaded in D₂ or H₂ gas to loading ratios of 0.68 and 0.75 respectively. The cycling regime consisted of constant-current charging (loading) and discharging with currents between 10 and 30 mA (current densities of ca. 5 to 15 mA cm⁻²). The cell voltage (Pd vs. Pt) during discharge was not allowed to exceed + 0.8 V to keep the formation of oxide layers on the Pd to less than a monolayer [37] and to avoid O₂ evolution on the Pd. The pertinent currents for the seven charging and six discharging events are given in the figure caption.

In general, each additional cycle leads to higher loading but the increments become smaller. The charging curve segments show a tendency to reach a limit in loading ratio if the charging period is long. After 250 h of cycling, of which 90% is loading, the H/Pd loading ratio is 0.95. Similarly, after 280 h of cycling, the D/Pd ratio is 0.96.

The loading ratios of the eight 2 mm Pd wires, four cycled in 0.5 M D₂SO₄, and four in 0.5 M H₂SO₄ are summarized in Table 1. Seven electrodes attained a loading ratio of unity (within an error of ± 0.05) and one electrode attained a value of 1.07.

Loading ratios of unity and above have been attained by other groups, employing one of four methods: (1) low temperature electrolysis in electrolytes with organic solvents [39-41], (2) long-term electrolysis at ambient temperatures [13,33,42], (3) loading in the gas phase at pressures of several 10000 atm [43,44] and (4) hydrogen ion bombardment of thin Pd films, followed by sample quenching from 300°C in liquid N₂ [45].

Neutron diffraction and scattering studies show that D and H occupy the octahedral sites in the f.c.c. structure of Pd [46-48] corresponding to a loading ratio of unity. However some evidence has been presented that H and D may occupy the tetragonal sites, particularly at very low temperatures (< 55 K) [45,49,50], resulting in loading ratios of 1.33 [45].

While it cannot be excluded that tetragonal sites in the Pd are occupied by D or H in the present study, it is regarded as more likely that some D or H is contained in internal voids or microcracks, or that D or H clustering has occurred at dislocations. Excess volume (beyond that due to lattice expansion) up to 32% has recently been found in Pd that had been exposed to repeated loading-unloading cycles [28].

In another study [51], employing 2 mm diameter Pd wires from the same supplier (Hoover & Strong) but conducted in a cell of very different design, we have not been able to attain D/Pd ratios exceeding 0.84. This could be due to the fact that the Pd electrodes were only 1.8 cm long and that the Pt anode was very close to the Pd cathode. This could have encouraged the loss of D from the ends of the Pd electrode owing to lower current densities and hence smaller overvoltages at the ends.

TABLE 1

Tritium analysis of electrolyte, Pd and gas

Experiment	1		2		3		4	
Time at D/Pd > 0.8/h	163.8		169.7		144.4		483.5	
Electrolyte	D ₂ SO ₄ +Li ₂ SO ₄	H ₂ SO ₄ +Li ₂ SO ₄	D ₂ SO ₄	H ₂ SO ₄	D ₂ SO ₄	H ₂ SO ₄	D ₂ SO ₄	H ₂ SO ₄
Loading ratio								
D/Pd, H/Pd	0.99	1.03	0.96	0.95	1.02	1.07	0.98	1.01
T in electrolyte/10 ¹⁰ atoms								
Before	0.38	ND	0.29	ND	10 *	ND	0.24	ND
After	19	ND	8.0	ND	14	ND	10	ND
T in Pd/10 ¹⁰ atoms								
Before	ND	ND	ND	ND	ND	ND	ND	ND
After	1.7	ND	16	ND	21	ND	4.7	ND
T in gas/10 ⁸ atoms								
Before	1.8	NM	1.8	NM	1.8	NM	1.8	NM
After	1.8	NM	8.3	NM	62	NM	NM	NM
T total/10 ¹⁰ atoms								
Before	0.4	ND	0.31	ND	10	ND	0.26	ND
After	21	ND	9.7	ND	17	ND	15	ND
T generated/10 ¹⁰ atoms								
Enhancement factor	52.5	ND	31.2	ND	1.7	ND	57.7	ND
Specific T yield/10 ¹⁰ atoms cm ⁻²	11	ND	4.5	ND	4.3	ND	8.8	ND
Average rate of T generation/10 ⁴ atoms cm ⁻² S ⁻¹	20	ND	7.4	ND	8.3	ND	5.1	ND

* Batch of D₂O with high T content.

