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Possible excess tritium production on Pd codeposited with deuterium

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Abstract

Tritium production was measured in the liquid and gas phases on Pd codeposited with deuterium from $\text{PdCl}_2 + \text{LiCl} + \text{D}_2\text{O}$ solutions. During two weeks of electrolysis, in four out of six cells, average excess tritium levels of 1.9 times in the gas phase and 1.6 times in the liquid phase were found over those expected from the separation factor. The largest excess of tritium found was three times that calculated theoretically from the separation factor. The excess tritium observed exhibited a 'burst' nature, both in the gas and liquid phases. On two occasions, where tritium production was within classical limits, no bursts were observed. A separation factor of 1.6 was measured in these two cells. This method has the advantage that the tritium concentration in the bulk of Pd was measured in solution before the Pd was deposited on an Au substrate.

INTRODUCTION

A knowledge of separation factors for hydrogen and deuterium (D) as well as for hydrogen and tritium (T) has been used frequently in the past to study the mechanism of hydrogen evolution reaction on metal substrates [1,2], particularly on Pd [3]. It is also of value in heavy water enrichment experiments. In the past two years, since the Fleischmann and Pons claims of excess tritium as well as heat and neutron production during heavy water electrolysis on Pd [4], more than 40 reports have appeared on the electrolytic production of tritium in excess of that expected from deuterium/tritium separation factors [5–8]. Most of these report amounts of tritium only 5–10 times above the background but, in some cases,

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amounts of tritium over 100 times (sometimes 10^4 times) above the background have been found. However, the percentage of successful attempts to reproduce the observed phenomena still rarely exceeds 30%. Recently, two different approaches have been shown to yield more reproducible results in excess tritium findings: one is performed in the gas phase loading of Pd/Si layers [9] (reproducibility above 50%) and the other by simultaneous electrolytic deposition of Pd from dissolved PdCl_2 and deuterium [10,11] (reproducibility approaching 100%). This second approach, due to Szpak and Boss, has the advantage of giving the total background of T at the beginning of any experiment, *thus completely excluding any possibility of Pd contamination*.

This paper reports on excess tritium production on Pd codeposited with deuterium as found in four out of six experiments.

EXPERIMENTAL

The experimental set-up for the codeposition of Pd and deuterium and for the simultaneous measurement of tritium both in the liquid and gas phases, is shown in Fig. 1. Three different sizes of cells were used: 7, 11 and 23 ml respectively. Care was taken to keep the ratio of the solution volume to working electrode area constant in all the experiments (15–20). $\text{D}_2 + \text{TD}$ and O_2 gases were recombined on a C-supported Pt catalyst (E-Tek). Concentrated sulfuric acid was used as a

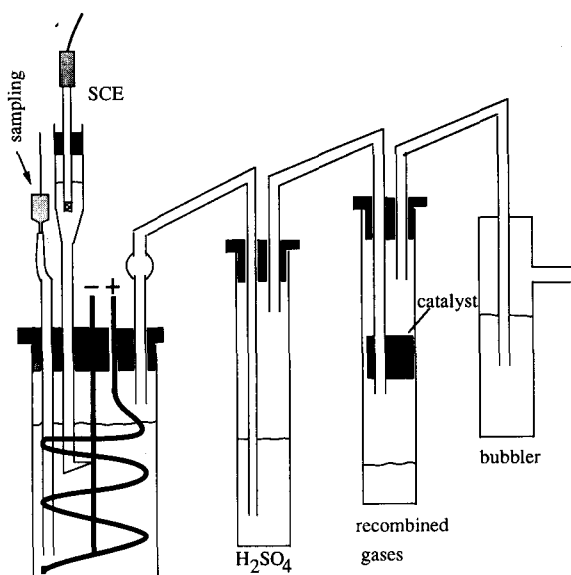


Fig. 1. Experimental set-up for codeposition of Pd and deuterium, for electrolysis and for simultaneous measurements of tritium in the liquid and gas phases.

trap for solution vapors. A bubbler at the end allowed the whole system to be isolated from the atmosphere. In correct operation of the cell, all the gases should be recombined and no bubbling of gases out from the cell should occur.

