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STUDIES OF ELECTROLYTIC AND GAS PHASE LOADING OF PALLADIUM WITH DEUTERIUM

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Highlights are presented of recent results obtained on deuterium and hydrogen loading of palladium both in electrolytes and in the gas phase. Reproducible tritium generation has been found on palladium cathodes with deuterium loadings approaching one deuterium atom per palladium atom. Tritium generation has been observed on four out of four such highly loaded cathodes. No tritium has been observed in four light water control cells operating simultaneously. Total tritium analysis was performed on all hermetically sealed cells before and after each experiment. Tentative evidence is presented for neutron generation and a single anomalous heat excursion. A novel high-pressure electrochemical cell is also described which employs a fuel cell approach, thereby avoiding oxygen evolution. Two anomalous heat excursions have been observed in this cell with excess power values up to 30%. Gas phase experiments of the Wada-type have been performed on palladium, using electrical discharges to activate the palladium. Neutron bursts up to 280 neutrons in 128 microseconds and tritium enhancements in the palladium of up to 25X background have been observed in the palladium. In both electrolytic and gas phase experiments, the tritium distribution in the palladium wires was found to be non-uniform.

INTRODUCTION

Since Fleischmann and Pons first reported on cold nuclear fusion in cells containing palladium cathodes and heavy water electrolyte [1], many groups have confirmed the occurrence of nuclear reactions in deuterium-loaded metals by identifying some of the nuclear by-products formed. In particular, a large number of groups has reported evidence for neutrons [2-5] and tritium [6-9]. While neutrons have generally been detected at only very low levels, tritium generation has been reported at 10^7 to 10^9 higher levels. Unfortunately, these findings are not generally reproducible or predictable, which has made systematic research of cold fusion phenomena most difficult. The present study reports on the reproducible generation of significant levels of tritium on Pd cathodes in acid electrolytes. Reproducibility of tritium generation has been achieved by developing a method to reproducibly attain deuterium to palladium loading ratios near and sometimes slightly higher than unity. This study also reports on tritium and neutron findings in palladium, loaded with deuterium in the gas phase.

EXPERIMENTAL

In contrast to cell designs generally used in cold fusion studies, the cell used in most of our electrolytic experiments, Fig. 1, employs a fritted (porous) glass cylinder to separate the Pd cathode from the Pt anode, thus avoiding O_2 gas evolved on the anode to come into contact with the Pd. Furthermore the cell is hermetically sealed, employs a catalyst to recombine D_2 and O_2, and has provisions to continuously measure the D:Pd loading ratio. A simple water-filled manometer, comprised of two burets which are connected at their lower ends with flexible tubing, serves to determine volume changes in the gas volume above the electrolyte. The volumetric technique, developed earlier by NCFI Engineering [10], allows reliable measurement of the D:Pd loading ratio during electrolysis. A key feature of the technique involves evacuation of the cells and refilling with deuterium or hydrogen gas prior to conducting electrolysis. Before and after each experiment, which generally lasted for about one week, the electrolyte, Pd electrode and gas were analyzed for tritium. Since the cell is sealed during the experiment, any

increase in tritium level can only result from tritium generation in the experiment itself. Considerations regarding deuterium-tritium partitioning between gas, electrolyte and Pd are therefore eliminated. A light water control cell was always run in electrical series with each heavy water cell.

In other electrolytic experiments, we employed the cell design #2 shown in cross-section in Fig. 2. A Pd wire of 2mm diameter is wrapped with battery separator material, followed by a cylindrical fuel cell anode and another layer of separator material. The porous battery separator is pre-wetted with D_2SO_4 (or H_2SO_4) and reaches into a glass cup filled with electrolyte. The cell is contained in a pressure vessel which is evacuated prior to an experiment and then refilled with deuterium or hydrogen of typically 3 atm pressure. When loading the Pd with D by making it the cathode, D^+ ions are reduced to D atoms which may enter the Pd or form D_2 gas. On the Pt anode, D_2 gas is oxidized to D^+ ions and no O_2 gas is evolved if the cell voltage is kept below approximately 1.2V. The D_2 pressure in the pressure vessel decreases during Pd loading and affords continuous measurement of the deuterium loading ratio.