ND, not detected

NM, not measured

Tritium yield

A total of eight experiments were carried out, involving 16 cells on which tritium analyses were performed. In every experiment, one Pd cathode (of identical origin) was employed in each of a heavy water cell and a light water control operated in electrical series. Three different types of Pd electrodes were used: (a) 1 mm diameter Pd wires from Johnson Matthey (three

experiments), (b) 2 mm × 0.5 mm Pd + 5% Li alloy ribbons (one experiment) and (c) 2 mm diameter Pd wires from Hoover & Strong (four experiments). No tritium generation was observed on the 1 mm Pd wires and the Pd + Li alloy, despite the attainment of loading ratios of unity in all cases but one (where the cycling time was insufficiently long). In contrast, all Hoover & Strong 2 mm Pd wires in D₂SO₄ showed tritium generation well above background, whereas none of the four identical Pd control electrodes in H₂SO₄ showed any detectable tritium.

Table 1 summarizes the results of all four experiments conducted with 2 mm diameter Pd wires from Hoover & Strong. Deuterium loading or charging always preceded tritium analysis. In the second line of the table, the times are given for which the cells were operated at an average D/Pd ratio greater than 0.8. For the low current densities (5-15 mA cm⁻²) and long charging times generally employed in this study, the D loading is expected to be rather uniform throughout the Pd so that the average D/Pd ratio will be fairly representative of the entire Pd. From further results, to be published elsewhere, it appears that tritium is predominantly generated when the average loading ratio exceeds 0.8. The total times at D/Pd > 0.8 were used to calculate average tritium generation rates, given at the bottom of the table. The total amounts of tritium generated in the four cells are surprisingly uniform, ranging from a low value of 7 × 10¹⁰ T atoms cm⁻² to a high value of 2.1 × 10¹¹ T atoms cm⁻² of Pd surface. Alternatively, when referred to unit weight, the values range from 8.4 × 10¹⁰ to 2.1 × 10¹¹ T atoms g Pd)⁻¹. Although the results of this study (see below) in conjunction with those of others [12,14,28,42] favor the generation of tritium in the Pd interior rather than at its surface, the yield in this study is referred to unit area to allow ready comparison with the results of other authors who usually mention an electrode area but no electrode weight.

Below the tritium yields in Table 1 are given tritium enhancement factors which express the ratio of the total tritium present in the cell after the experiment to the total tritium present before the experiment. Three of the four cells show enhancement factors ranging from 31 to 58. The fourth cell has an enhancement factor of only 1.7, owing to the fact that in this cell a new batch of heavy water with a tritium level 30 times larger than the tritium content of the heavy water in the other experiments was inadvertently used. It is interesting to note that, independent of the 30 times higher initial tritium content of the electrolyte, the amount of tritium generated per unit area and time is not much different from the other electrodes. This result is not surprising if the tritium is generated inside the Pd and if the T/D ratio is significantly larger in the Pd than in the D₂SO₄, as will be shown below.

Table 1 also summarizes average tritium generation rates, averaged over the time at which the electrode had a loading ratio exceeding 0.8 ± 0.05 and related to unit area. The values run from 5.1 × 10⁴ to 2 × 10⁵ T atoms cm⁻² s⁻¹, equivalent to values from 0.9 × 10⁵ to 3.7 × 10⁵ T atoms g⁻¹ s⁻¹.

Among the groups that have found tritium in heavy water electrolysis on Pd (all in LiOD solutions), the results are highly variable among different groups and even within the same group. Fleischmann et al. [1] reported relatively low tritium accumulations of 50-100 dpm ml⁻¹, corresponding to 3 × 10⁹ to 6 × 10⁹ T atoms cm⁻². Packham et al. [11] found values from 5.1 × 10¹¹ to 1.8 × 10¹⁴ T atoms cm⁻² in the electrolyte of nine cells and no tritium in 12 other

cells. The highest value is 1×10^{15} T cm⁻², reported by Bockris et al. [18]. The values found by various groups at BARC [12] in 21 cells ranged from 4×10^9 to 1.7×10^{14} T cm⁻². In nine of these cells, the values ranged from 8×10^{10} to 6×10^{12} T cm⁻². Adzic et al. [11] found tritium generation in six out of nine cells with yields ranging from 3.1×10^{10} to 3.1×10^{11} T cm⁻², equivalent to enhancement factors ranging from 6.2 to 50. Storms and Talcott [14] performed experiments on a large number of cells and generated tritium in 11 out of approximately 100 cells. The tritium yield ranged from about 5×10^{10} to 3×10^{11} T cm⁻². Values of 1.2×10^{11} - 1.9×10^{11} [6], 1×10^{10} [20] and 2.5×10^{10} - 3×10^{10} T/cm² [24] were reported by three other groups.

