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TRITIUM GENERATION IN PALLADIUM CATHODES WITH HIGH DEUTERIUM LOADING

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ABSTRACT

Tritium up to fifty times background has been observed upon electrolyzing 1N D₂SO₄ in four out of four cells when using Pd cathodes "of a certain type". No tritium was detected in four control cells, containing H₂SO₄ in H₂O, employing Pd cathodes cut from the same wire spool. Tritium amounts were from 7×10^{10} to 2.1×10^{11} atoms, corresponding to average generation rates from 5.1×10^4 to 2×10^5 atoms/sec/cm². In all cases, D/Pd and H/Pd loadings of 1 ± 0.05 were attained. A cyclic loading/unloading regime rather than the usual continuous constant current regime was applied to attain these high loadings. Tritium analysis was performed in Pd, electrolyte and the gas head space of the sealed cells. Maximum tritium concentrations of 8.9×10^{10} atoms/g Pd, 180 times the detection limit, were found in the D-loaded Pd cathodes, none in the H-loaded Pd. Also, no tritium within detection limit was found in 150 unused Pd pieces. Of these, 13 were cut randomly from the same wire spool as the four D-loaded Pd cathodes. The probability that the tritium in the latter was due to random spot contamination is computed as 1 in 2,380. It is concluded that the tritium was generated by nuclear reactions in the Pd. However, no tritium was detected in four D-loaded Pd cathodes of a different type in spite of attaining loadings D/Pd = 1. Different metallurgical history and impurity contents may play an important role.

I. INTRODUCTION

Low-level tritium generation during D₂O electrolysis with Pd cathodes, was first reported by Fleischmann and Pons,¹ followed by many others,² but has proven sporadic and irreproducible. It has been suggested³ that the tritium found in these types of experiments is not due to nuclear reactions in the Pd cathodes but to spot contamination of the as-manufactured Pd. This paper reports on the results of studies aimed at (1) exploring the conditions leading to the reproducible generation of tritium, (2) minimizing the chances for accidental contamination during the experiments and (3) evaluating the statistical probability of spot contamination of the Pd prior to the experiments, that is, in their as-manufactured condition.

II. EXPERIMENTAL

All experiments were performed in tightly closed two-compartment glass cells in which the Pd cathode (wire of 2 mm diameter and 2.6 cm length) was surrounded by a fritted glass cylinder and a platinized Pt cylinder anode. A Pt-catalyzed fuel cell electrode was positioned in the gas head space above the anolyte and served as D₂-O₂ recombination catalyst. The gas spaces above anolyte and catholyte were connected with glass tubing.

The electrolytes were 1N D₂SO₄ or 1N H₂SO₄, the cathodes 99.9% pure Pd wire, as-drawn, supplied by Hoover & Strong and the gases in the pre-evacuated head spaces D₂ (0.05-0.14 nCi/l) or pre-purified H₂.

Cell temperature was maintained at $27 \pm 0.02^\circ\text{C}$. Cathode and anode temperatures were monitored with thermistors, bonded to the electrodes, with a precision of $\pm 0.02^\circ\text{C}$. Charge and discharge currents were controlled by a precision constant current source.

A volumetric technique, using water-filled manometers to measure the occluded D₂ or H₂ volume,^{4,5} was employed

to determine the D/Pd or H/Pd loading ratio continuously to a precision of ± 0.05 . Tritium analysis was performed with a Beckman LS 5000 TD liquid scintillation counter with a sensitivity of 1×10^7 tritium atoms.⁶ Pd was analyzed for tritium, employing an acid digestion technique, followed by distillation and catalytic hydrogen isotope oxidation in a closed system.⁷

The following experimental procedure was employed: two cells, one containing 1N D₂SO₄ and the other 1N H₂SO₄ as a control, were always run in one experiment at the same time in electrical series connection. Four experiments, lasting from 164 to 484 hours, were conducted. All eight Pd cathodes of 2.6 cm length each were cut randomly from the same spool of 2 mm diameter wire and 60 cm total length. Nine control pieces of ~ 3 mm length each were also cut from the same spool, with locations adjacent to the Pd cathodes, and analyzed for tritium in their as-manufactured state. The Pd cathodes were palladized (~ 1 μ m Pd black layer) and gas-preloaded in 1 atm D₂ or H₂ gas, just prior to starting electrolytic loading with D or H. The D₂ gas in the head space and the electrolyte (D₂SO₄ and H₂SO₄) were analyzed for tritium before and after an experiment. Pd control pieces were analyzed before and the actual Pd electrodes after an experiment.