In both cells, experiments were carried out on 99.9% pure 2mm Pd wires (Hoover & Strong) in 0.5M H_2SO_4 control cells and 0.5M D_2SO_4 for the heavy water cells. The heavy water had a typical tritium content of 36ppm/ml. The acid solutions were prepared from reagent-grade chemicals. D_2 gas was electrolytic grade and contained 0.13 to 0.14 nCi/liter tritium according to our own analysis. Temperatures were measured with Thermometrics thermistors to ±0.2°C. Pd wires were palladized and pre-loaded in D_2 gas; the Pt anodes in cell #1 were platinized and Pt fuel cell anodes for cell #2 were purchased from Giner, Inc.

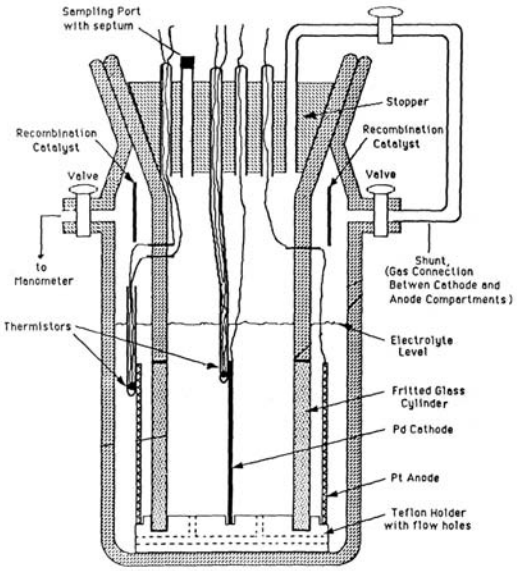


Figure 1. Electrolytic Cell#l

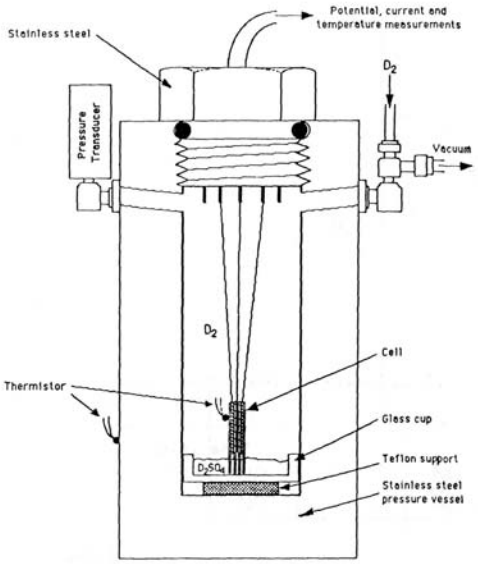


Figure 2. Electrolytic Cell #2. Cross Section and Pressure Vessel.

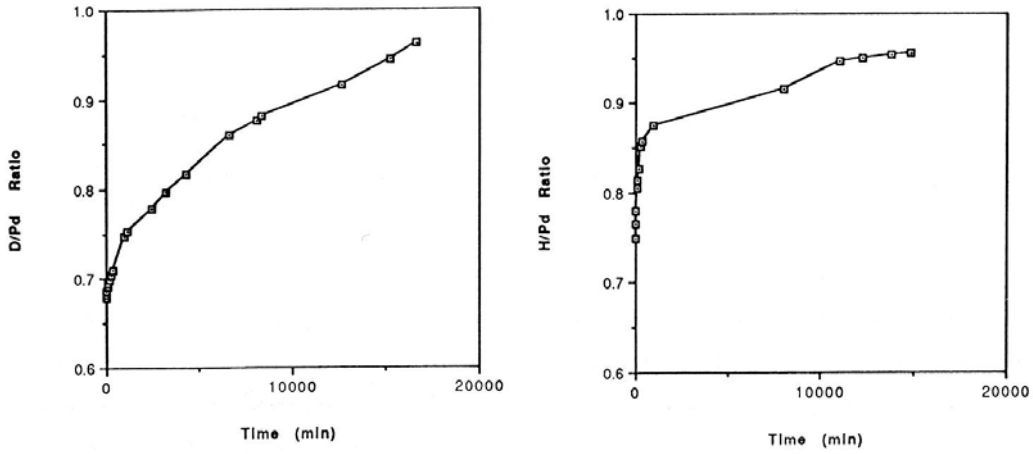
In the gas phase experiments described here, a simple cyclindrical glass cell was employed that could be evacuated to 10^{-3} torr pressure and refilled with D_2 to 3 arm. Coiled Pd wires (Hoover & Strong) of 1m length and 0.5mm diameter were used as electrodes and pre-etched with aqua regia. The Pd was "activated" by applying a 1.2kV a.c. discharge between two Pd coil electrodes in vacuum, followed by a second discharge at ~0.1 atm of D_2 gas. After cooling in vacuum, the Pd was loaded with D at an initial pressure of ~2 atm. The decrease in pressure during loading allowed continuous measurement of the loading ratio.