Pd was deposited galvanostatically on Au wire 0.5 mm in diameter (99.9%, Aldrich) from solutions of 0.05 M PdCl₂ (Aldrich) and 0.3 M LiCl (Aldrich) in D₂O (pH 3.4). Two different D₂O samples were used: 99.9% Cambridge Isotope Laboratories (tritium background content, 190–210 DPM ml⁻¹) and 99.9% Isotech Inc., Matheson (tritium background, 12–18 DPM ml⁻¹). It is extremely important that the same bottle of D₂O is used throughout the experiment. In this way, any dilution or concentration of tritium owing to the additions of heavy water of different background level is avoided. Results reported here are free of such error. (One run, showing excess tritium, was discarded on that basis.) The anode was a Pt wire (0.5 mm, 99.9%, Aldrich) with a surface area about 4–5 times larger than that of the Au working electrode. The reference electrode used was a saturated calomel electrode. It was tightly fitted in a Luggin capillary filled with electrolyte from the cell, thus minimizing possible contamination with light water. All the potentials are referred to the reversible hydrogen electrode (RHE) in the same solution. The PdCl₂ and LiCl were obtained under an Ar atmosphere and were kept in an Ar glove box to minimize light water contamination.

Both the deposition of Pd and electrolysis were performed galvanostatically using a PAR 173 potentiostat/galvanostat and the potentials were recorded on a Houston Instruments, Model 2000 recorder.

Tritium samples (0.5 ml) were taken by attaching the syringe with a disposable 100 μl pipetting tube to the cell sampling tube which had a Teflon holder with a hole (Fig. 1). This was repeated five times. The disposable pipetting tube fitted well into this hole. Pressing the small latex tube before and after sampling with the syringe allowed for minimum air and/or light water contamination. It was shown earlier [12] using nuclear magnetic resonance (NMR) spectroscopy that an open arrangement of the top of the cell allowed light water from the atmosphere to enter the cell. The light water content was 1.6% and 9.8% after three and 22 days of electrolysis respectively. It was found that, if the cell is closed, the light water contamination from air is reduced to less than about 2% in two weeks of electrolysis. The original light water content of D₂O used in this work was 0.1%. With the arrangement shown in Fig. 1, where the inner diameters of the tubing entering the cell were 2 mm or less, and with all precautions employed during the experiment (use of latex tube for sampling, dry chemicals, etc.), it is assumed that the light water content in the cells after two weeks of electrolysis (a typical duration of one run) was about 1%. A tritium sample from the gas phase was taken in a similar way from the recombiner vessel. After each sampling, the recombiner vessel was emptied. Fresh D₂O was added to the cell daily through the same sampling tube.

The tritium concentrations were measured on a Wallac LKB 1410 scintillation counter as described elsewhere [12]. The counting time was 1 h, which yielded a relative standard error deviation of the tritium concentration of 3% [12]. Intercali-

bration of the liquid scintillation counter with similar instruments in other laboratories was performed earlier [12,13].

RESULTS AND DISCUSSION

A change in tritium concentration during electrolysis in open cells occurs, owing to the additions of fresh D_2O containing background levels of tritium and owing to the removal of tritium by electrolysis. This removal depends on the isotopic separation factors of tritium and deuterium. When the amount of tritium added to the solution is equal to the rate of removal of tritium by electrolysis, the following equation describes the build-up of tritium concentration in the electrolyte during long-term electrolysis [13]:

$$\frac{n_T(t)}{n_T(0)} = S - (S - 1) \exp\left(-\frac{t}{\tau}\right) \quad (1)$$

where τ is the tritium build-up time constant, such that

$$\tau = SnV/R \quad (2)$$

where V is the volume of the cell, n is the concentration of D_2O (mol dm^{-3}) and R is the rate of the production of deuterium in solution ($R = I/2F$). The isotopic separation factor of deuterium and tritium on Pd, according to Corrigan [14], may be found within the range 1.7–2.2. Here, a value of 2 was taken.

Electrolysis was started at low current densities of 2.5 mA cm^{-2} (expressed per geometrical surface area) to avoid the Pd dendrite growth being too fast. The current was then gradually increased (within about 5 h) up to 25 mA cm^{-2} , when a