III. RESULTS and DISCUSSION

A. Hydrogen Loading

When charging Pd wires in D₂SO₄ or H₂SO₄ continuously with a constant current, loading ratios generally between 0.6 and 0.7 were observed. This is in agreement with the results of an extensive study⁸ in which only 15 out of 62 experiments, spontaneously and unpredictably, yielded loading ratios close to 1.

However, when repeatedly loading (charging) and unloading Pd with low current densities, we were able to attain loading ratios of 1 ± 0.05 reproducibly on 16 out of 16 Pd electrodes.^{9,10} The results of such cyclic loading are shown in Fig. 1 for the case of D and H in Pd; loading ratios of 0.96 were achieved in the seventh loading event. Unloading was performed to a cut-off cell voltage of 0.8V, thus avoiding the formation of Pd surface oxides or molecular oxygen. Also, deep discharge into the α -phase region is avoided, thereby minimizing lattice strain.

Similar results as shown in Fig. 1 were obtained in three other D₂SO₄ and three more H₂SO₄ cells as well as on a total of six 1mm Pd wires and two Pd-Li alloy ribbons. Saturation of the loading near values of D/Pd or H/Pd = 1 was observed in all cases.¹⁰

B. Tritium Yield

The tritium yields for the four heavy water cells, after D₂SO₄ electrolysis with 2mm Pd cathodes, are comprised of the sum of the tritium amounts in the gas head space, the electrolyte and the Pd. The amount in the head space is negligible, whereas the electrolyte contained between 2 and 10 times more tritium than the Pd. Electrolysis was always terminated with a charging event.

The tritium yields were found to lie in a relatively tight band from 7×10^{10} to 2.1×10^{11} tritium atoms. This corresponds to specific tritium yields from 4.2×10^{10} to 1.1×10^{11} T atoms/cm² of electrode surface. No tritium was found in any of the four light water control cells, within the detection limit of the analytical method, that is, 4×10^8 T atoms in 40 cm³ electrolyte. The tritium generation rates, referred to the time of D/Pd > 0.8, were between 5.1×10^4 and 2×10^5 atoms/sec/cm².

Compared to our values from 4.2×10^{10} to 1.1×10^{11} T atoms/cm², the results of ten other groups run from about 3×10^9 to 1×10^{15} T atoms/sq cm,⁹ with the majority (seven groups) reporting values from about 2.5×10^{10} to 6×10^{12} T atoms/cm².