Tritium analysis was performed by employing a closed-system analytical procedure described elsewhere [11]. Neutrons were measured with a ^{3}He detection system. In the electrolytic experiments, two ^{3}He were employed for each cell. The counting efficiency was approximately 2% and the time gate 8μsec. In the gas phase experiment described here, a system with 34% efficiency and a 120μsec time gas was used [2].

RESULTS AND DISCUSSION

Electrolytic Cell Employing Volumetric Technique.

Typical results of our loading ratio measurements as a function of time are presented in Figs. 3a and 3b for D and H, respectively. Similar results were obtained in three other experiments. The electrolytic deuterium loading experiment was performed for 12 days employing current densities of generally 10 and 20mAcm^2. At the start of applying an electrolytic current, the loading ratio already had a finite value which for the deuterium cell was 0.68 and for the hydrogen cell 0.75. The figures show only a small fraction of the large number of data points taken. Both curves show a continuous rise in the loading ratio to values of about 0.95. The loading ratio in the deuterium cell appears to continue increasing, whereas the H/Pd appears to be saturating. Actually it is the tendency to saturate that is observed in most cases.



Figures 3a and 3b. D/PD and H/Pd loading ratio as a function of time for 2mm Pd wires of experiment #2. Only fraction of data points shown. Details omitted.

The electrolyte, palladium and gas above the electrolyte in each D_2 cell were analyzed for their tritium content before and after each experiment. In the H_2 cells, only electrolyte and Pd were analyzed. Table 1 summarizes the tritium analysis results for all four experiments. We have found in experiments to be reported elsewhere, that tritium is generated predominantly at loading ratios in excess of 0.85. Table 1 lists the times at which this loading ratio is attained. The table also gives the maximum loading ratios that were achieved in the four D_2 cells and four H_2 cells. It is noted that the loading ratios lie between 0.95 and 1.15, with an experimental uncertainty of ±0.05. Tritium was not detected in any of the four H_2 control cells. On the other hand, significant tritium enhancements are found in all four D_2 cells, in particular, in the electrolyte and in the palladium. The total amount of tritium contained in the gas phase is relatively small. The palladium cathode area in all four cells was approximately 2cm^2 and the number of T atoms generated in the four cells is in a relatively tight band, from 4.3 x 10^{10} to 1.1 x 10^{11} T atoms/cm^2. These values are in good agreement with those obtained by several research groups at the Bhabha Atomic Research Center in Bombay, India [7]. Their values run from a low of 5 x 10^9 to a high value of 1.7 x 10^{14} T atoms/cm^2. Predominantly, however, their values are in the range from 10^{10} to 10^{11} T atoms/cm^2. These experiments were run for comparable lengths of time as our experiments. The average tritium generation rate in our experiments varies from 5.8 x 10^4 to 2.0 x 10^5 T atoms/cm^2/sec and the tritium enhancement factor (tritium after to tritium before the experiment) attained values of up to 52.

