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INVESTIGATION OF LOW-LEVEL TRITIUM GENERATION IN Ni-H₂O ELECTROLYTIC CELLS

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The generation of tritium during the electrolysis of aqueous light water alkali carbonate (K₂CO₃ and Li₂CO₃) solutions by nickel cathodes, first reported by us at the International Conference on Cold Fusion-3 (Nagoya, Japan, October 1992) has once again been verified and confirmed. During 1993, 10 out of 23 cells, whose electrolytes were analyzed using a newly set up dedicated liquid scintillation counting unit, indicated low tritium levels in the electrolyte, in the range of 0.5 to 4.8 Bq/ml. Except one cell, which contained 25% D₂O, the remaining nine cells, which produced tritium, were charged with natural light water solutions only. Two of these cells, which were monitored for tritium every few days, and excluding cell OM-3, which was set up in 1992, indicated tritium level variations in a sawtooth fashion, suggesting the possible presence of an as yet unidentified mechanism responsible for periodically removing tritium from the electrolyte.

INTRODUCTION

At the International Conference on Cold Fusion-3 (Nagoya, Japan, October 1992), we reported¹ observing relatively large amounts of tritium (46 to 3390 Bq/ml) in the electrolytes of 18 out of 29 aqueous carbonate electrolytic cells at the end of several weeks of operation. These cells had nickel cathodes and platinum anodes and contained either H₂O or D₂O or a mixture of H₂O and D₂O (the D₂O component being either 25 or 50%) in the form of 0.57 M K₂CO₃ or 0.1 M Li₂CO₃ (natural lithium or 54% enriched ⁶Li) solutions. The tritium activity in the electrolyte samples was measured using standard liquid scintillation counting techniques. All samples were

distilled under vacuum prior to adding scintillation cocktail for counting. Tritium was observed both in cells having some D₂O content as well as in cells containing only natural H₂O.

With the idea of studying the temporal variation of tritium buildup, several cells were set up using separation funnels so that electrolyte samples could be periodically drained from below. No calorimetry was carried out in these so-called “OM series” cells, which were set up specifically to study the time behavior of tritium generation. Of these, cell OM-3 with 0.1 *M* enriched Li₂CO₃ solution in H₂O, showed a steadily increasing tritium level in the electrolyte, reaching a maximum value of 225 Bq/ml at the end of ~1 month of operation (see Fig. 8 of Ref. 1). Evidence of continuous buildup of tritium gave us confidence in the overall reliability of the measurements.

FURTHER STUDIES WITH CELL OM-3

Cell OM-3 continued to be operated and monitored for tritium even after the Nagoya meeting. The last tritium activity reported in the Nagoya paper was that of October 6, 1992. Over the next 45 days, the tritium data points of cell OM-3 were found to oscillate in a sawtooth fashion between a minimum value of 150 Bq/ml and a maximum value of 240 Bq/ml. Table I summarizes these tritium results, and Fig. 1 depicts the full history of time variation of tritium activity of the electrolyte of cell OM-3. Figure 1 appears to suggest saturation of tritium level at an average value of 190 ± 40 Bq/ml, implying cessation of tritium generation in the cell. However, the rather high magnitude of the fluctuations of the measured tritium activities is puzzling.

As mentioned in Ref. 1, the aforementioned tritium measurements were carried out by experts at the Isotope Division of the Bhabha Atomic Research Centre (BARC) to whom samples of the electrolytic solution were sent. This group, however, also handles tritium from other research departments. In view of the fact that observation of tritium in light water cells was being reported for the first time by any group, we were conservative and reported only tritium levels above 10 Bq/ml (thrice background counts) at Nagoya. This way we hoped to avoid criticism that the observed tritium activity could have been due to either electrolytic enrichment or cross contamination occurring during the process of distillation and counting.

DEDICATED TRITIUM COUNTING SETUP

To once again independently verify and confirm tritium generation in light water cells, a new dedicated low background liquid scintillation counting setup was procured in May 1993 and installed in Engineering Hall No. 5 (of the Chemical Engineering Division) where no other tritium or radioactive sources are handled. The stability and calibration of this new counting setup were checked by recording background counts (26 ± 2 count/ min) and counts with standard tritium solution (2300 dpm/ ml), almost daily over a 2-month period. Table II presents a summary of these data counts. The counting efficiency of this new setup is seen to be ~22%. Note that the background counts are equivalent to a sample solution activity of ~2.0 Bq/ml.