Thus the results from 10 groups vary from 3×10^9 to 1×10^{15} T atoms cm⁻², with seven of these reporting values from 2.5×10^{10} to 6×10^{12} T atoms cm⁻².

Tritium distribution between the three phases

According to Table 1, the largest amount of tritium accumulates in the liquid phase and by far the smallest amount in the gas phase. However, the distribution of tritium in the three phases is usually compared on the basis of the T/D atomic ratios. This has been done in Table 2. Also given in Table 2 are the ratios of the T/D values in metal/liquid etc. To distinguish these ratios from equilibrium separation factors, they have been designated as “non-equilibrium distribution factors.” The T/D distribution factors Pd/gas and Pd/liquid have very large values, ranging from 37 to 233. In contrast, typical equilibrium isotopic separation factors D/H and T/H between Pd and gas are 0.42 and 0.37 respectively (at 25°C) [52]. Values between 0.2 and 0.3 have been determined for the separation factor D/H (metal/ solution) at 25°C [53]. The large values of the distribution factors found in the present study indicate that tritium has been generated in the Pd and that there has been insufficient time for it to diffuse out. Therefore the distribution over the three phases is far removed from equilibrium conditions, as described by the equilibrium separation factors.

Results obtained by Storms and Talcott-Storms [28] on deliberately tritium-doped Pd cathodes tend to confirm this interpretation. A Pd button had a T/D ratio of 1.22×10^{-8} prior to use as a cathode in 0.1 M LiOD, i.e. about 10^4 times larger than the values in this study. After 120 h of cathodic polarization at 35 mA cm⁻², the T/D ratio in the solution was 1.8×10^{-13} , in the D₂ gas it was 2×10^{-12} and in the Pd it was almost unchanged at 1.21×10^{-8} . Thus the non-equilibrium distribution factors were T/D (metal/ liquid) = 6.7×10^4 and T/D (metal/gas) = 6×10^3 , even larger than in the present study. Clearly, most of the tritium in the Pd had not diffused out during 120 h, thus maintaining a highly non-equilibrium distribution over the three phases.

TABLE 2

T/D ratios and non-equilibrium distribution factors

Experiment	1	2	3	4
10^{14} (T/D) liquid	7.6	3.2	5.6	3.5
10^{12} (T/D) metal	2.8	2.6	3.5	7.8
10^{14} (T/D) gas	1.2	5.5	41	NM
T/D (metal/liquid)	37	81	63	223
T/D (metal/gas)	233	47	85	NM
T/D (liquid/gas)	6.3	0.6	0.14	NM

NM, not measured.

At least two groups [12,42] have shown that tritium continues to be released for many days into the electrolyte or into fresh D_2O from D-loaded Pd after long-term cathodic polarization in LiOD solutions. This behavior corresponds to slow diffusion of tritium from the interior of the Pd into the liquid phase with a diffusion coefficient of the order of $10^{-8} \text{ cm}^2 \text{ s}^{-1}$, a value well within the range of known diffusion coefficients [54], particularly for highly loaded Pd [55].

Local tritium distribution in Pd wire cathodes

A closed-system acid digestion method described elsewhere [30] was used to determine the tritium in the Pd quantitatively. Figures 3(a) and 3(b) show the tritium spectra of a tritium standard (1000 dpm ml^{-1} of tritium in H_2O) and of a solution containing the distillate and recombinant from a piece of the Pd cathode used in experiment 3 of Table 1. The spectrum of the distillate has its maximum at the same channel 225 as the standard, identifying the species extracted from the Pd as tritium.

The tritium distributions in the four Pd cathodes are shown in Fig. 4. In the three experiments where the ends of the palladium wires were analyzed separately from the center sections, comparatively much less tritium is found at the ends of the wires compared with the center. The eight pieces near the centers of the four electrodes show a surprisingly narrow band of values namely, from 1.2×10^{10} to 8.9×10^{10} T atoms $(\text{g Pd})^{-1}$. It appears that the ends of the Pd wires either did not charge as efficiently as the center regions or that tritium escaped from the ends more readily.