Table 1
Tritium Analysis of Electrolyte, Pd and Gas

Exper. #		1		2		3		4	
Time at LR>0.85 [h]		163.8		169.7		144.4		161.3	
Electrolyte		$D2SO_4$ $+Li_2SO_4$	H_2SO_4 $+Li_2SO_4$	D_2SO_4	H_2SO_4	D_2SO_4	H_2SO_4	D_2S0_4	H_2SO_4
Loading Ratio Atom Fraction		0.99	1.030	0.96	0.95	1.02	1.07	1.15	1.01
#T atoms Electrol.	Before	$3.8x10^9$	ND	$2.9x10^9$	ND	* $1.0x10^{11}$	ND	$2.4x10^9$	ND
	After	$1.9x10^{11}$	ND	$8.0x10^{10}$	ND	$1.4x10^{11}$	ND	$8.7x10^{10}$	ND
#T atoms in Pd	Before	ND	ND	ND	ND	ND	ND	ND $4.7x10^{10}$	ND
	After	$1.7x10^{10}$	ND	$1.6x10^{10}$	ND	$2.1x10^{10}$	ND		ND
#T atoms Gas	Before	$1.8x10^8$	NM	$1.8x10^8$	NM	$1.8x10^8$	NM	$1.8x10^9$ NM	NM
	After	$1.8x10^8$	NM	$8.3x10^8$	NM	$6.2x10^9$	NM		NM
#T atoms Total	Before	$4.0x10^9$	ND	$3.1x10^9$	ND	$1.0x10^{11}$	ND	$2.6x10^9$	ND
	After	$2.1x10^{11}$	ND	$9.7x10^{10}$	ND	$1.7x10^{11}$	ND	$1.3x10^{11}$	ND
T Generated [# atoms]		$2.1x10^{11}$	ND	$9.4x10^{10}$	ND	$7.0x10^{10}$	ND	$1.3x10^{11}$	ND
Enhancement Factor		52.5	ND	31.2	ND	1.7	ND	50.0	ND
T Generated [# atoms/cm^2]		$1.1x10^{11}$	ND	$4.5x10^{10}$	ND	$4.3x10^{10}$	ND	$6.5x10^{10}$	ND
T Generate Rate [# atoms/cm^2/S]		$2.0x10^5$	ND	$7.4x10^4$	ND	$8.3x10^4$	ND	$5.8x10^4$	ND

* = Batch of D_20 with high T content
ND = Not Detected
NM = Not Measured
LR = D/Pd or H/Pd Loading Ratio

The tritium analysis of the palladium cathodes was carried out by analyzing several small pieces cut from the entire electrode. The tritium distributions in the four Pd cathodes are shown in Fig. 4

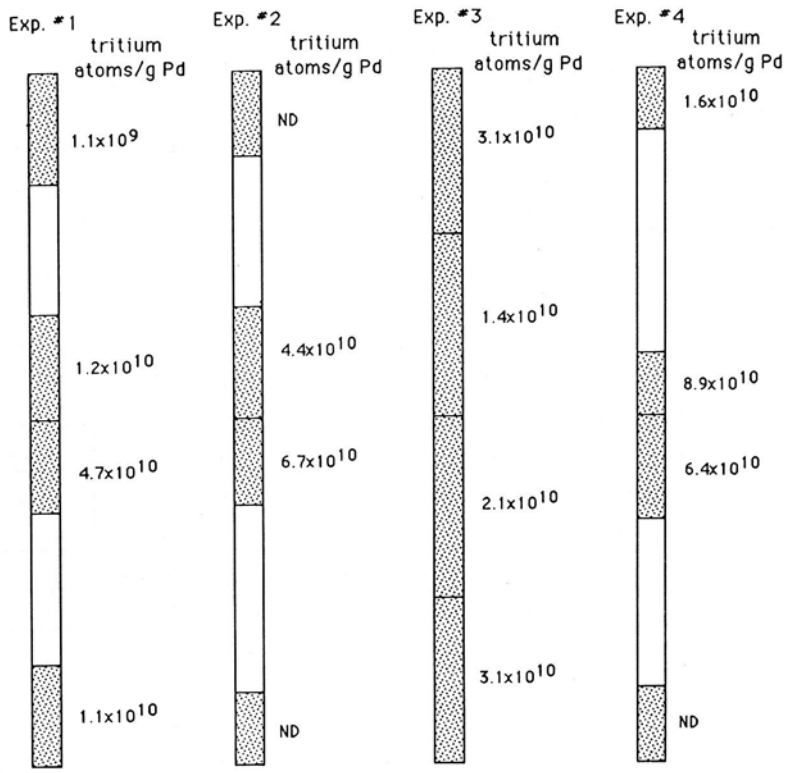


Figure 4. Tritium distribution in Pd cathodes after D_2O electrolysis. ND = not detected; detection limit is 5×10^8 tritium atoms/g.