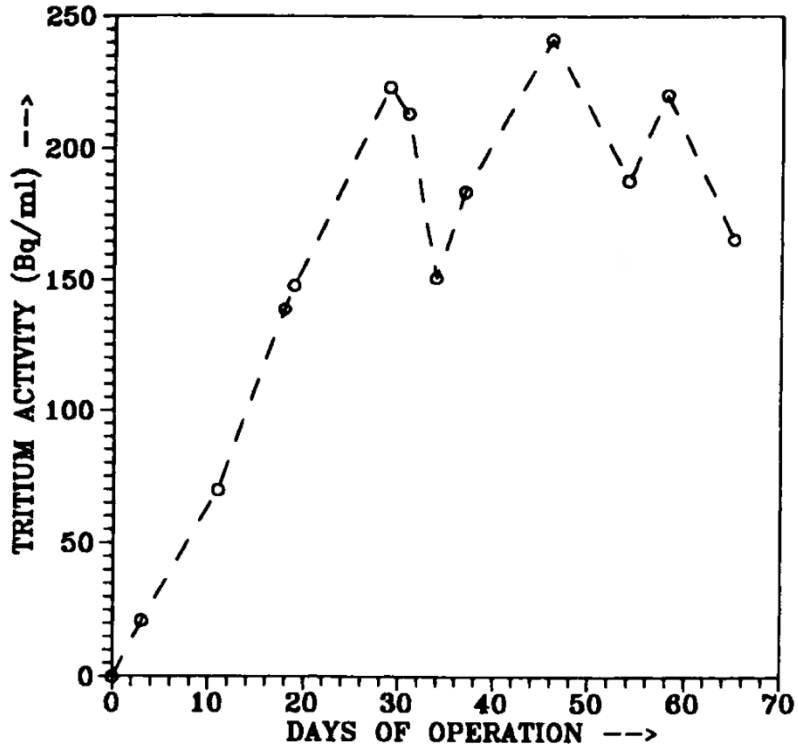


Fig. 1. Variation of tritium level of electrolyte in cell OM-3.

TABLE I
Tritium Buildup in Cell OM-3*

Date of Sampling (1992)	Days of Operation (days)	Tritium Level (Bq/ml)
September 5	0	Nil
8	3	21 ^a
16	11	70
23	18	139
24	19	148
October 4	29	223
6	31	213
October 9	34	151
12	37	184
21	46	241
29	54	188
November 2	58	220
9	65	166

*Sintered porous nickel cathode, 0.1 M Li₂CO₃ in H₂O.

^a Recombined water up to this time showed 42.3 Bq/ml.

TABLE II
Performance of Dedicated Liquid Scintillation Counting Unit (Stability Data)

Date (1993)	Background (count/3 min)	Standard Source ^a (count/3 min)
August	75	1680
20	84	1644
23	72	1566
24	72	1539
September	70	1539
1	81	1533
6	75	1629
7	79	1560
8	70	1539
13	72	---
21	72	---
22	72	---
23	72	---
28	73	---
Average	79.5 ^b	1605

^a 2300 dpm/ml.

^b 110 dpm/ml equivalent.

To avoid carryover of alkali during microdistillation, only ~1.5 ml of distilled solution was collected starting from an initial sample volume of ~5 ml, which was loaded into the small distilling flask. Then, 10 ml of freshly procured triton X-100-based scintillation cocktail was mixed with 1 ml of the distilled sample for counting. All stock solutions of the electrolyte, namely, 0.57 M K₂CO₃ and 0.1 M Li₂CO₃, were freshly prepared and double-checked for the presence of any initial tritium activity prior to charging into the electrolytic cells. In all, over 100 samples were distilled and counted from June through September 1993, using the newly dedicated tritium counting setup.

