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Preliminary note

Production of tritium from D_2O electrolysis at a palladium cathode

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INTRODUCTION

In the present communication, we report data that may be relevant to the phenomenon of room temperature fusion [1]. It is the contention of the authors that the alleged phenomenon is better characterized by the production of nuclear particles than by the measurement of bursts of heat. Here, we describe the observation of tritium produced in eleven D_2O electrolysis cells at levels 10^2–10^5 times above that expected from the normal isotopic enrichment of electrolysis. Particular attention has been paid to possible sources of contamination.

EXPERIMENTAL

Pd cathodes of diameters 1 to 6 mm were subjected to D_2 evolution from $D_2O + 0.1$ M LiOD electrolysis. The resulting solutions and the gases were examined for tritium.

Samples of liquid electrolyte were measured using liquid scintillation counting.

In all cells, measurements were made for the activity of ^3H in solution, and in one cell, gases evolved were recombined external to the cell using 0.5% platinum on alumina catalytic beads (recombination catalyst). The resulting liquid was analyzed in the same way as the electrolyte samples.

Twenty four electrochemical cells were fabricated using 15 ml Pyrex centrifuge tubes. The ends of the tubes were sealed with Viton rubber septa, through which electrode connections were made. Palladium samples supplied by Hoover and Strong (Richmond, VA), via the Texas Coin Exchange, 1 mm by 4 cm, and 3 mm by 4 cm in dimension (99.9% purity) were prepared as shown in Table 1. 6 mm × 4 cm electrodes were obtained from SurePure Chemetals Inc. All electrode connections were made using 99.9% pure nickel wire (0.5 mm), spot welded to the palladium wires. The nickel connections were fed through the septa, to form an air-tight seal.

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Nickel gauze anodes (99.9% pure), used in *all* cases, were washed in 5 M HCl, then in D_2O, and allowed to dry in air. A 0.1 M LiOD solution was prepared using 99.9% pure lithium metal from Alfa associates, which was added to 1 liter of 99.9% pure deuterium oxide (Aldrich Chemical Co.), in an atmospheric bag containing argon. Addition to the cells (D_2O, LiOD refilling) were made through the rubber septum using disposable syringes (one use only), equipped with stainless steel needles. Gases evolved during electrolysis were allowed to escape through a needle, pierced through the septum, attached via Tygon tubing to a mineral oil bath to avoid light water contamination. In general, the 1 mm cells were at first run galvanostatically at 50 mA cm^{-2} for 14 to 16 days, the 3 mm electrodes being charged for up to 28 days. Throughout this period, additions of D_2O were made (1 to 2 ml per day at low current density and up to 3 to 4 ml h^{-1} at high current density). The potential and current density through each cell was monitored 24 h a day. After the time stated, the current density was increased to 500 mA cm^{-2} for periods up to 12 h. Samples of electrolyte were withdrawn for tritium analysis from the cell using a sterile syringe (later discarded).

Tritium analysis was performed on the alkaline electrolyte by in-situ Liquid Scintillation Counting (LSC). Three counters were used in these analyses. The first of these is a Wallac LKB model 1219 LSC; the second, a Wallac LKB model 1410, and the third an instrument constructed in the Cyclotron Institute. A water soluble scintillation cocktail (Biosafe II, Research Products International Corporation, 15 ml) was added to 1 ml of sample, and allowed to stand under cover for 30 min before counting, which was found to be sufficient for elimination of chemiluminescence contributions for the work reported here. The samples were then analyzed in a double-blind fashion (with respect to the operator of the counter). Multiple blank samples of H_2O, D_2O, and 0.1 M LiOD were included for analysis. Evidence for chemiluminescence of the scintillation cocktail had been discovered when samples of 1 M LiOD had been analyzed. Therefore, a test was made using samples ranging from 1 M to 0.01 M LiOD, and including samples that had been neutralized by potassium hydrogen phthalate (KHP). Results of these experiments are shown in Fig. 1, which set the criterion for eradication of chemiluminescence. Samples run 24 h later, showed no significant change in activity levels. The efficiency of the model 1219 detector for tritium in the samples was 33%, for the model 1410 around 40%, and for the counter constructed in the Cyclotron Institute, around 30%. 1 min- and 10 min analyses (some samples were run overnight) were performed. A detailed analysis of the energy spectra from the Cyclotron Institute counters yielded the correct β energy end point for tritium (18 keV). The results are given as counts per minute (cpm) per ml of sample, and as disintegrations per minute (dpm) per ml of samples. The conversion factor is given by:

$$\mathrm{dpm\ ml}^{-1} = \left(\mathrm{cpm\ ml}^{-1}_{\mathrm{sample}} - \mathrm{cpm}_{\mathrm{cocktail}}\right) \cdot (V/E)$$

where E is the efficiency of the detector and V is the volume factor to give results per ml of sample.

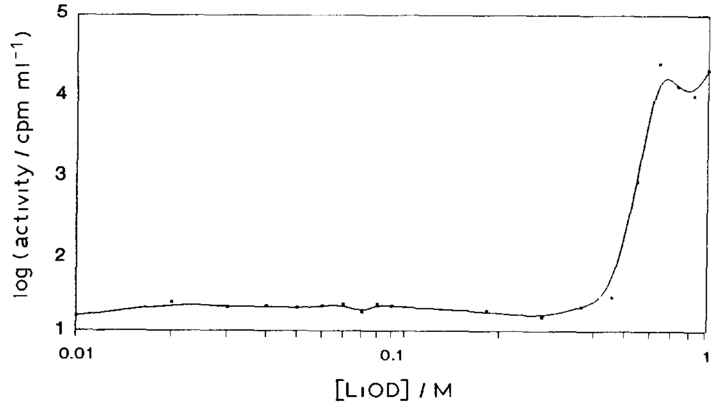

Fig. 1. The effect of electrolyte concentration on chemiluminescence of the scintillation cocktail.

After the analysis at Texas A&M, an examination of the tritium content of liquids resulting from the electrolysis, including a tritium (HTO) standard and blanks of LiOD and D_2O, was made by Los Alamos National Laboratory (National Tritium Center), Argonne National Laboratory, Battelle Pacific Northwest Laboratory and at the General Motors Research Laboratory. These results are shown in Table 2 below.

One of the cells used in the experiment (cell A8) also featured an external gas recombination arrangement using 0.5% platinum on alumina pellets which gave close to 100% recombination at low current densities (50 mA cm^{-2}).

The tritium production of this cell was followed for a further period of time. It had been charged at low current density (50 mA cm^{-2}) for 16 days, and then put to 500 mA cm^{-2} for 8 h, after which it was returned to the charging current, since the levels of tritium were at background. After 4 weeks, the recombination catalyst was put in place, and the recombinant was collected for 2 weeks. After this, the activity in the recombined gas and the electrolyte was measured on the 1410 LSC, resulting in the highest level found in all 9 cells. These results are shown in Table 3b below.

Another cell (cell A2) was tested for tritium over an extended period of time. It was run initially at low current density for 16 days, followed by a 10 h period at high current density, after which, tritium was *not* produced. The cell was then transferred to the Cyclotron Institute where it remained at low current density for another week, with no tritium production. On 6 May 1989, the current was increased to 110 mA cm^{-2} for 2 h, increased again to 300 mA cm^{-2} for 20 min, decreased to 90 mA cm^{-2} for seven days at which point it was returned to 50 mA cm^{-2} until 22 June. The tritium content of the solution was monitored during this time and the results are shown in Fig. 2, which limits the apparent production period to approximately 2 days.

In one of the cells (cell A7) the build up to tritium as a function of time was followed in more detail at high current density. The results shown in Fig. 3 place a limit on a period of production of approximately 12 h.