Comparatively much less tritium is found in the ends of the wires as compared to the center. The 8 pieces near the center of the 4 electrodes show a surprisingly tight band of values, namely, from 1.2×10^{10} to 8.9×10^{10} T atoms/g Pd. 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. Since the detection limit of our analytical procedure is 5×10^8 T atoms/g Pd, the tritium levels are up to 180 times larger than the maximum possible contamination level before electrolysis.

The results of our neutron measurements are presented in Table 2. It is seen that the number of triples monitored in three of the four D_2 cells is consistently between a factor of 2.0 and 2.6 higher than in the H_2 cells. In the entire two month period of observation, the total number of triples is 40 for the four D_2 cells and 18 for the four H_2 cells.

Table 2
Triple and Quadruple Neutron Counts in D_2SO_4 (D) and H_2SO_4 (H) Cells

Experiment*	1		2		3		4	
	D	H	D	H	D	H	D	H
# Doubles/24h	77	36	61	32	62	34	44	39
# Triples	13	5	14	7	13	5	0	1
# Quadruples	1	0	0	0	1	0	0	0

The total number of neutron events and the difference in numbers for D_2 and H_2 cells are small. Further, the role of one Pb brick each, used as a weight in the vicinity of both cells in all four experiments, needs to be explored. Reassuringly, removal of the bricks in a fifth experiment, lasting 22 days, resulted in 11 triples in the D_2 and only 5 triples in the H_2 cell.

Figures 5a and b show the electrical input power into the cell and the temperature of the Pd cathode and Pt anode as a function of time for the D_2 cell in Fig. 2 for the time interval from 15,430 to 16,030 minutes. The electrical input power to the cell increases steadily with time. Whereas the temperature of the platinum anode stays constant at 26.84°C during the entire time period of 700 minutes, the temperature of the Pd cathode shows a relatively constant values of 26.7°C only in the first 370 minutes of the time period shown. The relatively sudden temperature excursion of the Pd cathode from 26.7°C to 27.7°C followed by less elevated temperatures in the subsequent 70 minutes represents an increase in temperature which cannot be explained on the basis of the smoothly rising electrical input power. On the basis of a temperature-power input calibration performed on the cell, the temperature excursion in Fig. 5b corresponds to an excess power excursion with a peak value in excess of 10W, representing a 187 times increase over the electrical input power. The excess energy produced during this power excursion amounts to approximately 5 x 10^4 Joules. Operation of the thermistor was verified as correct after the conclusion of the experiment. However, the cell is not set up to do precise calorimetry and these results should be regarded as tentative.

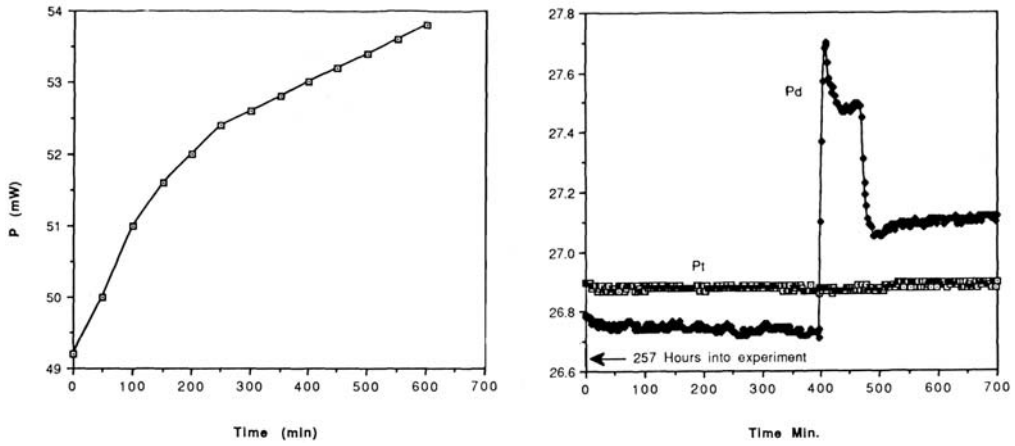


Figure 5. (a) Electrical power input of D_2SO_4 cell in experiment #2.
(b) Observed temperature - time curve of Pd Cathode and Pt anode.

