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On an electrode producing massive quantities of tritium and helium

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Abstract

A Pd electrode has been examined which produced a concentration of tritium in a 0.1 M LiOD solution around 10^3 times above background. Tritium production at a given potential ceased after a few days, but could be restarted by a small increase of the deuterium overpotential. Correspondingly, He^4 was found in 9–10 pieces of the Pd electrode at 2–100 times background. Addition of fresh amounts of D_2O quenched the T production which began again spontaneously after 1–2 days. If the T had come from contamination, ^3He would have been found in the electrode: it was absent. Loss of charge by the nucleus takes place when the fugacity of D in voids exceeds 10^{17} atm (Lifshitz and Pitaevskii, 1963). Sporadicity of function arises from the state of the surface, which is difficult to reproduce. The surface state controls the mechanism of D_2 evolution; only some mechanisms give a fugacity high enough to cause fusion. Only one electrode out of four examined produced T and ^4He . The surface of this electrode contained a Cu-mosaic structure, not seen on the inactive electrodes.

INTRODUCTION

Since March 1989, groups in many countries have been active in carrying out experiments on Cold Fusion. There are (Feb. 1992) around 380 published papers and reports from Government Institutes which give accounts of positive observations on Cold Fusion (e.g. reviews in refs. 1–4). Thus, there is evidence for the production (after some hundreds of hours) of excess heat in the region of 10–30% ($0.5\text{--}100 \text{ W cm}^{-3}$, with reports up to 1 kW cm^{-3}); neutrons in the range $1\text{--}10 \text{ n s}^{-1} \text{ cm}^{-2}$ with occasional reports of $10^6 \text{ n s}^{-1} \text{ cm}^{-2}$ in bursts; tritium, several

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times above background with 20% of the reports amounting to 10^3 – 10^5 above background; helium in the electrode at up to 100 times background. Gamma and X-ray emission have also been reported [5].

The successes are accompanied by considerable difficulties.

(1) The phenomena, when they are seen, are associated with an initiation time of several hundreds of hours.

(2) Even so, the majority of attempts fail to manifest anomalous phenomena at all.

It would be desirable to make simultaneous measurements of heat, neutrons, tritium, helium, X-rays and gamma rays. Economic considerations have made it necessary to measure one or two of these quantities. Thus, the most obvious and direct proof of fusion is the production of tritium from deuterium and we have gone principally in this direction [4].

More than 40 reports exist from different groups concerning the formation of T above the enrichment [2].

We have recently observed an electrode which yielded T at $\sim 10^4$ times above background. Production of tritium continued for three weeks and was intentionally interrupted.

EXPERIMENTAL

Experimental cell

The cell (Fig. 1) could contain 80 cm³ of solution, and possessed a Teflon cap in which there were three small holes for the emission of gases. The glass was conventional borosilicate glass. It was washed several times in distilled water before use.

Temperature control

The average temperature value varied between approx. 21 and 23°C.

Electrical

The total potential applied to the cell was controlled and measured by a dc power supply (BK Precision, Model 1635, Maxtec International Co. (Chicago, IL)). The cell potential, Pd electrode potential and current were measured by using Digital Multimeters (Keithley, Model 616) and continuously monitored on XY-t recorders (Houston Instruments, Models 100 and 200).

Electrodes

Pt wire (99.95%), 0.5 mm in diameter, 100 cm in length, was used as the anode. A saturated calomel electrode (Radiometer, K401) served as a reference electrode.

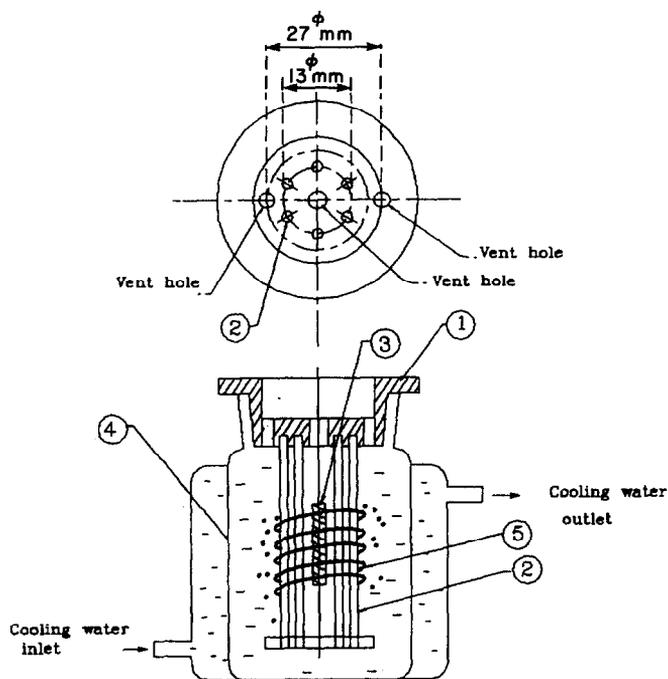


Fig. 1. Scheme of the electrolysis cell. (1) Teflon cap; (2) glass rod; (3) Pd rod; (4) glass beaker; (5) Pt coil.

The Haber–Luggin capillary used a 0.5–1 mm working distance. Electrode potentials were obtained in a secondary way from a simulated experiment in a dummy cell in which electrode potentials were measured under the same conditions.

The palladium electrode was 1.6 cm in length and 1 cm in diameter (99.99% Pd). All electrodes investigated were fabricated from palladium purchased from Elecmat Co. (Plainfield, NJ, USA). Palladium rods were made by melting the palladium ingot at about 1700°C under a nitrogen atmosphere, then casting in a high-temperature resistant ceramic shell, and shaping into rods. Palladium was obtained from original bullion and not refined from scrap [6]. The distance between the working and counter electrodes was approx. 2 mm, and yielded an electrolyte resistance of about 10 Ω .

The palladium electrodes were pretreated by acid etching and then electrochemically in the following way.

(1) *Acid etching.* The Pd rod was immersed in dilute nitric acid solution (1.3–1.6 M) for 50 h or until the Pd surface lost its lustre. The electrode was washed with triply distilled water and silver soldered to a Cu wire contact (Fig. 2). It was acid etched (for another day) and the washing procedure repeated. The Cu wire was not brought into contact with the etching solution. Residual acid was washed off

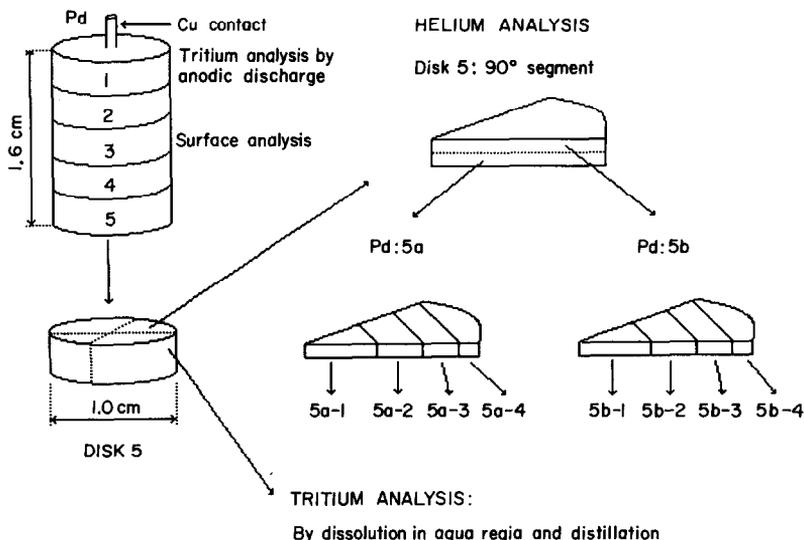


Fig. 2. Pd electrode which produced tritium: cutting diagram and annotation of samples used in subsequent analysis.

with distilled water and the electrode stored in a reservoir of distilled water above the Cu wire for about 2 weeks*.

