Preliminary note

The observation of tritium in the electrolysis of D_2O at palladium sheet cathodes *

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(Received 27 November 1990; in revised form 25 February 1991)

INTRODUCTION

Although the exact nature of the processes inside palladium cathodes under D_2O electrolysis remains to be established, systematic studies carried out since the first announcement [1] tend to confirm that neither chemistry nor classical physics can account for the enthalpy excess sometimes observed [2,3]; abnormal amounts of tritium are found sporadically in the electrolyzed D_2O [4,5].

The irreproducibility of the phenomena evidently requires iterated confirmations through manifold research efforts.

As part of this process, we present here some observations on tritium measurements in the $D_2O + 0.1$ M LiOD/Pd system. Although tritium is probably only a by-product of much more complex phenomena [6,7], the formation of this species can scarcely be questioned as evidence of nuclear phenomena providing fortuitous contamination can be ruled out.

We have used Pd sheet electrodes since deuterium loading is faster than in the rod electrodes used in the original work [1]. The large and variable area/volume ratios should eventually allow discrimination between surface and bulk reactions.

EXPERIMENTAL

(a) Materials

Pd sheets (99.9%) of 0.005, 0.01, 0.02, 0.05 cm thickness and Pt coil (99.9%), $\varnothing = 0.1$ cm were obtained from Johnson Matthey through Metalli Preziosi (Milan, Italy).

Ni coil (99.5%), $\varnothing = 0.1$ cm was obtained from Carlo Erba (Milan, Italy).

D_2O was mainly from a single supply from Jansenn Chimica (Belgium); the ^3H level lay in the range 20–40 dpm ml^{-1}. The single D_2O batch $\simeq 80$ dpm ml^{-1}, used for system 1 (see below) was from a different source.

LiOD was prepared by dissolution of Li metal (Fluka) in D_2O.

H_2O, used in some runs, was of Millipore grade; the electrolyte was LiOH (Merck, Germany).

The liquid scintillator cocktail (LSC) was Pico-Aqua ^{TM} from Canberra-Packard (Milan, Italy).

(b) Apparatus and procedure

The electrolytic cells were assembled using centrifuge tubes in Duran glass of internal dimensions $h = 10.5$ cm, $\varnothing = 3.4$ cm. Cathodes were made from the Pd sheet by cutting squares having an extra strip along one side, 3.0×0.1 cm^2, to serve as the electric connection. The strip was fixed with Araldite epoxy resin to the inside of a Pyrex tube ($\varnothing = 0.3$ cm), so that only the square was in contact with the electrolyte.

A Ni or Pt coil anode surrounded the cathode; its area was about 15 times that of the cathode.

The cells were sealed with Teflon lids supporting the electrodes. The lids contained two other glass tubes; one, sealed by a Viton septum, allowed periodic sampling and refilling of electrolyte; the other tube passed the electrolytic gas to a bubbler containing paraffin, which insulated the system from the atmosphere. The cells were charged with 35 ml of electrolyte.

The Pd/Pt electrodes were used as supplied; the Ni anodes were left in 0.5 M LiOH solution for 2 h followed by drying in air for 24 h.

Electrolysis in D_2O was carried out galvanostatically using a Model 55 Potentiostat by Amel (Milan, Italy). The same instrument coupled to a Model 731 Amel Integrator was used for potentiostatic measurements (vs. SCE) in H_2O.

(c) Tritium analysis

^3H was determined by counting the β decay of the solutions with a liquid scintillator, using a high-sensitivity spectrometer, designed and assembled in the Department of Physics of the University of Padova. High-amplitude resolution analysis of the sample spectra allowed detection and correction of counting interferences; high time-resolution pulse analysis combined with delayed-coincidence counting corrected the spectral results simultaneously for chemiluminescence and spurious counts. The full energy of the sample and chemiluminescence were col-

lected and displayed on a Multichannel 5600 Ortec–Nerland Analyzer for quick identification of β energy spectra and simultaneous spurious pulse distributions. The spectrometer efficiency was around 40%, as determined from authentic tritiated standards.