DESCRIPTION OF ELECTROLYTIC CELLS

Six new cells of identical design labeled OM-5 to OM-10 similar to OM-3 were set up and operated from June through September 1993. The outlet gases from each of these cells were led to separate traps containing platinum-based recombination catalysts that in turn were connected to paraffin oil traps for isolation from the atmosphere. Three of these cells had some D₂O component. All of the electrode assemblies were of a flat plate type with nickel cathodes and platinum wire (0.1-mm-diam) anodes mounted on Teflon U-frames. The cell voltages were in the 2.0- to 2.5-V region, and currents were <100 mA. Some cells were powered by an intermittent direct-current pulser similar to that used by Mills and Kneizys.² Table III summarizes the characteristics of these cells. The electrolytes of all these cells were monitored for tritium content at intervals of 3 to 10 days. Cell OM-9 was charged with 0.1 M natural Li₂CO₃ solution, which already contained some initial tritium activity (up to ~1.8 Bq/ml) from a previous experiment. The recombined water from all these cells was also analyzed for tritium activity.

RESULTS OF THE NEW OM SERIES OF EXPERIMENTS

Of the six new OM cells, two cells, namely, OM-7 (Li_2CO_3 in 25% D_2O) and OM-9 (Li_2CO_3 in H_2O), showed detectable levels of tritium. Counts were up to three times background values. These results are summarized in Tables IV and V and are plotted in Figs. 2 and 3. Both of these cells also indicated the characteristic oscillatory type of tritium level variation observed by us earlier in cell OM-3. However, the absolute magnitude of tritium activity in these two cells is relatively low: <3.5 Bq/ml.

The fact that during the increasing or decreasing phase of tritium activity several data points fall on a near straight line clearly indicates that the oscillatory behavior is genuine and not attributable to any counting errors or experimental artifacts. Also, the fact that none of the remaining four OM series cells, namely, OM-5, OM-6, OM-8, and OM-10, which were also operated, sampled, distilled, and counted for tritium in an identical manner, showed any detectable tritium rules out contamination from “BARC atmospheric air” (a commonly voiced concern) or from other samples containing small quantities of tritium stored in the laboratory.

MEASUREMENT OF TRITIUM IN CELLS WHEREIN CALORIMETRIC STUDIES WERE CARRIED OUT

Calorimetric studies were carried out³ in a number of aqueous carbonate Ni-H₂O cells at the Process Instrumentation and Systems Division of BARC. All of these cells were of the open type employing desilvered double-walled glass dewars and planar geometry electrode assemblies. The nickel cathodes were 2×6 cm² in area and 0.5 mm thick. The platinum anode wire (0.3 mm in diameter) was wound over the Teflon frame holding the cathode plates with a 3-mm interelectrode gap. The operating cell voltages and currents varied in the region from 2.0 to 4.0 V and 0.1 to 2.5 A, respectively. The corresponding current density range was 5 to 100 $\mu\text{A}/\text{cm}^2$. A bank of five cells and an identical dummy cell were operated at a time. A pair of thermocouples was located in each cell for temperature measurement. The difference in average cell temperature at steady state between operating and dummy cells was used to deduce the heat generation rate in the cells. The cells were calibrated using resistance heater coils. While most experiments were carried out with H₂O solutions, some runs used a mixture of H₂O and 25% D_2O . The calorimetric technique and other details are described elsewhere.^{1,3}

TABLE III
Summary of Cells Operated Specifically to Study Tritium Level Variations (June Through September 1993)

Cell	Electrolyte Volume (ml)	Alkali	Solvent	Electrodes	Duration of Operation (days)	Maximum Tritium Level (Bq/ml)
OM-5	100	Li ₂ CO ₃ ^a	H ₂ O	Porous nickel	54	Nil
OM-6	100	Li ₂ CO ₃ ^a	H ₂ O	Electrolytic nickel	44	Nil
OM-7	100	Li ₂ CO ₃	25% D ₂ O	Porous nickel	64	~2.6
OM-8	100	Li ₂ CO ₃	D ₂ O	Fibrex nickel	54	Nil
OM-9	50	Li ₂ CO ₃	H ₂ O	Porous nickel	46	~3.2
OM-10	20	LiOD	D ₂ O	Milton Roy palladium tube	17	Nil

^a 54% enriched ⁶Li.

TABLE IV
Tritium Level Variation of Cell OM-7*

Duration of Operation (days)	Raw Count/9 min (Average of 3)
1	260
2	316
3	360
12	542 ^b
16	381
19	310
29	503
36	377
39	376
48	364
54	390
65	332

Note: Background counts: 238

Standard source counts: 4815.

*Porous nickel-platinum wire, enriched (54%) Li₂CO₃ in H₂O

^a For recombined water.