The possibility that tritium was present in the D_2O, and the Li is ruled out by the results of Tables 3a and b. Each batch of D_2O that was used for refilling the cells

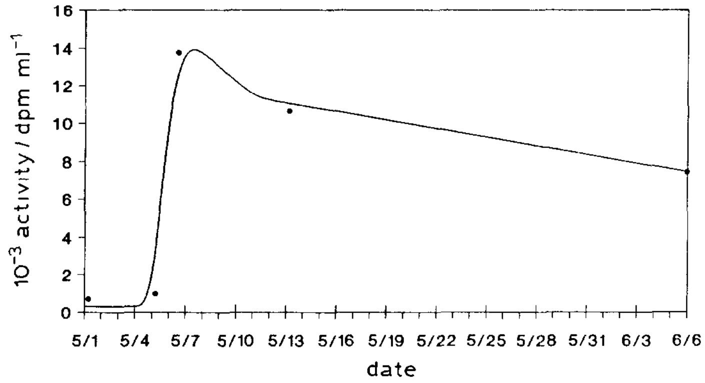

Fig. 2. The production of tritium in the electrolyte of cell A2 as a function of time (ordinate gives date: 5/1 means 1 May, etc.).

was analyzed for tritium content, both on the 1219 instrument (Table 3a), and the 1410 (Table 3b, shown as a mean of 10 results). Several experiments were run in which *no tritium was observed*, including identical cells to the ones which did produce tritium, except for the electrolyte, *which was 0.1 M LiOH in H_2O* (Tables 3b and 4). Possible contamination from the nickel anode was examined by dissolving an unused piece of nickel from the same large sheet used for all counter electrodes in concentrated nitric acid, followed by neutralization and then counting, with negative results.

Samples of virgin palladium and nickel of the same batch used for all 1 mm Pd cells were sent for analysis to Los Alamos National Laboratory. Thermal descorption mass spectrometry was used and no tritium was found in either electrode material (and likewise use for the last 4 entries in Table 4., i.e. D_2O and H_2O blanks). In addition, palladium is used throughout as a *cathode*, the electrochemical

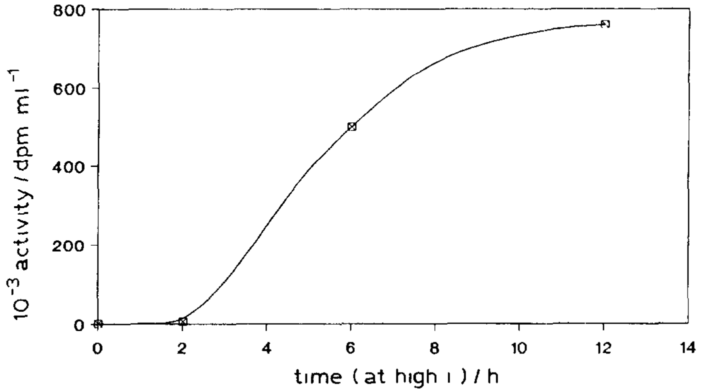

Fig. 3. The production of tritium in the electrolyte of cell A7 as a function of time.

nature of which would tend to drive H (D, T) *into* the cathode, rather than evolve tritium from within the electrode.

Interference with the experiments is considered improbable because of positive

TABLE 1

Cell identification, electrode treatment, solution type and tritium activity of electrolyte samples performed on 1219 LSC