(2) *Anodic treatment.* The acid-treated Pd rod was mounted in the electrolysis cell and 0.1 M LiOD solution introduced to fill the cell to the top of the Pd rod, again avoiding contact between Cu and the solution. Anodic treatment consisted of applying a positive electrode potential of 2.0 V for 2 h, then the potential was raised to 2.3 V for 30 min. After this pretreatment, electrolyte (0.1 M LiOD) was added up to the volume of 80 ml and the Pd rod was used in D_2O electrolysis.

Materials

D_2O was from Isotech Inc., Matheson, with a low tritium background of 12–18 DPM ml^{-1} . Its original H_2O content was 0.1%. 0.1 M LiOD electrolyte was prepared by dissolving Li metal (Johnson & Matthey, 0.38 mm thick Li foil, 99.95%).

The liquid scintillation cocktail (LSC) was Bio-safe II from Research International Product Co. (Mount Prospect, IL). The tritium background of 6.5 ml of scintillation cocktail, normally used for T analysis, was 26 ± 3 DPM ml^{-1} .

* There was contact between the solution and copper when the electrode was resting in distilled water. XPS measurement showed Cu on the electrode.

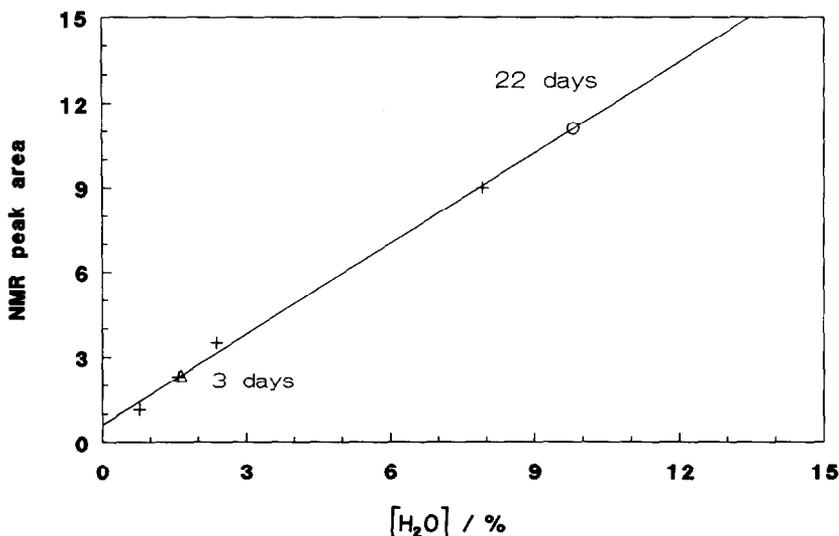


Fig. 3. NMR light water determination at different stages of electrolysis. (+) 0.1 M LiOD calibration; (Δ) after 3 days of electrolysis; (○) after 22 days.

Light water content in D₂O

The open design of the cell allowed H₂O from the atmosphere to enter the cell through the vent holes. Therefore the H₂O content in the electrolyte was checked by using NMR spectroscopy (NMR spectrometer, Model XL200E). Sample preparation was done in a glove box under an argon atmosphere. Standard samples were sealed in NMR tubes and calibration repeated each time the sample was measured.

The straight line (Fig. 3) is the calibration curve (obtained versus prepared standards) and two points on the graph represent the H₂O content at different times of electrolysis. The first point (Δ) shows 1.6% H₂O content after only 3 days of electrolysis. The H₂O content increased up to 9.8% (second point, ○) after 22 days of electrolysis.

Cutting the palladium specimen for ³He, ⁴He and surface analysis

After the electrolysis was stopped intentionally a Pd electrode which produced tritium was transferred into liquid N₂ (1–2 s). The electrode was kept in liquid N₂ for one week. Then it was removed and cut into five pieces for further analysis. A rotary cutter was used. The cutting operation was performed quickly, the time the Pd was out of liquid N₂ was less than 1 min, the Pd rod remaining well below room temperature. Figure 2 shows how the Pd electrode was cut and the position of cut

discs used for surface analysis and for ^3He and ^4He analysis. The first piece (No. 1 in Fig. 2) with the Cu contact attached was used in an anodic dissolution experiment. The second and fourth, (Nos. 2 and 4, Fig. 2) sections were preserved in liquid N_2 for further analysis. Disc No. 3 was used for surface analysis. Disc No. 5 was cut for ^3He and ^4He analysis. Two 90° segments from disk No. 5 were cut further (as shown in Fig. 2 for one of the 90° segments) into smaller pieces of approx. 30 mg, and analyzed for ^3He and ^4He .

XPS and EDS surface analysis

XPS and EDS analyses were performed on palladium disc-shaped samples. A first set of samples was cut from the electrode from cell B (Fig. 2). A second set was from the same original source and was not preserved in liquid N_2 . It consisted of samples which were pretreated only chemically in the same way as those from cell B. The third set consisted of samples which had been electrolyzed and had not given tritium. The fourth set of samples was from the original source and represented a virgin Pd sample, with no pretreatment.

All palladium samples were allowed to remain under high vacuum in an Edwards Coating System E306A for 24 h at pressures lower than 5×10^{-6} Torr prior to analysis to avoid outgassing during the measurement.

XPS analysis

XPS was carried out using a Perkin-Elmer 5500 photoelectron spectrometer. The system was equipped with a dual anode (Mg and Al) X-ray source and operated at 10^{-9} Torr. The XPS spectra were taken applying Mg $K\alpha$ ($h\nu = 1253.6$ eV) irradiation, with an angle of incidence of 45° , as the photon source (300 W, 15 kV).

To obtain a depth profile, the palladium surface was sputtered by Ar ion bombardment and spectra were collected in the centre of the etched area. XPS analysis was performed alternately with sputtering. During sputtering the pressure of the argon ion gas was 4.5×10^{-8} Torr, the emission current of the ion gun was 25 mA, and ion gun voltage 3 kV.