In the high-pressure cells employing fuel cell anodes (Fig. 2), D:Pd loading ratios were consistently lower than in cells of type 1, minor tritium was found only in one of three experiments with 2mm Pd wires, and no neutrons were detected. However, two excess heat events occurred during a 12-day experiment employing 2mm Pd. These two events are shown in Fig. 6 in the time interval 8000 to 17,000 minutes. The cell had been calibrated, yielding a temperature change of 0.035°C/mW/cm^2. The power output exceeds the power input in two events, from 10,500 to 12,775 minutes and from 14,200 to 16,939 minutes. The apparent excess power excursions go to highest values of 13mW as compared to an electrical power input of 10mW, thus amounting to excess power values of up to 30%. The apparent energy generated in the two time intervals amounts to approximately 300 Joules. It should be emphasized that (1) these are the results of a single experiment at this time, (2) the temperature excursions are very small, (3) there was only one thermistor measuring the temperature and (4) light observed temperature and power excursions as tentative observations that require considerable verification.

In gas phase loading experiments of Pd wires with D, employing the Wada technique, we have found evidence for neutron and tritium generation. The most successful experiment was performed in collaboration with S.E. Jones at Brigham Young University. After Pd activation and D_2 gas loading, four neutron bursts were observed in a time period of 100 hours. These corresponded to bursts of 20, 20, 30 and 280 source neutrons (detection

efficiency 34%) in a 128μsec time gate. This is shown in Fig. 7.

The tritium distribution in Pd electrodes used in our Wada-type of gas loading experiments was usually highly non-uniform. Figure 8 shows the results of our tritium analysis on the Pd wires used in the experiment of Fig. 7. In "hot spots", we observed tritium levels of up to 10^{10} atoms/g Pd. Before the experiment, the Pd did not contain tritium within the detection limit of the analysis, that is, ~4 x 10^{8} atoms/g Pd.

Of twenty "valid" (equipment debugged, procedures developed) experiments with Pd, nine or ten exhibited elevated levels of neutrons and/or tritium, representing a success rate of 45 to 50%.

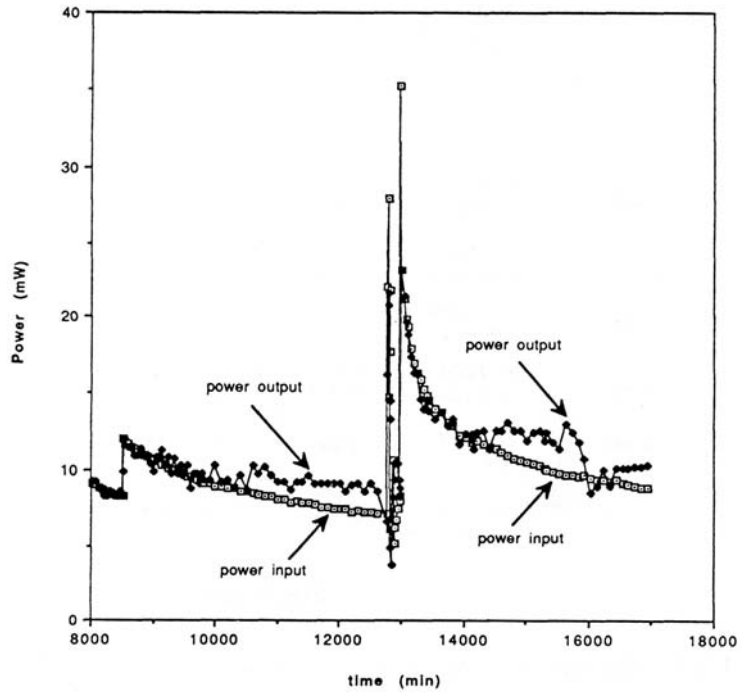


Figure 6. Measured electrical power input and calculated power output (from measured cell temperature) when deuterium loading 2mm Pd wire.