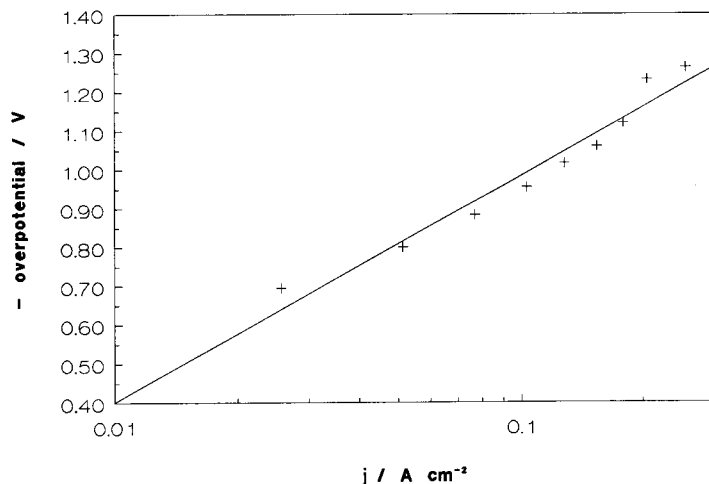


Fig. 2. Current vs. potential curve on Pd–Au electrode in $0.05 \text{ M PdCl}_2 + 0.3 \text{ M LiCl}$ (cell A) after Pd^{2+} deposition was completed (solution discolored). $b = 580 \text{ mV/decade}$.

large change in the potential from approximately -0.02 to -0.8 V vs. RHE occurred. Comparing this potential (-0.8 V) with data published previously for D_2 evolution on Pd [15,16], it is obvious that the Pd deposition took place with simultaneous deuterium evolution at very high overpotentials. This assured that each Pd layer deposited was loaded with D_2 . The current of 25 mA cm^{-2} was kept constant until the solution was completely discolored, i.e. all the Pd from solution was deposited on the electrode. A highly dendritic layer of Pd (2–3 mm thick) was visible at the electrode. This happened within the first 40–50 h of electrolysis. The current density was then usually increased to 250 mA cm^{-2} . Figure 2 shows the changes in potential during the gradual increase in the current from 25 to 250 mA cm^{-2} . A current vs. potential curve thus obtained exhibited a high so-called Tafel slope of 580 mV/decade , which may be associated partly with the limiting current deposition from H_3O^+ .

Figures 3, 4 and 5 show the change in tritium concentration, both for the liquid and gas phases, in the three cells A, B and C during two weeks of electrolysis. Theoretical lines calculated from eqns. (1) and (2) are also shown for comparison. All the changes in the applied currents during electrolysis are taken into account in the calculations and are marked in each graph. A ‘burst’ type of excess tritium production in the gas phase was observed, followed by or simultaneously occurring with the bursts in the solution. A summary of the tritium excess observations for the four positive cells out of six investigated is given in Table 1. Two criteria were applied to judge the excess tritium production. The first criterion was the ratio of the tritium concentration observed to the value calculated theoretically from eqns. (1) and (2), for both the gas and liquid phases. These values are taken at burst

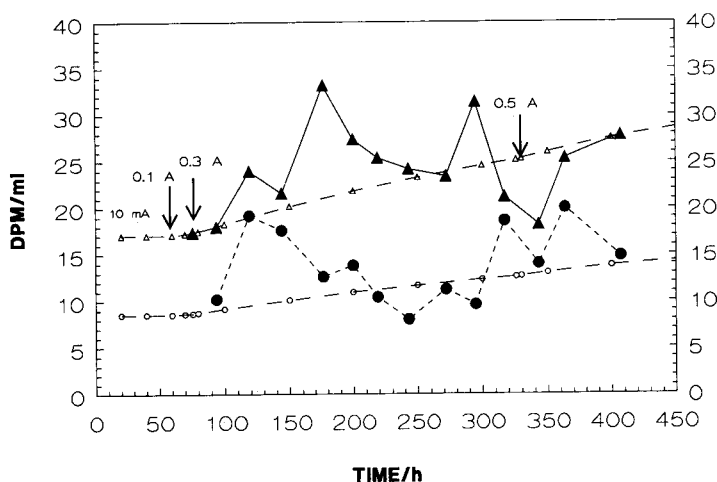


Fig. 3. Tritium bursts in the liquid and gas phases in cell A during two weeks of electrolysis in $0.05 \text{ M PdCl}_2 + 0.3 \text{ M LiCl}$. Dashed lines with open symbols represent theoretical values for the liquid and gas phases calculated according to equations (1) and (2); \blacktriangle , \triangle , solution; \bullet , \circ , gas.