The standard procedure was to dilute 1 ml samples of electrolyte (without prior neutralization) with 15 ml of pseudo cumene-based LSC in a standard low K 40 borosilicate glass vial. Counting experiments were then carried out for 1000 s and averaged over 3–5 determinations. Samples run weeks after the first determination showed no significant change in activity.

The data reported in the tables below represent the ^{3}H increases over the solution level before electrolysis; they are all background-subtracted and corrected for spectrometer efficiency:

$$\text{dpm ml}^{-1} = \left(\text{cpm ml}^{-1} \text{ sample} - \text{cpm ml}^{-1} \text{ blank} - \text{cpm ml}^{-1} \text{ LSC}\right)/0.4$$

RESULTS

H_2O / LiOH electrolysis

Experiments were carried out in $H_2O/0.1$ M LiOH to measure the conversion Pd $\rightarrow$ PdH$_x$. A single $0.50 \times 0.50 \times 0.01$ cm^3 Pd cathode was charged potentiostatically at -2.00 V for 4 h; this should exceed by more than ten times the time necessary for charging if this is controlled by hydrogen diffusion into the metal ($t = (d/2)^2/D$, where $d = 0.01$ cm and $D = 10^{-7}$ cm^2 s^{-1} [8]).

The hydride content was determined by anodic stripping; linear sweep voltammetry at 1–2 mV s^{-1} gave a drawn-out wave having its onset at $\simeq -0.9$ V and a limiting current towards 0.40–0.50 V. Potentials $\geqslant 0.80$ V caused oxidation of the

TABLE 1

Data for a set of successive charge–discharge cycles (potentiostatic reduction at -2.0 V (SCE) for 4 h followed by hydride stripping at $+0.5$ V (SCE); electrolyte $H_2O/0.1$ M LiOH; H/Pd stoichiometry based on Pd weight determined: (a) post mortem; (b) from the geometry ($\sim 0.5 \times 0.5 \times 0.01$ cm^3))

Run	Q_{red}/C	Q_{ox}/C	[Poison]/mol l^{-1}	H/Pd atomic ratio	
				a	b
1	200	30.5	–	0.88	1.05
2	111	24.3	–	0.70	0.83
3	149	28.5	–	0.82	0.98
4	180	19.5	–	0.56	0.67
5	225	23.4	–	0.67	0.80
7	297	17.4	As$_2$O$_3$ (5×10^{-5})	0.50	0.60
8	498	32.3	As$_2$O$_3$ (5×10^{-5})	0.93	1.11
12	592	28.8	–	0.83	0.99
20	495	29.2	NH$_2$CSNH$_2$ (10^{-3})	0.84	1.00

metal, so stripping was performed by stepping the electrode from -2.00 V to 0.50 V with integration of the current. N_2 was bubbled into the electrolyte to minimize any interference by molecular H_2 and O_2.

In Table 1 are listed the data of a set of successive charging–discharging runs (the electrode was cleaned using distilled H_2O between runs).

The cathodic charge (column 2) increases progressively presumably because of roughening due to charge–discharge cycles. In fact, the oxidative charge (column 3) is not related to the reductive one: the highest value in 0.1 M LiOH alone was obtained in the first run, the later runs showed extensive variation. Experiments 7, 8 and 20) were carried out in the presence of typical recombination poisons [10]. The highest and lowest values of stripping charges were both measured 5×10^{-5} M As_2O_3 solution.

Column 4 of the table gives the apparent stoichiometry of the hydride, obtained from the oxidative charge and electrode mass. For the data in (a) the mass was 0.0384 g, as determined by weighing the electrode post mortem; for the data in (b) the mass was 0.0300 g, as determined by electrode geometry. The values in (b) are preferred since those determined by weighing are affected by deposition of material from the solution.