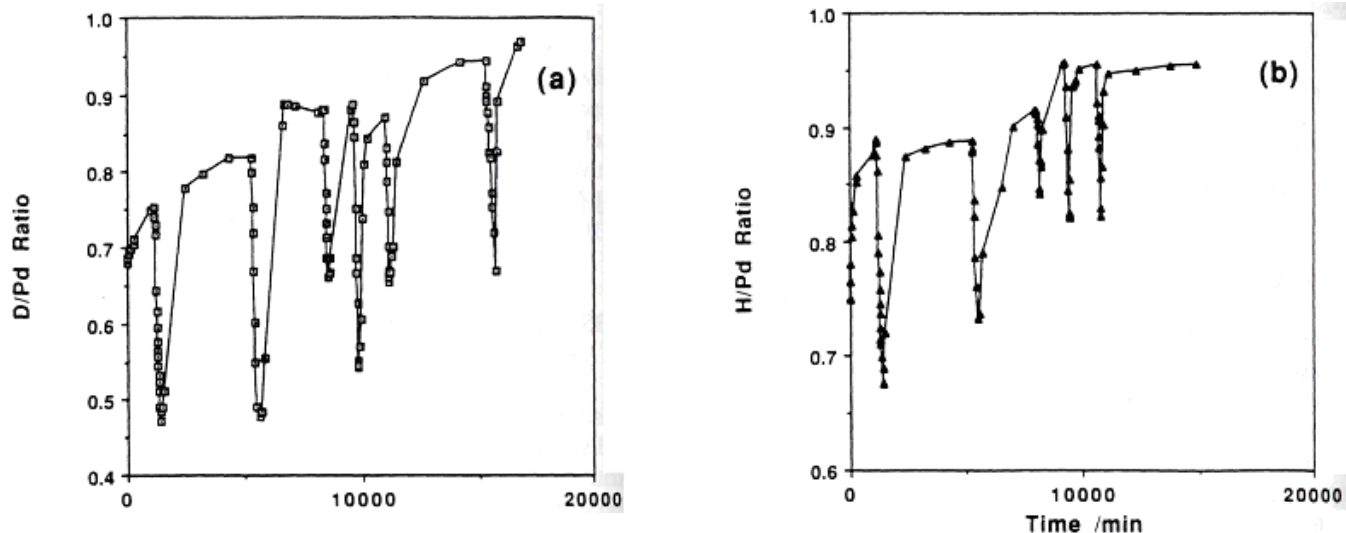


Fig. 1. D/Pd (a) and H/Pd (b) loading ratio versus time. Charging with 10 to 30 mA; discharging successively at 30,20 and 10 mA. Electrode area 2 cm².

C. Tritium in Palladium and its Identification

Scintillation counting of the clear neutralized aqueous solutions, resulting from the distillation and catalytic hydrogen isotope oxidation of the acid-digested Pd,⁷ yielded values (except near the edges) from 1.2×10^{10} to 8.9×10^{10} T atoms/g dissolved Pd, compared to a detection limit of 5×10^8 T atoms/g dissolved Pd. T/D atomic ratios were found⁹ to be 37 to 223 times larger in the metal than in the electrolyte. If the two phases, metal and liquid, were in equilibrium, the T/D ratios would be 2 to 5 times smaller in the metal.⁹ This was taken as evidence⁹ that the tritium had been generated inside the Pd and had insufficient time to equilibrate with the electrolyte. These findings rule out any possibility of accidental or deliberate contamination of the electrolyte (or the gas) as source of the observed tritium.

To demonstrate that tritium was the source of the observed scintillation counts, beta spectra were recorded of (1) pieces of Pd cathodes after use in D₂SO₄ electrolysis; (2) a secondary tritium standard prepared in-house; and (3) a commercial tritium standard (Beckman). The secondary standard was prepared by adding 1 ml of tritiated light water (activity 1000 decompositions/min-DPM) to 10 ml scintillation cocktail (Beckman pseudocumene/xylene). The primary standard had been supplied by the manufacturer of the scintillation counter (Beckman); it consisted of a tritium-containing organic solution (toluene) of scintillation-grade fluors.

Figures 2-4 show the relevant spectra in plots of counts (detected in five-channel increments) versus channel number. The relationship

$$N = 72 + 280 \log E \text{ [keV]} \quad (1)$$

permits conversion from channel number N to kinetic energy of the electrons. The standard method for identifying an unknown beta emitter from its spectrum is to determine its end point energy by producing a Fermi-Kurie plot¹¹ of the data and comparison with table values.

For spectra obtained with scintillation counters, this technique is not reliable, due to the quenching of the electrons by the scintillation fluid. The end point energies determined from the plots in Figs. 2-4, using equ. (1), lie in the range from

17.5 to 20.6 keV (channels 420 to 440), compared with a table value of 18.6 keV. Among all known beta emitters, only Pb^{210} (15 keV) and Pu^{241} (21 KeV) have endpoint energies close to this range.

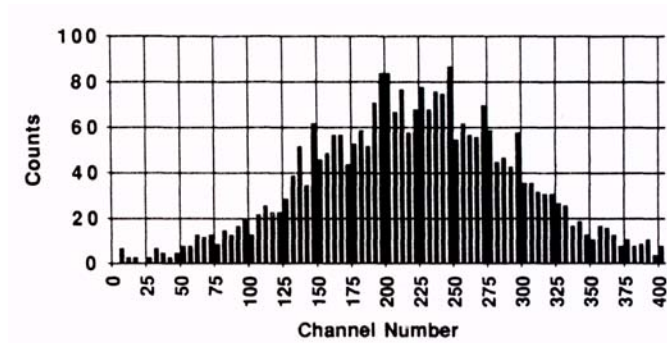


Fig. 2. Beta spectrum of Pd cathode piece after D_2O electrolysis and application of closed-system analytical method.⁶ Ordinate: Incremental counts per 5-channel interval in 20 minutes.