EDS analysis

A JEOL JSM-6400 SEM equipped with a Tracor Northon (NORAN) I-2 (EDS/Image processing) system with the atmospheric thin window which allows detection of light elements down to boron was used to analyse the bulk of palladium electrode to a depth of $1 \mu\text{m}$. The voltage used was 25 kV with an angle of incidence of 34° . EDS conditions were the same for all regions analyzed with the 100 s count time.

Compositions were calculated by use of a built-in standard analysis program including sensitivity corrections for each element.

Helium analysis

Palladium samples which had shown tritium production, platinum anode samples and non-electrolyzed Pd electrode samples were sent, packed in solid CO₂, to Rockwell International, Los Angeles, CA, for ³He and ⁴He analysis by mass spectrometry. Cut palladium discs (Fig. 2) were kept in liquid N₂ for 16 days (samples of series 5a and 5b) and 66 days (samples of series 5c), respectively, before sending them for ³He and ⁴He analysis. The 90° disc segments were further cut into smaller pieces of about 30 mg. Samples 5c were cut in the same way as shown for samples 5a and 5b, but from another 90° segment (Fig. 2). The helium content was determined following vaporization in a resistance-heated tungsten-wire crucible in one of the mass spectrometer system's high-temperature vacuum furnaces [7]. Details of the calibration procedures, determination of the background helium release from the system, including hot and cold blank tests, analysis of the Rockwell Control Pd specimens, as well as virgin Pd and Pt anode samples will be published separately [8]. It was observed, despite three Zr-Al alloy hydrogen getters in the system, that enough deuterium (from a fully charged Pd electrode) made its way into the mass spectrometer to produce an HD artifact which interfered with the signal for ³He [8]. In the case of ⁴He such interference does not occur because of better resolution between ⁴He and hydrogen isotope signals. Samples 5b and 5c were thus pretreated thermally by baking in a vacuum oven (< 10⁻⁴ Torr) at ~150°C for 24 h prior to analysis. In this way the mass spectra collected were free from any interference of residual hydrogen isotopes.

Tritium analysis

Samples were taken about one to two times per day, each sample being 0.5 ml syringed by a micropipet. Disposable Eppendorf flex tips (Brinkmann Instruments, Inc. New York) of 0.1 ml were used for sampling.

Two amounts of fresh D₂O (see above) were added to the cell, one 14 ml (at 148 h of electrolysis) and the other 30 ml (at 406 h of electrolysis). The 0.5 ml sample was added to a vial and then 6.5 ml of the Biosafe cocktail (26 ± 3 DPM) made up the basic measuring vial. This was kept in darkness for 3 h and measured for 10 min in a Wallac LKB 1410 liquid scintillation counter.

The natural decline of the radiation was about 0.5% per month.

The liquid scintillation counter was equipped with a chemiluminescence counter and indicated its own efficiency.

The calculation of the tritium content was made in the following way:

$$\text{DPM ml}^{-1} = (\text{CPM/ml}_{\text{sample}} - \text{CPM}_{\text{cocktail}}) \times (V/E) \quad (1)$$

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

Errors

The counting errors were as follows. At low count rates, and with 10 min counting, the random errors in counting were up to 10%, whilst at high count rates (~ 20000 DPM/ml), this figure dropped to less than 2%. Samples of low count rates (approx. 35 DPM/ml) showed 38%, 9.9% and 2.8% relative standard deviation error for 1, 10 and 60 min of counting time, respectively. Ten minute analyses were usually performed.

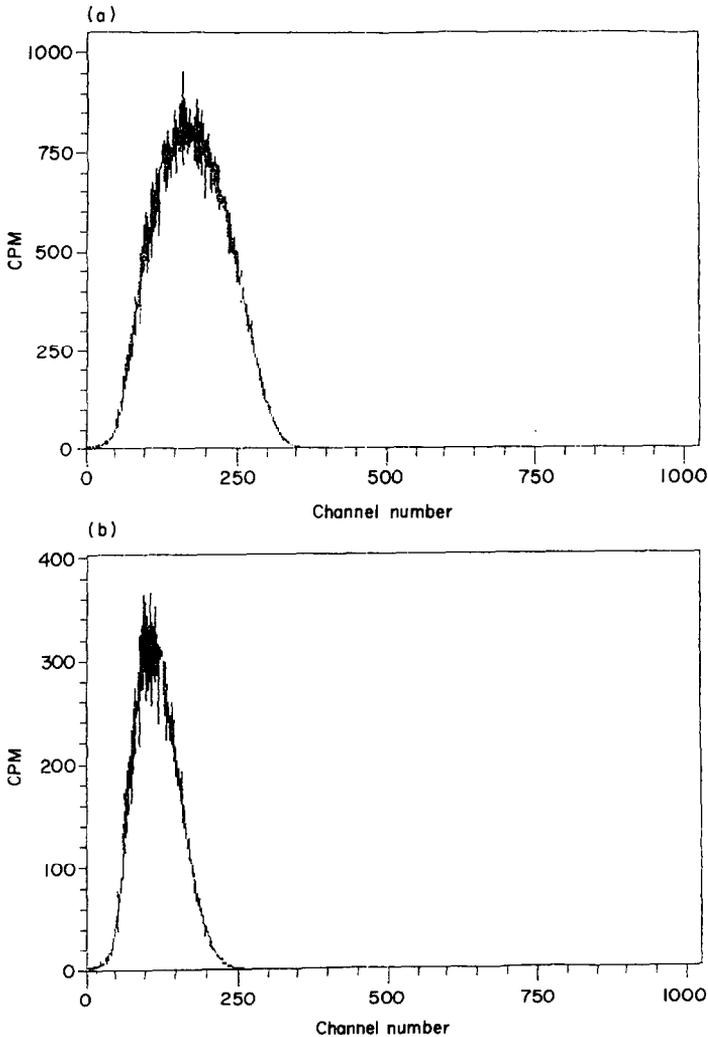


Fig. 4. Tritium energy spectra of: (a) standard tritium aqueous solution, (b) tritium sample taken at the end of electrolysis.

A detailed analysis of the sample energy spectra yielded the correct beta energy end point for tritium when compared with a standard tritium sample. Figure 4(a) shows a standard tritium spectrum (activity 200 000 DPM) and Fig. 4(b) a T sample taken before the electrolysis was stopped. Both spectra exhibit the same pattern with maxima within the same energy range or at the same corresponding channel numbers (130–150).

The tritium background of the scintillation cocktail was determined as 26 ± 3 DPM. A typical value for D₂O (Isotech Inc.) was 32–35 DPM/0.5 ml (or, as background corrected value, 12–18 DPM/ml). When the tritium samples showed a counting activity several orders of magnitude higher than the background value, a background correction was not taken into consideration. Positive tritium findings were measured independently on a Wallac 1210 liquid scintillation counter, in the laboratory of Prof. M. McLaine (Department of Nuclear Engineering, Texas A&M University).

RESULTS

Tritium analysis

Tritium measurements before the start of electrolysis

After careful Pd acid etching pretreatment and storing in distilled water, anodic pretreatment was performed in an 80 ml cell, filled up with 0.1 M LiOD, at 2.1 V for 2 h and at 2.3 V for 0.5 h. Results are shown in Table 1.