The data of Table 1 show the diversity of the H/Pd ratios for identical cathodic conditions, and that high H/Pd ratios of about 1:1 can be approached, although irreproducibly.

D_2O / LiOD 0.1 M electrolysis: ^3H measurements

Pd / Ni cells

Experiments 1, 2, 3, and 4 consisted of at least two cells connected in series and fed by the same galvanostat. The cells were identical were identical except for the thickness of the cathodes; "poisons" were added to some of the cells.

Table 2 lists the data of system 1, for $1.50 \times 1.00 \times 0.005$ cm^3 cathodes. Column 1 lists the sampling times for ^3H measurements; Columns 2 and 3 list the cell current and current density maintained during sampling.

Columns 4 and 5 give the H-level increments for cell A containing thiourea and B containing As_2O_3, respectively.

The initial ^3H content was higher than in the solution used to refill the cells ($\simeq 80$ as against $\simeq 20$ dpm ml^{-1}). If we assume the D/T electrolytic separation factor to be $\simeq 2$ [11], a drop in ^3H activity to $\simeq 50\%$ of the initial value for prolonged electrolysis would be expected.

The situation shown in Table 2 for cell B is somewhat different; after an initial decrease, a positive increment above statistical error is observed between 100 and 150 h. This is significant when considering that in this period, $\simeq 20\%$ of the initial solution had been replaced to compensate for losses due to electrolysis and sampling. The ^3H content in cell A may follow a similar trend. For electrolysis times in excess of 150 h, the predicted ^3H decrement was observed for both A and B.

TABLE 2

Tritium levels during electrolysis in $D_2O/LiOD$ 0.1 M (electrolyte, 35 ml/0.1 M LiOD: cell 1A + NH_2CSNH_2 10^{-3} M; cell 1B + A_2O_3 8×10^{-5} M. Activity of feeding $D_2O = 19.4 \pm 9.4$ cpm ml^{-1} Activity of feeding $D_2O/LiOD = 27.2 \pm 18$ cpm ml^{-1})

Electrolysis time/h	I [a]/ mA	i [a]/ mA cm^{-2}	Tritium activity in cell 1A /dpm ml^{-1}		Tritium activity in cell 1B /dpm ml^{-1}	
			(a) initial	(b) $\Delta\,^3H$	(a) initial	(b) $\Delta\,^3H$
–	–	–	81.4 ± 12.1	–	83.7 ± 3.0	–
46	90	30		3.2 ± 2.0		-26 ± 3.9
72	90	30		10.2 ± 21.7		0.25 ± 16.5
97	90	30		11.1 ± 11.3		25.1 ± 17.9
166	150	50		-18.9 ± 14.2		3.5 ± 3.2
188	350	127		-16.4 ± 24.1		-51.1 ± 7.2
216	550	183		-39.6 ± 7.9		-27.6 ± 5.2
243	750	250		-36.3 ± 4		-23.4 ± 2.7
337	150	50		-34.0 ± 9.5		-37.0 ± 7.5

[a] Current before tritium sampling.

Table 3 lists the data of system 2, in which cells A and B had cathodes of dimensions $1.00 \times 1.00 \times 0.01$ cm^3, and no poison in the electrolyte; the solutions used to fill and replenish the cell showed identical ^3H activities.

The ^3H levels measured at various electrolysis times are scattered around the initial value; even after 20 days. With total renewal of the initial 30 ml of electrolyte volume, no evidence was obtained of "electrolytic" ^3H enrichment.

Table 4 shows data for two systems having sheet cathode dimensions of $0.85 \times 0.85 \times 0.02$ cm^3 (system 3) and $0.70 \times 0.70 \times 0.05$ cm^3 (system 4). Cells 3A and 4A did not contain any poison, whereas cells 3B and 4B contained 5×10^{-5} M As$_2$O$_3$. The solutions used to fill and replenish the cells again showed the same ^3H activity $\simeq 40$ dpm ml^{-1}. After 4 days at 50 mA cm^{-2}, sampling of cell 3A indicated a ^3H

TABLE 3

Data for system 2 (Pd electrodes = $1.00 \times 1.00 \times 0.01$ cm^3. Electrolyte 30 ml/0.1 M LiOD; ^3H activity = 27.2 ± 18 cpm ml^{-1}.)