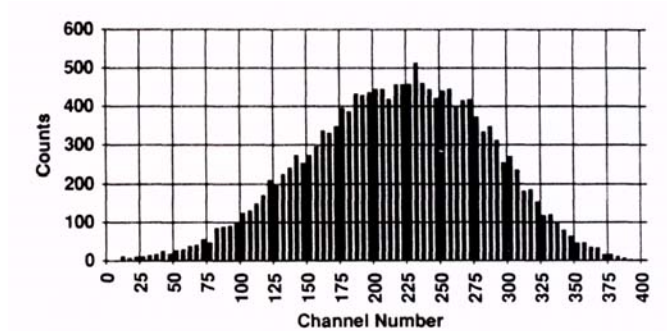


Fig. 3 Beta spectrum of secondary tritium standard: Tritiated H_2O (1000 dpm) in Beckman scintillation cocktail. Ordinate: Counts per 5 channels per minute.

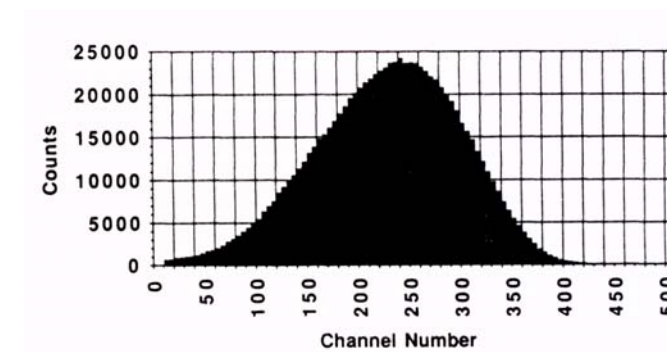


Fig. 4 Beta spectrum of water-free primary tritium standard supplied by Beckman. Ordinate: Counts per 5 channels per minute.

As the endpoint energies of tritium, Pb^{210} and Pu^{241} are quite similar, positive identification of tritium was made by a comparison of the spectra originating from the dissolved Pd cathodes with the spectra of tritium standards. Fig. 5 shows a superposition of the spectra of Fig. 2-4, normalized to the maximum number of counts. The maxima of the three curves for the primary standard, secondary standard and Pd cathode occur at channel numbers 238, 220 and 218, respectively, corresponding to energies of 3.9, 3.4 and 3.3 keV. There is good correspondence of the curves between secondary standard and Pd cathode. The shift of both curves toward lower energies as compared to the primary standard is caused by the additional quenching of the electrons by the 1 ml water added to the scintillation liquid. No water is present in the primary standard, hence, there is less quenching. The spectra of Pu^{241} and especially of Pb^{210} are sufficiently different from the spectra in Fig. 5 to rule out Pb^{210} with confidence and Pu^{241} with high probability as being the sources of the observed beta emission from Pd cathodes

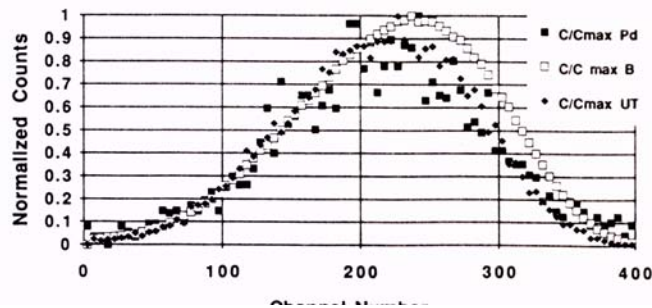


Fig. 5 Beta spectra of Pd cathode piece, primary (B), and secondary (UT) tritium standard, normalized to maximum number of counts,

D. Probability of Accidental Tritium Contamination

To evaluate the statistical probability that the tritium observed in all four D_2SO_4 cells employing 2 mm diameter Pd cathodes from Hoover & Strong could have been caused by chance contamination of the as-manufactured Pd wire rather than by nuclear reactions in the Pd, a number of controls from the same wire spool were also analyzed for tritium. In addition, a large number of as-manufactured Pd samples from other wire lots were analyzed.