Significantly, the four Pd cathodes cut from the same Pd wire and employed in H_2SO_4 under the same conditions and at the same time as the four Pd electrodes in D_2SO_4 did not show any tritium within the detection limit of the analysis, i.e. 5×10^8 T atoms $(\text{g Pd})^{-1}$.

In addition, 54 as-manufactured pieces of 2 mm Pd wire from the same supplier (Hoover & Strong) were analyzed for tritium and did not contain any tritium within the detection limit. Thus it appears that the tritium found in all four 2 mm Pd cathodes loaded in D_2SO_4 is due to accidental tritium contamination of the as-received material or to handling thereafter.

Lastly, the recombination catalyst has to be ruled out as a source of tritium since no tritium was found either in the four H_2SO_4 -filled cells or in the 54 as-received Pd samples employing the same type of catalyst in the analytical procedure as in the electrolyte cells.

Since (1) all four D_2SO_4 cells with 2 mm Pd electrodes showed considerably more tritium after than before the electrolysis and nothing was added to the tightly closed cells during the experiments, ** and (2) the four Pd electrodes have much higher T/D atomic ratios than the liquid or gas phase, the tritium was apparently generated in the highly D-loaded Pd. Only nuclear reactions occurring in the D-loaded Pd could have led to the observed tritium. While the nature of these nuclear reactions remains to be established, it is clear that deuterium and tritium are intimately involved in them.

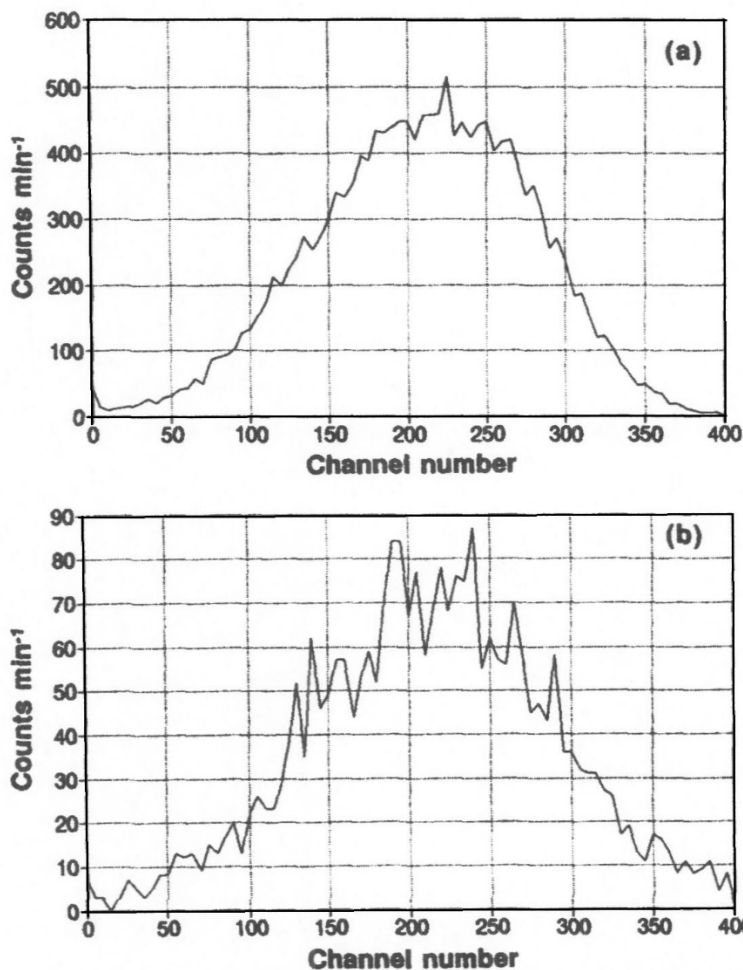


Figure 3. Tritium spectra: (a) tritium standard (1000 dpm ml⁻¹); (b) one of four Pd electrode pieces after experiment 3 of Table 1 applying a closed-system analytical procedure described elsewhere [29].