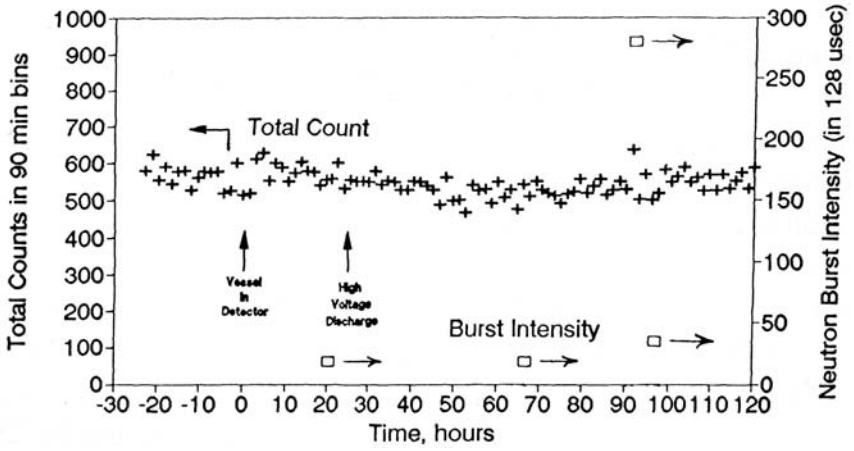


Figure 7. 90-minute total neutron count averages and neutron bursts (in source neutrons) on Pd wires in Wada-type D_2 gas loading experiment.

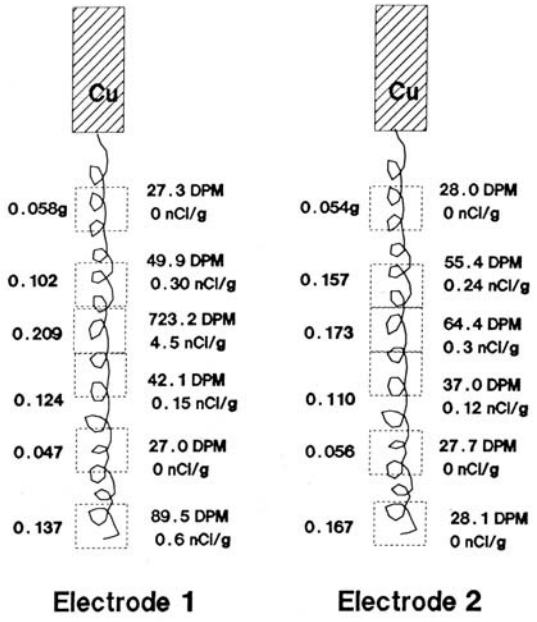


Figure 8. Tritium distribution in Pd wires used in Wada-type experiment of Fig. 7.

CONCLUSIONS

Employing a hermetically sealed electrolytic cell and a volumetric measurement technique for the D:Pd ratio, we have developed a procedure to attain loading ratios close to unity. With such high loading ratios, tritium generation has been observed reproducibly in four out of four heavy water cells whereas none of the four light water controls showed tritium generation. Tritium enhancements up to a factor 52 were observed. As we performed total tritium analysis on electrolyte, electrode and gas before and after each experiment, and as the cells are hermetically sealed, we conclude that the tritium can only have been generated by nuclear phenomena in the deuterium-loaded palladium during the experiment. Neutron generation has also been observed in these heavy water cells, but at very small levels. Excess heat generation has tentatively been observed in three cases: A 70-minute event with 10W excess power and $4 \cdot 10^4$ Joules energy on one of the four heavy water cells and two 38- and 46h events with up to 30% excess power and 300 Joules in one of our high-pressure electrolytic cells. In 45 to 50% of our "countable" Wada-type D_2 gas loading experiments on Pd wires, we have observed neutron and/or tritium generation. The most intense burst consisted of 280 source neutrons in a time gate of 128μsec. The largest amount of tritium was found near the center of one of the electrodes which had produced the 280-neutron burst. A tritium concentration equivalent to 4.5nCi/gPd or 10^{10} tritium atoms/g Pd was found. This compares to a maximum possible tritium contamination level in the Pd of 4×10^8 atoms/g Pd.

ACKNOWLEDGEMENTS

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