All eight Pd cathodes (four from D_2SO_4 cells (D) and four from H_2O control cells (H)) and nine as-made Pd control pieces were cut from the same 60 cm long, 2 mm diameter Pd wire. Cathodes were about 2.6 cm, control pieces about 0.26 cm long. They accounted for a total of 23.1 cm length. D cathodes and H cathodes were always cut alternately and control pieces were always cut adjacent to the cathodes. This meant that D cathodes, H cathodes and control pieces each *originated from various parts of the wire* rather than the D cathodes all from one part, etc. This *random cutting* is important for the statistical evaluation of the analysis results.

Average tritium concentrations from 35 to 94 times the detection limit (5×10^8 atoms/g Pd) of the analytical technique was found in all four D cathodes. No tritium was found in any of the four H cathodes or in any of the nine as-made Pd control pieces. If the tritium in the four D cathodes would have been due to chance contamination of the as-received material, the probability of having selected all four correctly out of 17 Pd pieces total may be calculated by two methods, depending on the assumptions made.

If it is assumed that potential tritium contamination is uniformly distributed along the entire wire, then the chance for randomly cut pieces to contain tritium is just as large as the chance not to contain tritium. The probability of correctly predicting the presence or absence of contamination is therefore $\frac{1}{2}$ for each piece, identically for all pieces. The overall probability of making all predictions correctly for 17 pieces is thus $(\frac{1}{2})^{17}$ or 1 in 131,072.

If random spot contamination is assumed, then for the presence of four T-contaminated Pd pieces in a total of 17 pieces, the probability of selecting these four pieces in four attempts is:

$$\frac{4}{17} \times \frac{3}{16} \times \frac{2}{15} \times \frac{1}{14} = 1 \text{ in } 2,380.$$

Thus, while chance contamination of the as-made Pd wire cannot be ruled out with certainty, the likelihood that the tritium observed in the four heavy water Pd cathodes is due to chance contamination is exceedingly small.

Wolf et al.³ reported finding tritium spot contamination in two out of 45 unused Pd pieces cut from one particular spool of as-made 1 mm Pd wire from Hoover & Strong. No tritium was found in 45 Pd pieces from a different lot of 1 mm Hoover & Strong or in 160 Pd pieces from other sources. In addition, Wolf et al. reported finding tritium in 2 out of 50 LiOD cells, 2 out of 50 LiOH cells and one Pd cathode from an LiOH cell. While the findings of Wolf et al. could be due to rare spot contamination of some of the as-received Pd, radioactive contamination during handling and experimentation cannot be ruled out, especially since (1) vented electrochemical cells were used which had to be topped off with D₂O daily for many weeks, (2) the tritium analysis in the Pd samples were carried out in open cells and (3) the laboratory was located near the cyclotron with a variety of radiation sources present. Concerns regarding false positive tritium readings in the open system analytical technique used have been expressed previously.⁶ By comparison, our results presented here and previously,^{7,9} employing closed electrochemical cells and closed-system analytical techniques, show no tritium in any of 150 unused Pd samples, comprised of wires from three different manufacturers as well as several foils and powders. More than 100 Pd samples originated from Hoover & Strong. In addition, no tritium was found in ten H₂O control cells employing 1 and 2mm Pd electrodes from two different suppliers.

IV. CONCLUSIONS

Tritium generation has been found in four out of four heavy water cells, employing Pd cathodes which had attained loading ratios D/Pd = 1 by applying a cyclic loading/unloading technique. The tritium concentrations ranged up to 50 times background in the electrolyte and up to 180 times in the Pd cathodes. No tritium was found in light water control cells or in a large number of unused Pd samples. Tritium was identified as such by analyzing the beta emission spectra and comparing them to controls. Four heavy water cells with Pd wires from a different supplier showed no tritium. This may be due to a different metallurgical history. Statistical evaluation of the data yields a probability of only 1 in 2,380 that the observed tritium is due to random spot contamination rather than to nuclear reactions in the highly D-loaded Pd cathodes. While the type of nuclear reactions resulting in the observed tritium is as yet unknown, cold fusion of deuterium atoms in the Pd lattice has to be ruled out due to the observation of a very small neutron signal.¹²

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