** With the exception of cell 4 where electrolyte samples were removed and fresh D_2O was added.

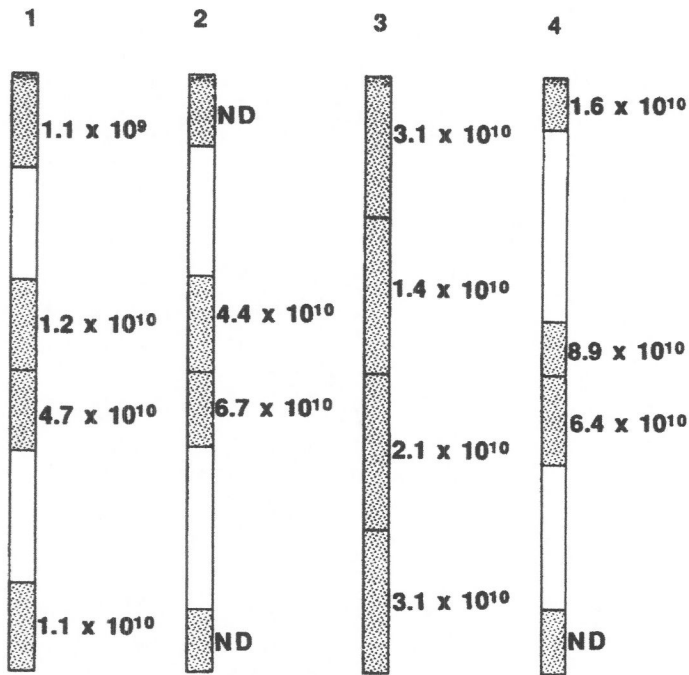


Figure 4. Axial tritium distribution in Pd cathodes after D₂O electrolysis in experiments 1-4 of Table 1 using analytical procedure described elsewhere [29]. ND, not detected (the detection limit is 5×10^8 atoms) (gPd)⁻¹. The numbers give the numbers of atoms per gram Pd.

CONCLUSIONS

A cyclic charge-discharge regime of Pd in aqueous sulfuric acid solutions, employing low current densities of typically only 5-15 mA cm⁻², leads to the reproducible attainment of H/Pd and D/Pd loading ratios of 1 ± 0.05 as observed for 16 out of 16 Pd electrodes. Tritium accumulations up to 57 times background were found in four out of four tightly closed heavy water cells, employing Pd electrodes of a certain type, whereas no tritium above background was found in four light water control cells run with Pd electrodes from the same wire under the same conditions and at the same time. No tritium was found in four heavy water cells employing Pd electrodes of another type or a Pd + Li alloy electrode, despite having attained D/Pd ratios of 1 ± 0.05 . D/Pd loadings exceeding 0.8 ± 0.05 appear to be a necessary but not sufficient condition for tritium generation. Metallurgical factors also appear to be significant. The difficulty in attaining D/Pd loadings exceeding 0.7 with continuous rather than cycling loading methods, coupled with the as yet unknown effects of the Pd metallurgy, probably account for the failure of many groups to observe measurable tritium generation. Specific tritium yields were between 4.3×10^{10} and 1.1×10^{11} atoms cm⁻² compared with a range of values from 2.5×10^{10} to 6×10^{12} atoms cm⁻² as determined by seven of ten other groups reporting tritium. Average tritium generation rates in the four heavy water cells ranged from 5×10^4 to 2×10^5 atoms s⁻¹ cm⁻². This is equivalent to an average power level of the order of 10^{-7} W, which is too small to be detected. The T/D distribution over the three phases—Pd, electrolyte and gas—is highly non-equilibrium, with the T/D ratio approximately 100 times larger in the Pd than in electrolyte or gas. This indicates that the tritium is generated inside the Pd, where it is found at levels of up to 9×10^{10} atoms (g Pd)⁻¹. Based on previous analyses of 54 as-manufactured Pd samples of the same type

of 2 mm wire from the same supplier, which had resulted in no measurable tritium within a detection limit of 5×10^8 atoms (g Pd)⁻¹, it appears that the tritium in the four Pd electrodes was not caused by accidental contamination of the Pd. Since up to 57 times more tritium was found in the tightly closed cells after heavy water electrolysis compared with that present before, the tritium must have been generated in the cells. Based on the large T/D ratios in the Pd electrodes, it is concluded that the tritium was generated inside the Pd; only nuclear reactions, whose nature is as yet unknown, could have produced the observed tritium.

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