Cell	Electrode pretreatment [a]	Solution	Corrected ^3H activity/ dpm ml^{-1}
A1	No treatment	0.1 M LiOD	3.8×10^4
A2	No treatment	0.1 M LiOD + 0.1 mM NaCN	
	After 16 days at 50 mA cm^{-2} then for 8 h at 500 mA cm^{-2} (5/1/89)		168
	50 mA cm^{-2} for 4 days (5/5/89)		134
	50 mA cm^{-2} for 3 h, 110 mA cm^{-2} for 2 h, 200 mA cm^{-2} for 20 min (5/6/89)		1.1×10^4
	50 mA cm^{-2} (5/7/89)		1.4×10^4
	(5/7/89–5/13/89)		1.1×10^4
	(5/13/89–6/6/89)		7.5×10^3
A3	Anneal	0.1 M LiOD	4.9×10^6
A4	Anneal	0.1 M LiOD + 0.1 mM NaCN	1.2×10^5
A5	Acid etch	0.1 M LiOD	3.7×10^6
A6	Acid etch	0.1 M LiOD + 0.1 mM NaCN	3.3×10^4
A7	Electrochemical	0.1 M LiOD	
	Before high current density		102
	After 2 h at 500 mA cm^{-2}		5223
	After 6 h at 500 mA cm^{-2}		5.0×10^5
	After 12 h at 500 mA cm^{-2}		7.6×10^5
A8	Electrochemical	0.1 M LiOD + 0.1 mM NaCN	
	After 16 days charging and 8 h high current density (5/1/89)		192
	Electrolyte levels after 6 weeks at 50 mA cm^{-2}		5.0×10^5
	Recombined gas levels after 2 weeks of external recombination at 50 mA cm^{-2}		5.0×10^7
B3 (3 mm)	Anneal	0.1 M LiOD	6.3×10^4
B5 (3 mm)	Acid etch	0.1 M LiOD	48
Cell 1 (6 mm)	No treatment	0.1 M LiOD	117

[a] Key for electrode surface pre-treatment: Anneal = annealing at 800 °C, 10^{-6} Torr, 8 h; Acid etch in 5 M HCl, 15 min; Electrochemical oxide removal, 2 h.

results from the Cyclotron Institute to which entrance is prohibited except by the usual personnel at the Institute. There are also no supplies of tritium at the Cyclotron. Inadvertent contamination is unlikely because no tritium work has been performed in either of the laboratories involved.

RESULTS

The results and noteworthy features of the cells are summarized in Tables 1–4, some features of which are listed below.

(1) Electrodes produced tritium in different time domains (i.e. cell A2 and A8), of which some electrodes required lengthy low current density treatment (up to 9 weeks) before production.

(2) Ni gauze (NiO_2) was the anode material in all experiments reported here, in contrast to platinum wire or gauze used by most investigators.

(3) The tritium concentration in solution (DT?) increases with time until it reaches an asymptote (Fig. 3), which can be interpreted in terms of the end point of production. Tritium production at the electrode ceases after some hours of activity (Figs. 2 and 3).

(4) Tritium from the $D_2 + DT$ mixtures evolved from the electrode gives rise, after recombination, to a solution concentration about 100 times greater than that with which the gas off from the electrode is in equilibrium.

DISCUSSION

It can be shown that [2] prolonged electrolysis of a solution regularly made up to constant volume by addition of D_2O gives an isotope enrichment equal to the known separation factor of H, D, T, i.e. at a negligible level compared to the results reported in Table 1 for the 9 most active cells.

Reports of tritium production can always be questioned as to contamination. Defence against each suspicion has to be made each time a new suspicion is

TABLE 2

Confirmatory results from outside sources on various samples

Institution	Corrected ^3H activity/dpm ml^{-1}				
Sample	Cell 1 [a]	Cell 2 [a]	HTO standard	0.1 M LiOD	D_2O
Texas A & M	2.13×10^6	1157	7.23×10^5	93	47
Battelle	1.96×10^6	1170	8.08×10^5	127	140
Argonne	1.96×10^6	1020	7.59×10^5	90	114
Los Alamos	1.97×10^6	800–1300	6.50×10^5	113	161
General Motors	1.80×10^6	1000	N.A. [b]	N.A. [b]	N.A. [b]

[a] Cell 1 corresponds to cell A1 in Table 1 approximately 1 week after the high current density treatment, cell 2 corresponds to cell A5 in Table 1 before high current density treatment.

[b] N.A. = not analyzed.