No increase in T activity was observed in the electrolyte after anodic pretreatment (Table 1). A high potential (2.3 V), although applied for 0.5–2 h, should cause tritium contaminants to be expelled from the electrode. No significant increase was seen.

Initiation period and commencement of tritium activity

After anodic treatment, charging was started at -0.05 V (vs. RHE) in the negative direction. No increase in tritium activity was observed (Fig. 5). After 35 h, the cathode potential was decreased to -0.10 V. This decrease in cathode potential triggers the reaction and a steady increase in tritium activity was observed after that. The initial, almost linear, relationship between tritium activity and time, is in Fig. 5, which presents results of two cells (A and B), run in parallel. One (cell B) out of four cells showed high tritium level production.

TABLE 1

Typical tritium activity analysis of the 0.1 M LiOD electrolyte before and after anodic pretreatment

T activity before anodic pretreatment /DPM ml ⁻¹	T activity after anodic pretreatment /DPM ml ⁻¹
12 ± 3	12 ± 3

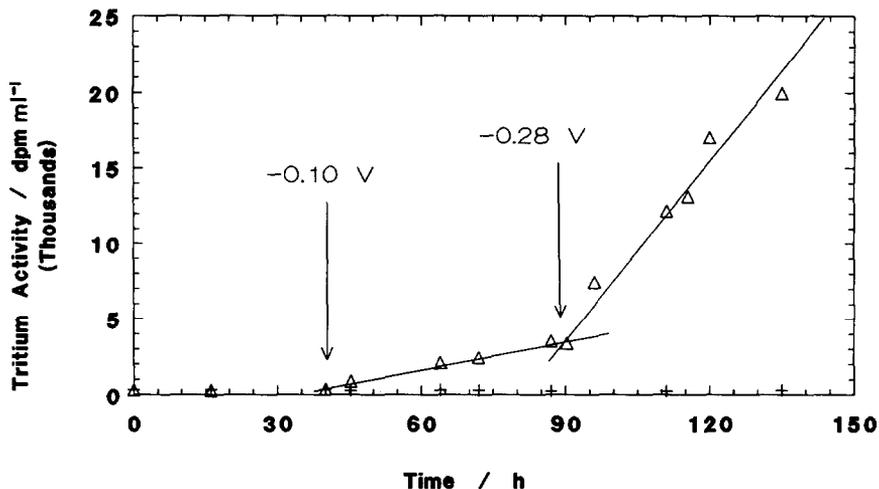


Fig. 5. Tritium activity measurements vs. time at the initial stage of electrolysis: (+) cell A, which showed no tritium in excess; (Δ) cell B, which showed high levels of tritium production. Numbers indicate cathode potentials vs. RHE.

The maintenance of a continuous increase in tritium activity, triggered by small increases in applied potential, seems not to have been recorded previously. In previous observations of T activity, tritium has appeared in a burst-like manner [9].

Rate of tritium production (Figs. 5 and 6)

When the cathode potential was in the range -0.05 to -0.10 V the rate was $\sim 2.1 \times 10^6$ T atoms $s^{-1} cm^{-2}$. When the potential was decreased to -0.28 V, the

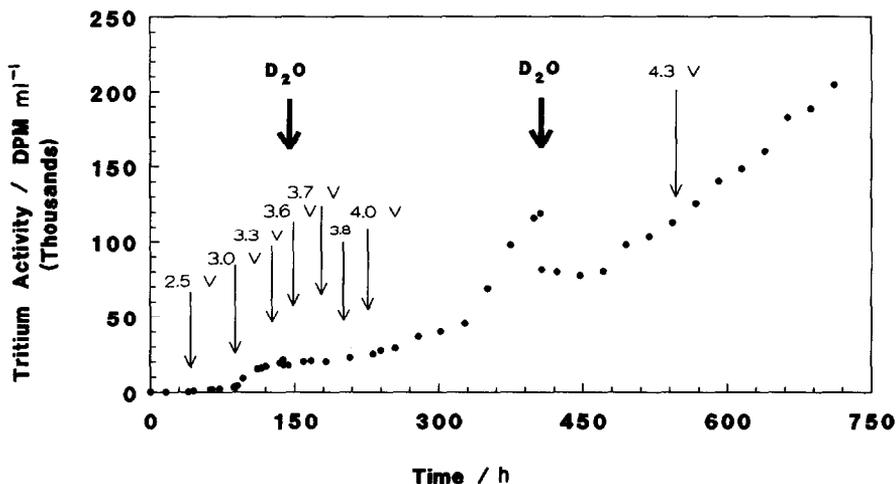


Fig. 6. Recording of the tritium events during one month of continuous tritium production in cell B. Arrows indicate voltage adjustment. Numbers indicate cathode potentials vs. RHE.

rate of production became 1.7×10^7 T atoms $s^{-1} cm^{-2}$. After lowering the potential to -0.44 V the tritium production rate increased (8.1×10^6 T atoms $s^{-1} cm^{-2}$). The tritium production reached its maximum of 3.8×10^7 T atoms $s^{-1} cm^{-2}$ at 327 h of electrolysis. The reaction was quenched at 406 h, when D_2O was added. Tritium production restarted again at 471 h of electrolysis with no potential increase. The tritium production rate observed was 2×10^7 T atoms $s^{-1} cm^{-2}$.

Quenching of tritium production

After the addition of make up heavy water (14 cm^3 added at 138 h), tritium production ceased for 2 days. The electrode potential was increased several times to trigger the reaction again. After raising the cathode potential from -0.42 to -0.44 V, at 232 h of electrolysis, tritium production re-commenced at 8.1×10^6 T atoms $s^{-1} cm^{-2}$. Thus, an incubation period is needed after the reaction is quenched. The reaction was quenched for the second time (at 406 h), when 30 ml D_2O was added. The decrease in T activity after D_2O addition is due to the dilution. An incubation period of 65 h was needed for the reaction to restart again (at 471 h). No potential triggering was applied this time.

Quenching of T production also occurs when a great deal of turbulence is introduced [10].

Cell potential, Pd electrode potential and current density changes during the electrolysis

Figure 7 shows the cathode potential as a function of time and current density. Current transients observed after increasing the applied potential are shown in Fig. 8.