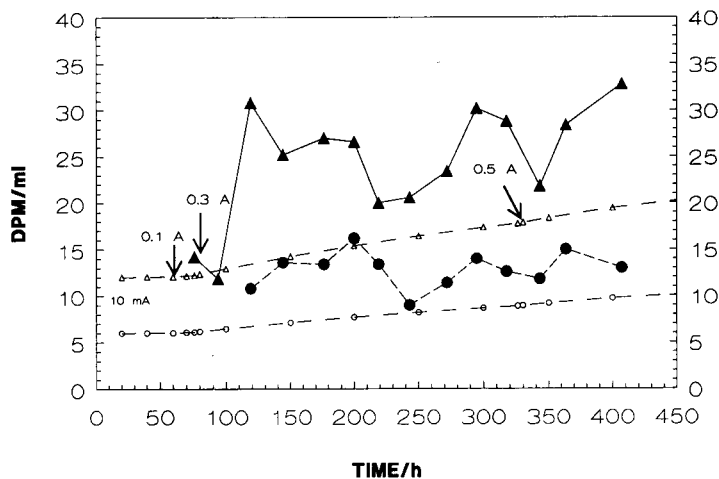


Fig. 4. Details as for Fig. 3, except results shown are for cell B.

maxima in the gas and liquid phase. The second criterion was the ratio of the tritium concentration found in the gas phase to that in the liquid phase. This ratio is measured at points where tritium in the gas phase was closest to the tritium found in liquid or exceeding that of the liquid.

The initiation time for the appearance of the tritium bursts, as shown in Table 1, is measured after the solution was discolored (Pd deposition completed). It should be noted that the check for possible effects of Pd-complex interference with the tritium measurements in PdCl_2 solutions was made by performing liquid scintillation analysis after distilling the samples in a closed distillation apparatus,

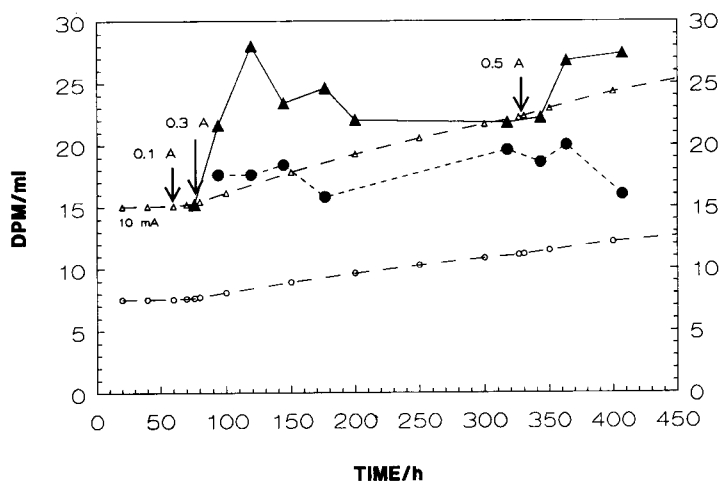


Fig. 5. Details as for Fig. 3, except results shown are for cell C.

TABLE 1

Summary of excess tritium findings in cells A, B, C and D

Cell	Initiation time /h	Burst no.	Burst duration /h	Gas phase $T_g/T_{g_{th}}$	Solution $T_s/T_{s_{th}}$	Ratio T_g/T_s	Comment
A	35	1	120	2.1	1.6	0.83	Bursts in gas phase precede bursts in solution
		2	80	1.8	1.3	0.93	
B	32	1	140	2.4	2.1	0.67	Both gas and liquid above T_{th} during whole experiment
		2	70	1.6	1.7	0.51	
C	17	1	130	2.1	1.7	0.80	Gas phase constantly about 80% above T_{th}
		2	90	1.6	1.2	0.91	
D	25	1	135	1.5	1.0	1.52	Tritium bursts both in gas and liquid phases; decreased with time of electrolysis

T_g is the tritium concentration in the gas phase.

$T_{g_{th}}$ the tritium concentration in the gas phase calculated from eqns. (1) and (2).

T_s the tritium concentration in the solution.

$T_{s_{th}}$ the tritium concentration in the solution calculated from eqns. (1) and (2).

$T_g/T_{g_{th}}$ and $T_s/T_{s_{th}}$ are measured at maximum tritium concentration in the burst.