TABLE 3

(a) Blank experiments during tritium analysis performed on the 1219 counter

Sample	Activity/cpm ml^{-1}	Activity/dpm ml^{-1} [a]
D_2O Analysis No. 1	65	48
D_2O Analysis No. 2	70	63
D_2O Analysis No. 3	67	54
D_2O Analysis No. 4	60	33
D_2O Analysis No. 5	50	3
D_2O Analysis No. 6	71	66
D_2O Analysis No. 7	75	78
D_2O Analysis No. 8	62	39
0.1 M LiOD Analysis No. 1	75	78
0.1 M LiOD Analysis No. 2	70	63
0.1 M LiOD Analysis No. 3	74	75
0.1 M LiOD Analysis No. 4	65	48
0.1 M LiOD Analysis No. 5	60	33
0.1 M LiOD Analysis No. 6	66	51
0.1 M LiOD Analysis No. 7	76	81
0.1 M LiOD Analysis No. 8	70	63
Neutralized 0.1 M LiOD	73	72
Neutralized 0.1 M LiOD + 0.1 mM NaCN	76	81
Dissolved nickel in acid Analysis No. 1	78	87
Dissolved nickel in acid Analysis No. 2	80	93
Dissolved nickel in acid Analysis No. 3	76	81
Scintillation cocktail	49	–

(b) Mean of 10 blank experiments during tritium analysis performed on the 1410 counter

Sample	Activity/cpm ml^{-1}	Activity/dpm ml^{-1} [a]
Biosafe II cocktail	170 ± 13	–
H_2O Analysis	161 ± 16	0
D_2O Analysis	210 ± 16	100
0.1 M LiOD Analysis	220 ± 20	125
0.1 M LiOH Analysis	157 ± 12	0
Dissolved nickel in nitric acid	140 ± 20	0
Tygon tubing in NaOH	105 ± 20	0
Rubber stoppers in NaOH	150 ± 20	0
Recombination catalyst in NaOH	140 ± 15	0
Dissolved shavings from cutters	160 ± 11	0
Dissolved shavings from vacuum chamber	164 ± 17	0
Dissolved shavings from spotwelder	155 ± 10	0

[a] Background corrected.

expressed. Tables 3 and 4 show that an extensive program of checks and blanks has been performed.

The electrode surface seems to be involved in the nuclear events implied here since, according to Storms [3], a tritium-producing Pd cathode, when made anodic in a virgin D_2O + LiOD solution, produced no tritium, i.e. none dissolved *from inside* the electrode.

TABLE 4

Details of cells that produced no tritium with 1410 LSC

Experiment	Corrected activity /dpm ml^{-1}
3 mm×3 cm Ti Cathode in 0.1 M LiOD with internal gas recombination	275
3 mm×3 cm Pd Cathode in 0.1 M LiOD with internal gas recombination	235
3 mm×3 cm Ti Cathode in 0.1 M LiOD with internal gas recombination	285
0.5 mm×1 cm Pd Cathode in 0.1 M LiOD with internal gas recombination	55
4 mm×2 mm Pd disc Cathode in 0.1 M LiOD with internal gas recombination	365
0.5 mm×1 cm Pd Cathode in 0.1 M LiOD with external gas recombination (recombined gases measured)	315
1 mm×4 cm Pd Cathode in 0.1 M LiOD with external gas recombination recombined gases measured 7/18/89)	75
1 mm×4 cm Pd Cathode in 0.1 M LiOD with external gas recombination (recombined gases measured 7/21/89)	33
1 mm×4 cm Pd Cathode in 0.1 M LiOH (H_2O) No gas recombination	0
1 mm×4 cm Pd Cathode in 0.1 M LiOH (H_2O) No gas recombination	18

In further support of the present observations, several others have been made [3–6].

We are aware that, according to the classical theory of nuclear physics, when D–D fusion occurs, the rate of neutron production should be approximately equal to that of tritium. This is not observed in the present experimental program [7]. We believe that it is important firstly to establish the *facts* about tritium production on electrodes. The theory of electrochemical confinement will be discussed elsewhere.

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