Electrolysis time /h	I [a] /mA	i [a] /mA cm^{-2}	Cell 2A: $\Delta\,^3H$ /dpm ml^{-1}	Cell 2B: $\Delta\,^3H$ /dpm ml^{-1}
95	90	45	6.2 ± 4.8	-2.7 ± 16.0
165	50	25	10.8 ± 5.3	-7.1 ± 1.5
190	200	100	6.0 ± 10.5	-4.2 ± 15.2
242	50	25	-4.0 ± 12.2	13.1 ± 6.2
312	200	100	1.7 ± 7.1	-2.2 ± 5.4
336	200	100	0.6 ± 13.8	-3.1 ± 4.5
410	500	250	10.5 ± 7.3	0.0 ± 4.0

[a] Current before ^3H sampling.

TABLE 4

Data for systems 3 and 4 (Pd electrodes: cell 3 $0.85 \times 0.85 \times 0.02$ cm^3; cell 4 $0.70 \times 0.70 \times 0.05$ cm^3. Electrolyte: 3A/4A 35 ml/0.1 M LiOD (^{3}H activity = 41.6 ± 6.4 cpm ml^{-1}); 3B/4B added of As$_2$O$_3$ $\sim 5 \times 10^{-5}$ M.)

Electrolysis time /h	i/mA cm^{-2}		Δ^3H/dpm ml^{-1}			
	Cells 3	Cells 4	Cell 3A	Cell 3B	Cell 4A	Cell 4B
94	50	50	473.3 ± 15.2	60.6 ± 9.1	356.4 ± 10.0	450.9 ± 17.3
360	variable current program from 50 to 450 mA cm^{-2}	50	364.9 ± 10.8	45.5 ± 11.4	288.9 ± 12.6	364.3 ± 17.3

increment which gave a count = 12 times higher than the background (corresponding to overall $\geqslant 1.5 \times 10^{11}$ ^{3}H atoms), whereas activity in 3B was far lower.

In system 4, the ^{3}H increment was 8 (A) to 11 (B) times the initial value. Prolonged electrolysis using either a variable current (cell 3) or a constant current (50 mA cm^{-2}) (cell 4), showed only a steady decline in ^{3}H levels (see the last sampling in Table 4).

The electrodes of system 3 (0.02 cm thick) had become very brittle, while macroscopic damage to those of system 4 appeared less evident. The latter electrodes, examined one day later using a PH Ortec Ge detector, exhibited some radioactivity due to low-energy γ-rays; during 4000 s, 8504 ± 92 counts were measured against a background of 7494 ± 86 counts.

Pd / Pt cell

Figure 1 shows how the ^{3}H activity of a Pd/Pt cell was found to vary with electrolysis time and current density. The cathode dimensions were $0.70 \times 0.70 \times 0.05$ cm and the initial ^{3}H content was $\simeq 40$ dpm ml^{-1} (electrolyte used to refill the cell had the same activity).

The tritium data (left ordinate) were corrected for ^{3}H losses of the solution caused by repeated sampling. The line at the bottom represents integrated current (right ordinate in moles of electrons) whose slope gives the current density passed at any time. As Fig. 1 shows, ^{3}H accumulated from the first few days of electrolysis, reached a maximum in 8–9 days and then started to decline, though there appears to be no direct relationship with the current density.

Instead, the decline in ^{3}H activity after prolonged electrolysis (which has also been observed in the previous systems) may be due to (i) the termination end of ^{3}H production or progressive loss of DT gas, and (ii) continuous refilling by D$_2$O at lower ^{3}H content.