T_g/T_s is measured at points where tritium in the gas phase was close or exceeded tritium in the liquid.

similar to the one described by Will and coworkers [17,18]. The distilled samples before Pd deposition and after complete deposition of Pd on the electrode did not show any significant increase in the tritium concentration. This test proved that there was no tritium contamination of the Pd bulk deposit. Also, after Pd deposition was completed, distilled and non-distilled solution samples exhibited the same tritium concentration, within the error of measurements. In this way, no Pd-complex interference with the tritium measurements is found in solutions where Pd is completely exhausted by deposition on the electrode surface. Therefore, most of the samples are measured without the predistillation step. The initiation time for the appearance of excess tritium ranged between 17 and 35 h, these values being in agreement with the shortest initiation times found in similar [10] and/or in other experiments [4-7,12].

In most of the cells, one or two bursts were observed, the first burst being usually longer than the second burst. In the gas phase, maximum values 2.1-2.4 times that expected from the separation factor of 1.3-2.1 were observed. In the

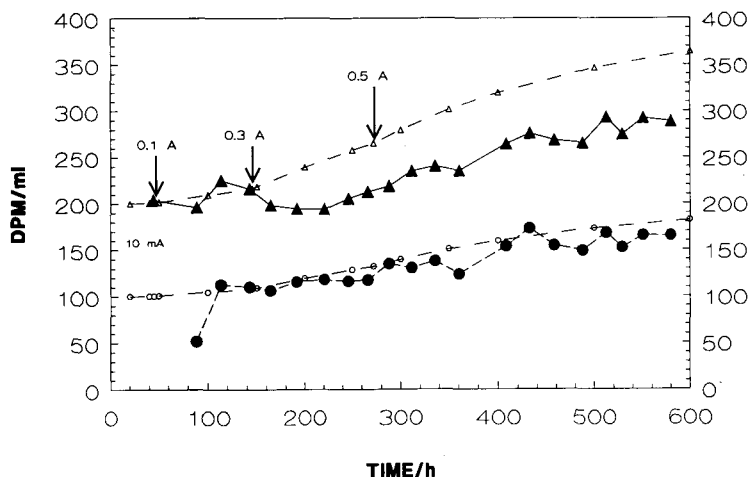


Fig. 6. Change in tritium concentration in the liquid and gas phases in cell E which did not produce excess tritium. 0.05 M PdCl_2 + 0.2 M LiCl ; dashed lines with open symbols represent theoretical values for the liquid and gas phases calculated according to equations (1) and (2); \blacktriangle , \triangle , solution; \bullet , \circ , gas.

liquid phase, excess tritium over that expected from the separation factor was generally lower than that for the gas phase. The ratio T_g/T_s (0.5–1.5) reflects how much tritium in the gas phase is found in excess over the theoretical ratio ($T_{g,th}/T_{s,th}$) expected from the separation factor (which is 0.5). Results expressed in this way are not subject to background variations during long-term electrolysis. In all the cells (except cell B, burst 2), the T_g/T_s ratios found were 30%–90% higher than that expected. The highest value found was that for cell D, where tritium in the gas exceeded that of the liquid by about three times.

In Fig. 6 is shown the cell which did not demonstrate excess tritium production. No bursts were observed and the ratio of tritium found in the liquid to that found in the gas phase stayed constant during two weeks of electrolysis. No dependence of the separation factor on the potential was observed. It is concluded that no anomalous phenomena occurred in this case. Another cell, not shown here, exhibited the same behavior. An average value of the isotopic separation factor thus measured was 1.7 and 1.5 for the two cells respectively. These values are lower than the theoretical value of 2 used in the calculations. In this way, data reported here on excess tritium findings are underestimated.

It has to be pointed out that, in both these cells, where no excess tritium is found, a Cambridge D_2O was used. The occurrence of cold fusion reactions has often been related to the source of D_2O and, indeed, positive results were found in the cases where Isotech D_2O was used [12,19], as is also the case in the present experiments. This again indicates that the impurity agglomerations in solution and their adsorption at the metal surface might be of major importance in understanding cold fusion phenomena. An explanation for the high tritium production on Pd, based on the effect of the amount and the type of impurities on the mechanism of

the deuterium evolution reaction on Pd surface, and, consequently the development of high fugacities inside the metal, was offered in a series of previous publications [12,15,16,20]. According to this explanation, the very high Tafel slope observed here, assuming that either a coupled-discharge combination or coupled-discharge electrochemical desorption mechanism is taking place, should promote conditions favorable to reach high fugacities inside the dendritically deposited Pd and eventually cold fusion reactions.

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