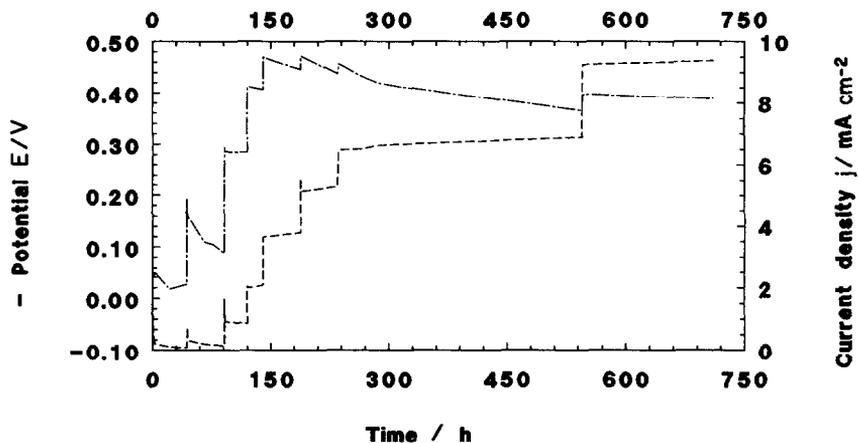


Fig. 7. Scheme of (—) the cathode potential changes, and (---) corresponding current density transients during a complete run.

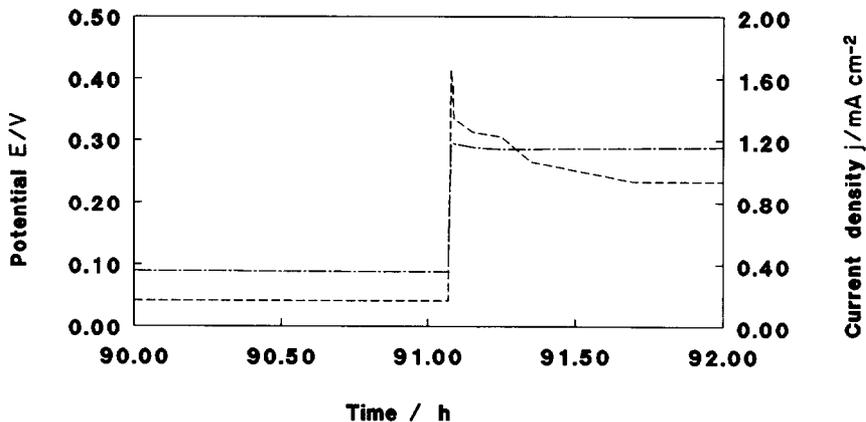


Fig. 8. (---) Typical current transients observed when the applied potential (---) was decreased from -0.29 to -0.38 V.

Dependence of tritium production rate on electrode potential

After 36 h (Fig. 4), tritium production was triggered by the increase in applied electrode potential to -0.1 V vs. RHE (Fig. 7). From Figs. 5 and 6, four intervals of constant rate of tritium production may be recognized.

The relationship between $\log j$ and η , where η is the overpotential is shown in Fig. 9(a). The relation between overpotential and the rate of tritium production is given in Fig. 9(b). The value of the slope is 4.5 V^{-1} ($F/(2 \times 2.303RT) \sim 8.2 \text{ V}^{-1}$).

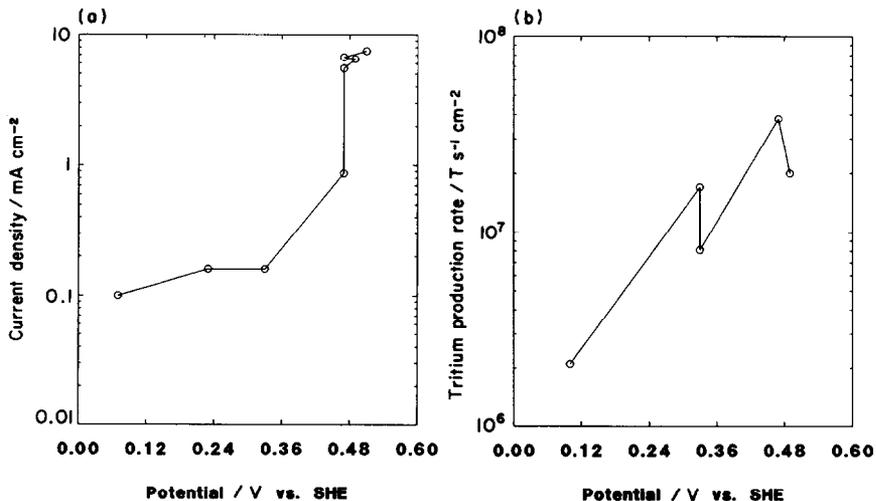


Fig. 9. (a) Current density, $\log j$, and (b) tritium production rate dependence on electrode overpotential.

In the sense of a Tafel slope, then, the present result $\approx 4RT/F$.

Once the reaction is quenched by the addition of fresh D_2O , tritium production restarts after a change in potential (e.g. from -0.42 to -0.46 , at 232 h, Fig. 4). However, a decrease of the potential too frequently (in time intervals of ~ 30 h, cf. 136 to 232 h) did not seem to affect the reaction rate.

Total amount of tritium produced

The total tritium amount produced in the electrolyte after 761 h of electrolysis may be calculated:

$$[T] = 204570 \text{ DPM/ml} \doteq 2 \times 10^5 \times 10^7 = 2 \times 10^{12} \text{ T atoms/ml}$$

total in solution:

$$[T] = 2 \times 10^{12} \times 80 \text{ ml} = 1.6 \times 10^{14} \text{ T atoms}$$

Tritium in the gas phase was not measured. There are several results published on the ratio of total tritium amounts measured in the gas phase and in the liquid. Ratios obtained were ~ 4 [11], 5–10 [12], 3–4 [13], respectively. Taking the average ratio between tritium in the gas phase and in the liquid as 5, one calculates that the total tritium produced is 10^{15} atoms.

Tritium contamination from the laboratory air

A study of contamination of the cells from the environment was performed by determination of the tritium picked up by an open non-working cell of the same design, placed next to the working cells. No tritium enhancement above the background value in this control cell was found in 250 h. Another cell, A, of the same design was run in parallel to cell B (which showed positive tritium results), but did not show tritium production (Fig. 4).

Tritium contamination of virgin Pd material

Virgin Pd was dissolved in aqua regia and liquid scintillation analysis made upon *distilled* samples, by the method developed by Cedzynska and Will [14]. The closed apparatus for dissolution of Pd and distillation was similar to the one described in ref. 14. Several Pd discs were cut from the original Pd rod, at

TABLE 2

Tritium analysis of the bulk of virgin Pd rod

Sample	10^8 T atoms/g Pd
1	4 ± 3
2	3 ± 3
3	4 ± 3

randomly chosen positions, and cut further into smaller samples (up to 300 mg). These were dissolved in aqua regia (~ 2 ml), distilled and analyzed by liquid scintillation counting. No difference in tritium activity was observed when the distillate was neutralized by NaOH.

A summary of results is shown in Table 2. No tritium above background is found.

Pd electrode examination after ceasing the electrolysis

Immediately upon ceasing electrolysis, the Pd electrode was quickly (1 s) put into liquid N₂. It was kept in liquid N₂ for one week and then cut as described above.

Tests for tritium content in the bulk of Pd were performed in two ways. The first used the method by Cedzynska and Will [14]. The other used a long anodic treatment to expel tritium from the Pd electrode.

Pd was also analyzed for He³ and He⁴ content.