The data of Fig. 1, replotted as the ratio of ^{3}H activity at any time $n(t)$, to the background value $n(0)$, $n(t)/n(0)$, are compared with the hypothetical ^{3}H enrich-
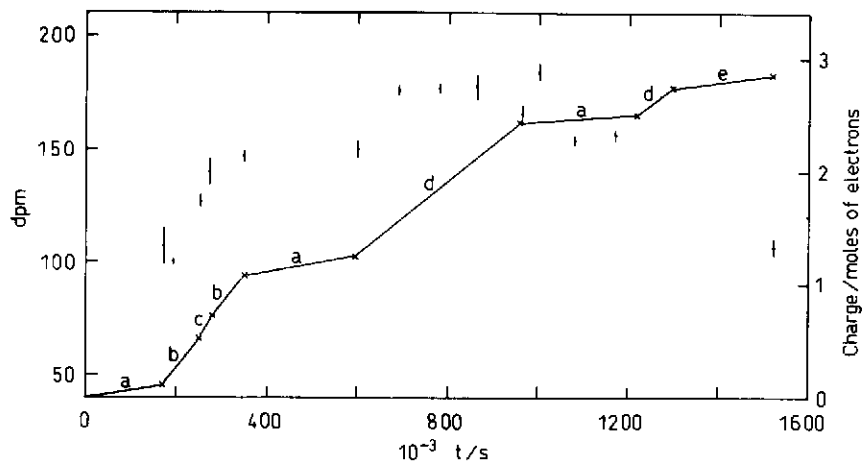
Fig. 1. Disintegration rate of tritium in (d/min ml^{-1}) referred to Pd/Pt cell as a function of electrolysis time (left ordinate, experimental points). Solid lines indicate the cathodic charge collected (right ordinate): a = 60 mA cm^{-2}; b = 500 mA cm^{-2}; c = 750 mA cm^{-2}; d = 300 mA cm^{-2}; e = 50 mA cm^{-2}.

ment due to D/T electrolytic separation in Fig. 2. The dotted line represents the equation:

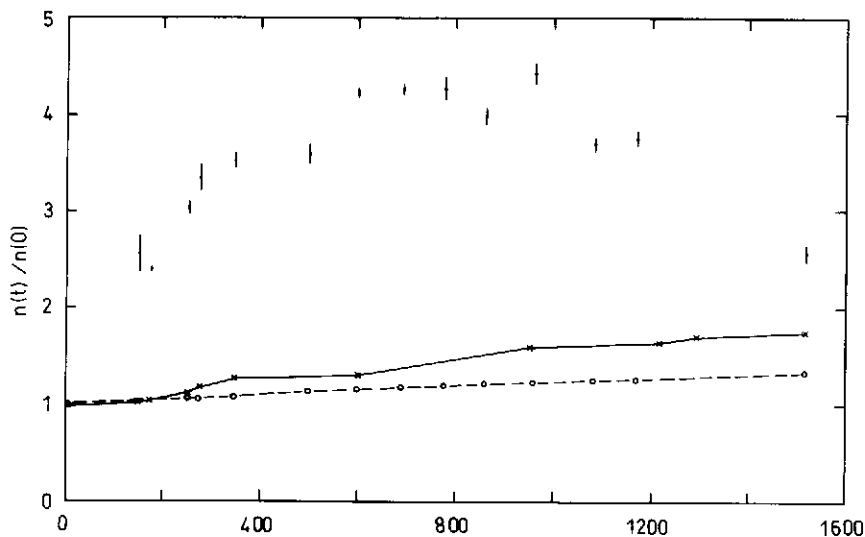$$n(t)/n(0) = S - (S - 1) \exp(-ti/2FSnV)$$