^b Maximum, corresponds to ~153 dpm/ml.

TABLE V
Tritium Level Variation of Cell OM-9*

Days of Operation	Count/9 min
0	460 ^a
7	298
13	252
20	217
26	240
28	430
31	613 ^b
33	494
35	484
38	438
41	386
46	431
Background counts	238

*Porous nickel-platinum wire, natural Li₂CO₂ in H₂O (July 23 through September 7, 1993).

^a Electrolyte contained 110 dpm/ml of tritium from a previous experiment.

^b Maximum, corresponds to 188 dpm/ml.

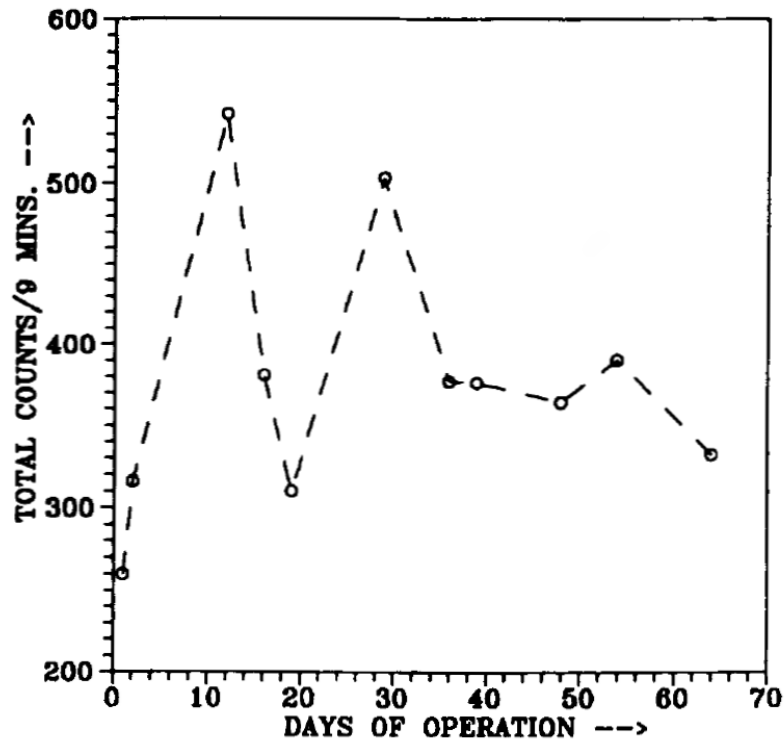


Fig. 2. Variation of tritium level of electrolyte in cell OM-7.

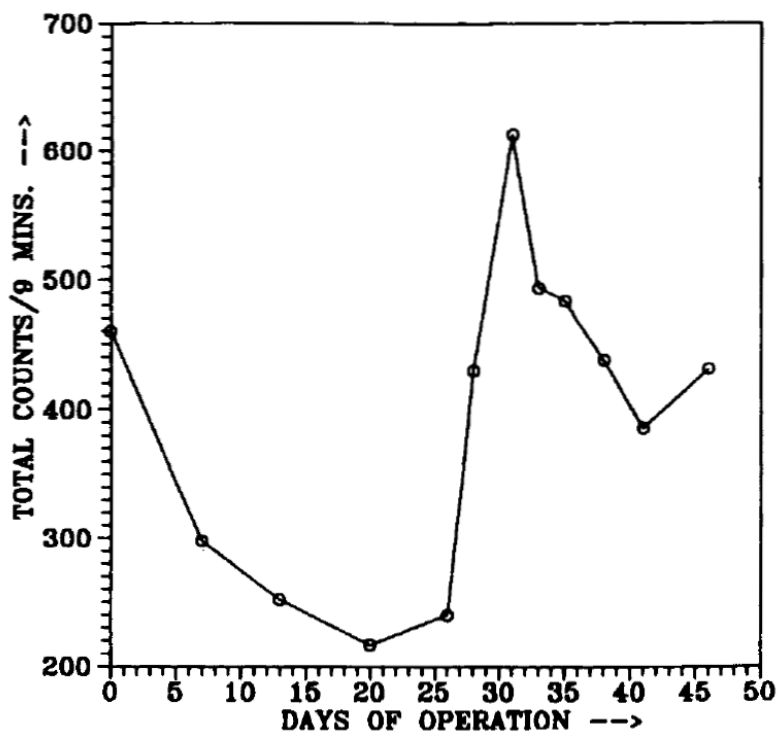


Fig. 3. Variation of tritium activity of electrolyte in cell OM-9.