Tritium analysis in the bulk of Pd

Dissolution in aqua regia

Pd samples (0.3 g) were dissolved in aqua regia solution in a closed distillation system and the solvent distilled into a collection vessel [14]. Samples of 0.5 ml were taken for scintillation measurement. The following results were calculated: Pd sample, 0.286 g; distillate volume, 1 ml; [T] measured = 101 DPM/0.5 ml; [T] in Pd = $[(101 - 28) \times 2 \times 10^7] / 0.286 = 5.1 \times 10^8$ T atoms / g Pd.

Result of anodic polarization of the cathode

A parallel procedure was used to treat another piece of Pd (approx. 4 g, see Fig. 2) as the anode to perform electrolytic dissolution of tritium into 0.1 M LiOH aqueous solution. The cell potential was maintained at 6 V for 3 days. The experiments were performed in a closed cell with a recombiner (Pt black on carbon) inside the cell to convert DT gas into liquid. The following result is obtained: the Pd sample (4.2559 g) was discharged anodically (6 V) for 3 days into 20 ml LiOH (0.1 M solution); [T in 0.1 M LiOH background] = 28 DPM/0.5 ml; [T] after anodic discharge = 113 DPM/0.5 ml; [T] in Pd = $[(113 - 28) \times 20 / 0.5 \times 10^7] / 4.2559 = 8 \times 10^9$ T atoms / g Pd. The corresponding amount by the Cedzynska and Will approach would have been 5×10^9 atoms T/gram.

Quenching of T production by D₂O additions as a test for T contamination of Pd

On two occasions (Fig. 6) after addition of make up D₂O T production was stopped for about two days. It is difficult to find any correlation between quenching of the reaction induced from the solution side and a possible source of T from spot contamination in the bulk of Pd. The same reasoning might be applied to quenching observed when a turbulence is introduced in the electrolyte [10].

TABLE 3

Summary of tritium results

T_{total} in electrolyte	T in gas phase (assuming $T_g / T_1 = 5$)	T in Pd (by dissolution in aqua regia)	T in Pd (by anodic discharge method)	Total amount of T produced (electrolyte, gas, bulk)
1.6×10^{14} T atoms	8.1×10^{14} T atoms	5.1×10^9 T atoms/g Pd	8×10^9 T atoms/g Pd	$\sim 10^{15}$ T atoms
or 1.5×10^{13} T atoms/g	or 5.4×10^{13} T atoms/g	(or total in Pd = 7.6×10^{10} T atoms)	(or total in Pd = 1.2×10^{11} T atoms)	or 6.9×10^{13} T atoms/g
or 2.5×10^{13} T atoms/cm ²	or 1.2×10^{14} T atoms/cm ²			or 1.5×10^{14} T atoms/cm ²

Attempt to restart T production after ceasing the electrolysis

A part of the electrode (Fig. 2) used as an anode to analyze T in the bulk of Pd, as described above, was then placed in a smaller closed cell containing 0.1 M LiOD. An attempt was made to restart the electrode as a T producer. However, no further T production was found.

Tritium results are summarized in Table 3.

The tritium content in Pd found by the two methods matched well (5.1×10^9 and 8.0×10^9 T atoms g⁻¹). These values are $\sim 10^4$ times below the tritium found in the electrolytic solution at the end of electrolysis (Table 3).

Helium analysis

Helium analysis in the bulk of electrolyzed Pd samples which produced tritium

After the electrolysis had been interrupted to analyze for other nuclear products in the bulk of the Pd electrode which produced tritium, the electrode was stored in liquid N₂ and then sliced. Samples 5a-1 to 5a-4 (see Fig. 2) were not treated thermally, while samples 5b-1 to 5b-4 and 5c-1 and 5c-2 were degassed at 150°C for 24 h. Samples 5a and 5c (outer slices) are those cut from the bottom of disc 5, having the largest area in contact with the solution during the electrolysis. In series 5b, only one side (inner slice) was exposed to the solution. Samples 5c were from another 90° segment (outer slice). Thus, series 5a and 5c are from the near-surface region.

Presence of ⁴He

All samples, with (5b and 5c) and without (5a) thermal treatment showed positive findings of ⁴He. Background values were obtained by repeating the calibration procedure before each analysis using Rockwell control Pd specimens, free of He [8]. To obtain the net helium released from each specimen, the ⁴He values from the Rockwell control specimens were averaged separately, for each

TABLE 4

Results of ^4He analysis in electrolyzed Pd samples which produced tritium. Average background value: 0.5×10^9 ^4He atoms

Samples near the surface (outer slices)			Samples away from the surface (inner slices)		
Sample	Sample mass ^a /mg	$^4\text{He}/10^9$ atoms or (10^{11} atoms/g)	Sample	Sample mass ^a /mg	$^4\text{He}/10^9$ atoms or (10^{11} atoms/g)
5a-1	30.92	3.8 ± 0.3 (1.2 ± 0.1)	1b-1	27.79	1.9 ± 0.3 (0.7 ± 0.1)
5a-2	39.70	166.8 ± 3.3 (42 ± 0.8)	1b-2	30.01	2.5 ± 0.3 (0.8 ± 0.1)
5a-3	42.37	3.4 ± 0.3 (0.8 ± 0.1)	1b-3	23.85	0.4 ± 0.3 (0.17 ± 0.12)
5a-4	20.22	2.1 ± 0.6 (1.0 ± 0.3)	1b-4	33.05	1.7 ± 0.6 (0.5 ± 0.2)
5c-1 ^b	44.63	1.9 ± 0.5 (0.4 ± 0.1)			
5c-2 ^b	30.40	-0.1 ± 0.5 -0.03 ± 0.1			

^a Mass uncertainty is ± 0.01 mg.

^b Samples of series 5b and 5c were pretreated thermally (150°C , 24 h, $< 10^4$ Torr).

days' runs, and then these values were subtracted from the ^4He amounts released by each specimen giving the net helium release data in Table 4, column 6. The data in column 6 therefore represent the amounts of ^4He released by the specimens that exceeded the average amount released or desorbed during the analysis of the Rockwell control specimens. Results are summarized in Table 4.

Excess ^4He was observed in 9 of the 10 electrolyzed palladium samples from electrodes which produced tritium. The amounts ranged from 0.4 to 166.8×10^9 atoms. The estimated analysis uncertainty averaged $\sim 0.5 \pm 10^9$ atoms (except for the highest result, where the uncertainty is $\sim 2\%$). No ^4He was observed (above background) in the non-electrolyzed (chemically pretreated) palladium (two slices from the same virgin Pd rod cut as in Fig. 2) or in the platinum anode material [8].