Fig. 2. The ratio of tritium activity (reported in Fig. 1) to the background value $n(t)/n(0)$ (experimental points) as a function of electrolysis time. The solid line represents hypothetical tritium enrichment due to D/T electrolytic separation factor $S = \infty$. The dotted line is for $S = 2$ ($i = 203$ mA cm^{-2}).
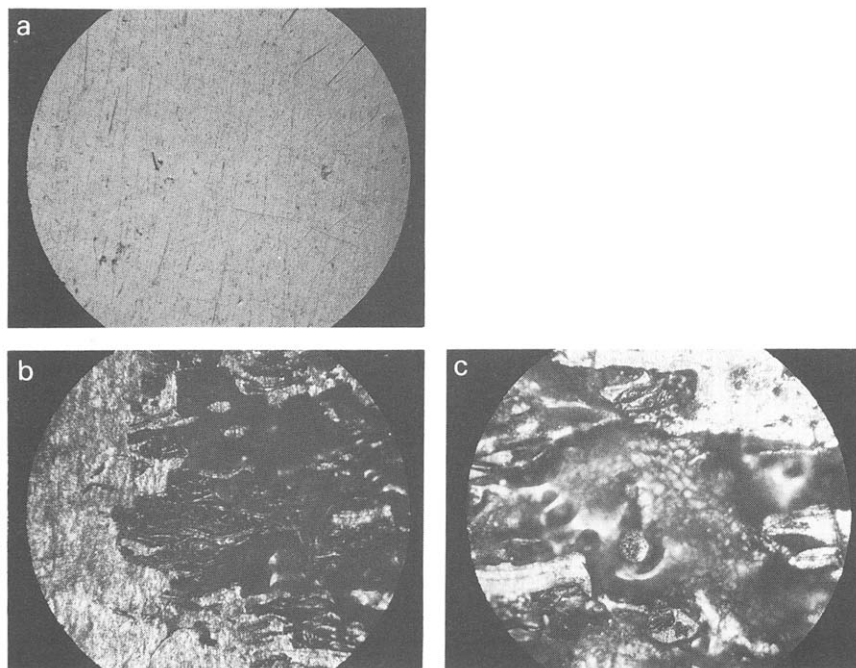
Fig. 3. Photographs of a Pd sheet, before (a) and after (b,c) ^{3}H release. Magnification (a,b) $3 \times$, (c) $6 \times$.

where S is the separation factor ($= 2$); n is the number of D_2O mol ml^{-1}; $V = 35$ ml; $i = 203$ mA cm^{-2} (the average current passed in the experiment).

The solid line was drawn assuming *ab absurdo* $S = \infty$; that is, all the ^{3}H added is that kept in the cell. Losses and refilling corresponding to the real current were taken into account. Clearly, the ^{3}H observed in the cell has nothing to do with any hypothetical electrolytic enrichment. In Fig. 2, losses due to evaporation and hypothetical enrichment due to D/T separation in the vapour were not considered. However, a major ^{3}H increase obviously occurred which commences during the first few days of electrolysis when (at 50 mA) heating was minimal and evaporation negligible.

A further phenomenon was observed in this cell when 2 mg of thiourea were added to the electrolyte: the ^{3}H-level doubled to a new pseudo-steady level in a few days.

During the experiment one side of the Pd sheet developed a visible swelling, with deep pitting underneath, as shown in Fig. 3.

Negative results

A number of cells (11 to date of this report) with Pd sheet electrodes 0.02 and 0.05 cm thick, gave no or only slight ^{3}H enrichment above the background, even after prolonged electrolysis (up to 2 months).

CONCLUSION

It is clear that ^{3}H excesses measured in some cells cannot be explained in terms of isotope enrichment due to D/T electrolytic separation.

An explanation in terms of fortuitous contamination is unlikely since numerous cells run concurrently did not show any (or only very low levels of) isotopic enrichment. We believe that this latter behaviour is the norm in the absence of tritium generation.

The poor reproducibility of the phenomenon compares with the sporadic occurrence of high H/Pd ratios observed in blank experiments.

ACKNOWLEDGEMENT

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