Electrolyte samples from these cells were analyzed for tritium at the end of the runs. Only samples from the 17 cells operated after June 1993, when the newly dedicated counting setup became available, were monitored for tritium. These results are summarized in Table VI. It is seen that 8 out of the 17 cells whose samples were counted have indicated low levels of tritium production, in the 30 to 290 dpm/ml range (corresponding to 0.5 to 4.8 Bq/ml).

SUMMARY AND CONCLUSIONS

The production of tritium during the electrolysis of aqueous carbonate solutions using nickel cathodes and platinum anodes first reported by us in Nagoya has been verified and confirmed once again using freshly setup cells and a newly acquired dedicated tritium counting setup. During these experiments, adequate precautions were taken to rule out any possibility of contamination from stray sources of tritium, if any. During 1993, 10 out of 23 cells indicated the generation of tritium at levels in the range of 0.5 to 4.8 Bq/ml. However, the magnitude of tritium activity in the post-Nagoya experiments is significantly lower. Electrolytic enrichment of the tritium isotope cannot account for this in view of the low currents, above ambient temperature of cell operation, and the addition of makeup water to maintain original solution levels. The generation of tritium in Ni-H₂O cells has since been corroborated by Notoya et al.⁴ at the International Conference on Cold Fusion⁴.

Of the OM series cells whose electrolytes were sampled and counted frequently, three cells (inclusive of OM-3) indicated tritium levels well above background counts. Interestingly, all of

these three cells, which were sampled and counted periodically, have displayed a characteristic oscillatory variation of the tritium activity. While an increase in tritium level can be understood as a production phase, the decreasing phase, lasting from 5 to 10 days (in one case up to 20 days), is difficult to understand. A close scrutiny of our sampling, distilling, and counting techniques confirms that the decrease in tritium level is genuine and not attributable to any artifact. We are strongly tempted to suggest that there is an as yet unidentified mechanism periodically “cleansing” the electrolyte of tritium. Oscillatory behavior of tritium level in Pd-D₂O electrolytic cells has also been reported by three other independent groups.⁵⁻⁷ It is puzzling that the tritium activity of the electrolytes of both Pd-D₂O and Ni-H₂O electrolysis cells seems to vary in an analogous oscillatory fashion.

TABLE VI

Tritium Generation in Cells Operated in the Process Instrumentation Division

Serial Number	Cell	Electrolyte ^a	Date of Sampling (1993)	Total Count/9 min	Tritium Activity (dpm/ml)
1	XO-1	K ₂ CO ₃	July 5	252	---
2	XO-2	K ₂ CO ₃	July 5	219	---
3	XO-3	(N)Li ₂ CO ₃	July 5	228	---
4	XO-4	(N)Li ₂ CO ₃	July 5	783 ^b	260
5	XO-5	K ₂ CO ₃	July 5	243	---
6	XP-1	(N)Li ₂ CO ₃	July 12	246	---
7	XP-2	(N)Li ₂ CO ₃	July 12	363 ^b	56
8	XP-3	(N)Li ₂ CO ₃	July 12	267	---
9	XP-4	(E)Li ₂ CO ₃	July 12	278	---
10	XP-5	(E)Li ₂ CO ₃	July 12	300	30
11	XQ-1	(N)Li ₂ CO ₃	August 7	327 ^b	40
12	XQ-2	(N)Li ₂ CO ₃	August 7	264	---
13	XQ-3	(N)Li ₂ CO ₃	August 7	396 ^b	73
14	XQ-1	(E)Li ₂ CO ₃	August 10	429 ^b	88
15	XQ-2	(E)Li ₂ CO ₃	August 10	360 ^b	56
16	XQ-1	K ₂ CO ₃	August 13	267	---
17	XQ-2	K ₂ CO ₃	August 13	870 ^b	290

^a Here, (N) denotes natural and (E) denotes enriched ⁶Li

^b Counts a.300 per 9 min is taken as indicative of the presence of tritium, in comparison to background counts, which were 238 per 9 min.

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