Absence of ^3He

Mass spectroscopy analysis for thermally non-treated series of samples 5a showed small amounts of mass number 3 species. Values obtained were within the range of 0 to 3.8×10^9 atoms per sample. The background value for ^3He ranged from 0.2 to 1.3×10^9 ^3He atoms (per approx. 30 mg of sample). Samples of series 5b and 5c were then treated thermally at 150°C for 24 h in vacuum, in order to expel highly loaded hydrogen isotopes from the Pd bulk. After this pretreatment, mass spectrometry analysis was again performed. Analysis of all the samples in series 5b and 5c now showed no isotopes of mass 3. It was concluded that isotopes of mass 3, found in samples 5a-1 to 5a-4, originated from HD species. This is highly probable, because NMR measurements showed up to 10% light water in the

TABLE 5
Summary of EDS analysis

Sample	Spot position	Pd/at. %	Cu/at. %	Zn/at. %	Pt/at. %	Si/at. %
"High tritium"	A	1.2	93.0	0	5.8	0
	B	8.0	89.2	0	2.9	0
	C	90.7	7.3	0	1.6	0
"No tritium"	A	0.0	93.2	4.2	2.5	0
	B	84.7	8.7	5.0	1.6	0
	C	37.4	14.1	45.7	2.8	0
	D	41.0	25.2	29.8	4.0	0
"Pretreated"	A	79.7	16.4	2.0	0	1.9
	B	89.8	9.2	0.6	0	0.4
	C	77.4	18.7	2.0	0	2.0
	D	98.8	1.0	0	0	0.3
"Untreated"	A	98.5	0.6	0.5	0	0.4
	B	98.7	0.5	0.4	0	0.4

electrolyte at the end of electrolysis. It has been shown that protium, once entered into the electrolyte, will be concentrated further in the palladium during electrolysis [15].

The total tritium found in the electrolyte, $N_0 = 1.6 \times 10^{14}$ T atoms is given in Table 3. Supposing this amount of T originated from *contaminated* Pd, one calculates the amount of ^3He produced through the decay:



Assuming an age of the Pd samples of only 6 months, a corresponding amount of ^3He produced and remaining in the Pd [16] will be:

$$\text{Number of } {}^3\text{He} \text{ atoms} = (1 - e^{-\lambda t}) N_0 = 4.5 \times 10^{12}$$

(where λ is the decay constant in units of month^{-1}).

It follows that the large amount of tritium found in the electrolyte was produced in or on the electrode and did not arise from contaminated palladium.

Surface analysis

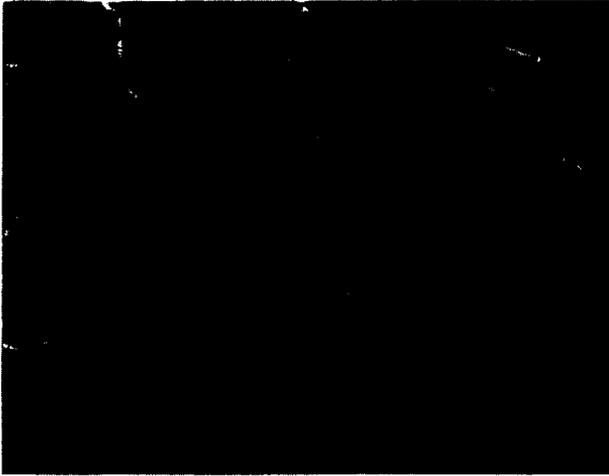
Results of XPS and EDS surface analyses

XPS and EDS analyses of the electrode surface were performed at several different spots. Table 5 summarizes the results of EDS analysis. The first analysis was accomplished on an untreated Pd electrode surface. The second was performed on the electrode pre-treated as described above. A third set of data, "no tritium", represents an electrode pretreated in a standard way, and which did not exhibit positive tritium findings after one month of electrolysis. The final, fourth,

set of data was obtained on an electrode which had shown high levels of tritium production. Different spots analyzed have symbols A, B, C, etc.

The "untreated" sample shows a relatively impurity-free Pd surface. The amounts of Cu and/or Zn may be regarded as negligible. The other samples show spots of pure Pd (above 90%) as well as spots contaminated by impurities, mainly Cu, where the Pd concentration was as low as 4–7%. In order to have this high concentration of Cu to a depth of 1 μm one calculates that there should be about

(a)



(b)



Fig. 10. SEM images of: (a) electrode which produced tritium; (b) "ball"-shaped deposits on the surface of an electrode which showed no tritium production.

10^{-5} mol of Cu in solution. Careful examination of the spots at the electrode surface close to the Cu contact (Fig. 2) shows very little Cu (see spot D for the "pretreated" sample in Table 5). Low amounts of Pt (up to 5%) were found after electrolysis on the "no tritium" and "high tritium" samples.

Particularly careful examination of the surface of the electrode which showed a high level of tritium production ("high tritium") and one which was pretreated in the same way, but did not give positive tritium results ("no tritium"), was done. By scanning different spots at the surface and combining SEM and EDS analyses, significant differences were found between these two samples. A difference in morphology was present. Well defined crystal deposits were found in the case of the electrode which produced tritium (Fig. 10a). EDS analysis for the spots focused precisely in the region where these crystals were formed, see Table 5 ("high

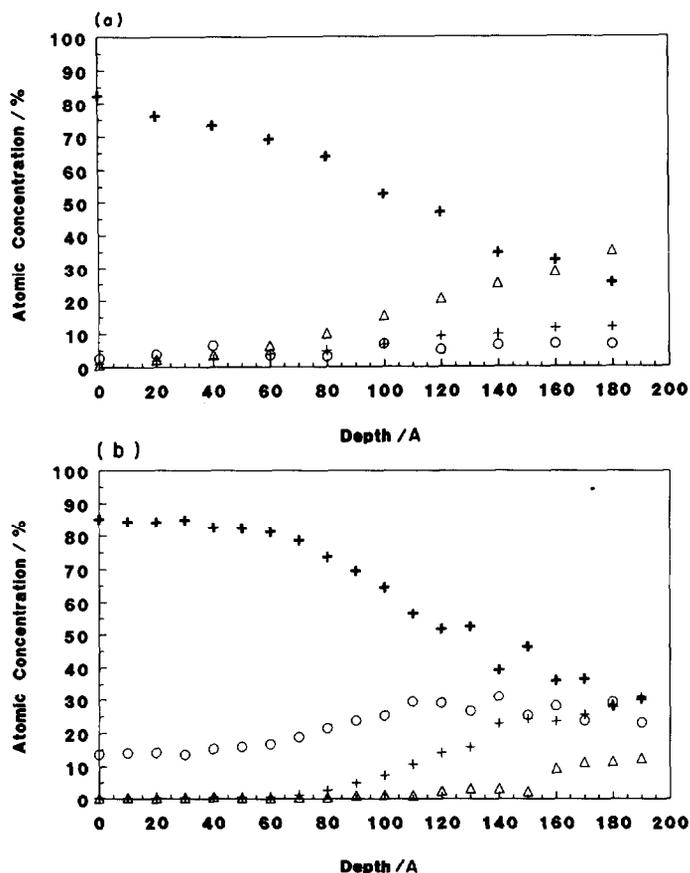


Fig. 11. XPS and depth profile investigations of: (a) pretreated sample (acid etched and stored for 2 weeks in distilled water) and (b) sample which exhibited high levels of tritium. (+) Pd; (Δ) Cu; (○) Si; (+) C.

tritium" spot A and B (B being focused directly on the crystal form)). The impurities were Cu, up to 92%, and Pt, up to 6%. High impurity spots found on the "no tritium" sample showed "ball"-shaped deposits on the surface (Fig. 10(b)). The impurity is again Cu, 93% (Table 5, "no tritium" sample, spot A). Here some Zn (4.2%) was found (spot A). Zn concentrations up to 45% (spots B, C and D) were found, depending on where the analysis was focused at the surface. Pt concentrations were found at about the same level in both cases.

XPS and depth profile investigations of a pretreated sample (acid etched and stored for 2 weeks in distilled water) and a sample which had exhibited high levels of tritium are shown in Figs. 11(a) and 11(b), respectively. A thick layer (over 200 nm) consisting mainly of C, Cu, Zn and Si was detected in both cases. Little Pd was found at the surface. Larger amounts of C were found on the electrolyzed sample.

DISCUSSION

Contamination

Precautions were taken to avoid contamination difficulties in the experiments. Four pieces of evidence attest to the absence of contamination.

(A) Three measurements of tritium in virgin pieces of the same kind of palladium as that which was used in the electrolysis experiment, applying a distillation technique [14] to avoid the effect of particle size and color in the solution, showed no case in which the tritium content was above background.

(B) We had samples examined at a competent institution with respect to the presence in them of ^3He which would come from tritium decay and the ^3He measurements were not above background. No production of ^3He was evident, and therefore no earlier tritium contamination had occurred.

(C) Pickup from surroundings: the reported experiment on tritium pickup from the air of the laboratory was negative.

(D) After the electrode, work on which is reported here, was switched off, it could not be re-started. If the mounting tritium was coming from the surroundings (or from spot contamination in the electrode), turning the electrode on and off would hardly affect the exit of T into the solution.

Electrochemical aspects of the processes concerned

The recorded rates [10,11,17] of T production vary from about 10^4 – 10^{10} atoms $\text{cm}^{-2} \text{s}^{-1}$.

Trivial calculation shows that 10^{10} atoms $\text{cm}^{-2} \text{s}^{-1}$ is equivalent to 10^{-9} A $\text{cm}^{-2} \text{s}^{-1}$ and as the electrolysis is being carried out at a current density of about 20 mA, the ratio of tritium to deuterium formation is about 10^{-7} .

From Fig. 9(b) the Tafel slope is $4RT/F$ (2.303), or about twice the normal Tafel slope for deuterium evolution. However, high Tafel slopes of this kind are often observed [18].

The tritium production rate can be turned into a reaction rate and the irregularity of the points in Fig. 9(b) may be explained as partial current densities. The logarithmic dependence of the rate upon overpotential and the rational slope indicate that the rate determining step for the passage of tritium into solution is a charge transfer mechanism which probably involves a reverse proton discharge mechanism.

This is consistent with the considerable increases of the rate of production obtained by changing the potential and the roughly logarithmic dependence of heat production upon potential as observed by Fleischmann et al. [19].

Surface

The appearance of the surface of the successful electrode was different from that of others which did not produce tritium. The successful electrode had a copper mosaic structure. The appearance of Cu is probably due to its corrosion during the storage procedure in distilled water.

Effect of water upon the reactions

Surprisingly, water did not affect the production of tritium up to a water content in the solution of 10%. This is consistent with the high fugacity in voids theory (see below and refs. 18, 20 and 21) for if the part of the deuterium in the voids is protons and not deuterons it will surely make little difference when the amount is in the region of 10%. On the other hand, in theories which depend upon adsorption of deuterium into the lattice, and binding of this deuterium to palladium atoms, H will always displace D and one would expect the water to diminish the tritium production [22].

Production of ^4He

^4He was found in spots, and these should surely be the cavities observed. The observed [23] ^4He was found in spots less than 1 mm from the surface (Table 4).

Speculations on mechanism

Cavities

The fact that a change of potential was found to trigger T production might be interpreted by the high fugacity theory [18,20,21,24].

In order for the Griffith crack [25] to spread it can be shown that:

$$p_{\text{D}_2} = \left(\frac{16 Y \gamma}{3 l} \right)^{1/2} \quad (3)$$

where Y is Young's modulus which for palladium is 1.17×10^{12} dyne cm^{-2} and the surface tension, γ , is 1500 dyne cm^{-1} . Taking the cavities as 10^{-5} cm the critical

pressure after which the cavity expands (and fugacity falls) would be 3×10^4 atm [25].

From the relation of fugacity of hydrogen in voids to the corresponding pressure, derived by Podgurski [26,27], it follows that very high fugacities can be associated with relatively low pressure so that there is no contradiction in assuming that it is possible to obtain in the void space fugacities of 10^{17} atm, whilst the pressure (cf. eqn. 3) remains below that for cracking. As the cavities fill and attain the critical fugacity needed for fusion [28], they also expand and therefore the fugacity falls and the critical condition is lost until a higher fugacity is tuned in by increasing the potential. This lasts for some time until the cavity again expands under this pressure, needing a further increase of potential, etc.

These calculations are inexact (assumption of Griffith type crack, etc.) and the very high *fugacity* ($\sim 10^{15}$ atm) which would correspond to a *pressure* in the crack is not far from that calculated by Lifshitz and Pitaevskii [28] for the beginning of loss of charge on the particles of the plasma assumed to constitute the interior of the voids (10^{17} atm).

There is evidence [9] that the phenomena reported depend upon *surface* structure. Thus, the surface structure would determine the path and rate determining step of deuterium evolution and this in turn is known to determine the fugacity developed in voids (cf. Table 1 in ref. 29). Thus, the high fugacity in voids theory connects up the times of waiting for switch-on, the sporadicity of the results, and the fact that clean solutions do not give good results but dirty ones sometimes do [30]. Correspondingly, the observation of one of us (Chien [10]) that high turbulence causes a quenching of the production of tritium is consistent with this: the high turbulence would destroy the surface structure by knocking off promontories and this in turn may change the mechanism of deuterium evolution on the substrate.

Effect of quenching

Adding fresh D_2O to the solution quenched the fusion reaction and it would not start again for some hours. It is possible that new D_2O dissolves some of the impurity on some entities on the surface. But it may be that these surface components, which determine the mechanism of the hydrogen evolution reaction, consequently determine the dependence of fugacity in voids within the metal upon overpotential. Subsequently, it may be assumed that the desorbed entity re-adsorbs. Therefore, the mechanism which gave the high fugacity is re-established and the tritium production begins anew.

CONCLUSION

It has been shown that at an electrode described in this paper, about 750 h of tritium production at about 10^7 atoms $cm^{-2} s^{-1}$ have taken place. After this time, the reaction was interrupted intentionally, and could not be re-started.

The facts reported are consistent with the achievement, as a result of a particular and specific configuration on the surface of the electrode, of a surface condition corresponding to high fugacity of D_2 in voids within the electrode.

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