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Tritium and neutron emission in D_2O electrolysis at Pd and Ti cathodes *

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Abstract

The possible emission of nuclear particles during the electrochemical loading/discharging of deuterium in/at suitable metals has been investigated by analyzing in succession four cells equipped with Ti rod, Pd tube and Ti plate cathodes. It was found that ^3H enrichment in the electrolyte purely due to electrolytic T/D separation seems to be related to the characteristics of D_2O used; notwithstanding the possible occurrence of this effect, three cells out of four showed (at least during the first week of the run) ^3H excess above the statistical error. A quantitative evaluation of neutrons from the cells was not tried owing to the high fluctuating background. However, from the statistical analysis of pulse frequency recorded during either long electrolytic or blank experiments, it appears that in the former case the background is overlapped by a phenomenon of higher frequency.

INTRODUCTION

We recently reported the sporadic observation of unaccounted for amounts of ^3H in the electrolysis of D_2O/0.1 M LiOD solutions at Pd sheet cathodes [1]. The preferred experimental design consisted of several cells (2–4, of 35 cm^3 each) equipped with similar Pd sheet cathodes and Ni coil anodes, run all at once in series.

Whereas in a large number of cells no significant ^3H increase took place during extended electrolyses (up to 2 months), after 4 days with 50 mA cm^{-2} applied,

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three cells (Pd cathodes $1 \times 1 \times 0.02$ cm^3 and $1 \times 1 \times 0.05$ cm^3) revealed β-activity in the range 350–450 dpm ml^{-1}, that is, about one order of magnitude above the background; no further ^{3}H increase was found on prolonging this experiment for 2 weeks.

Furthermore, the build-up of the ^{3}H level (3–4 times the background) which cannot be explained by electrolytic separation enrichment, could be followed in a single cell (Pd cathode $1 \times 1 \times 0.05$ cm^3; Pt anode): ^{3}H accumulated right from the start, reaching a maximum in about 1 week, and then declined, with no apparent relationship to the current applied (50–750 mA cm^{-2}). Some parts of this Pd sheet developed swelling with deep pitting underneath, which was never observed for a number of electrolyses in light water. This observation suggests that the nuclear reaction(s), if any, occur only on some spots on or near the surface of the metal deuteride, so that the chance of reproducing these events may increase when large electrodes are used [2,3].

The strategy of further investigation presented below was in agreement with the above consideration.

Since on both theoretical and experimental grounds [4] the generation of nuclear particles seems to be induced by non-equilibrium conditions, some experiments were designed with the cathode polarized in an asymmetrical current field (the gradient in electrochemical potential should establish a special form of steady-state non-equilibrium behaviour).

EXPERIMENTAL

Materials

Ti rods 99.5%, diameter = 1 cm, length = 3.5 cm were already available in the institute (for electrochemical and photo-electrochemical investigations).

Ti plate 99.6%, $3.0 \times 2.0 \times 0.1$ cm^3 and Pd tube 99.9%, diameter = 0.2 cm, thickness = 0.02 cm, were supplied by Goodfellow (Cambridge, UK).

D_2O 99.8% was from two different batches supplied by Jansenn Chimica (Belgium): ^{3}H activity was respectively 88 ± 25 and 260 ± 25 dpm ml^{-1}; the same firm supplied 40% NaOD in D_2O. The other electrolytes were LiOD, prepared by dissolution of Li metal (Fluka) in D_2O, and Li_2SO_4 (Fluka).

Pd supported on plastic pellets, as the catalyst for D_2/O_2 recombination, was supplied by Bayer.

Liquid scintillator cocktails (LSC) were Pico-Aqua™ for diluted D_2O solutions and/or recombined D_2O, and Hionic-Fluor™ for concentrated solutions, both supplied by Canberra–Packard (Milan, Italy).

Electrolytic apparatus

Ti rod and Pd tube electrodes were assembled inside glass centrifuge tubes, used as single compartment cells [1]. An Ni coil, diameter 0.1 cm, spiral-wound

around the cathode constituted the counter electrode: Ni/Ti and Ni/Pd area ratios were 5 and 10 respectively.

The Ti plate cathode was vertically coupled (again in a centrifuge tube cell) to a Pt sheet anode of the same area, 3.0×2.0 cm^2, at a distance of 1 cm.

Before use, the Ti electrodes were activated by dipping for 3 min in a boiling solution of 20% $(COOH)_2$ or 5% aqueous HF; this procedure frees the metal of thick oxide layers (formed on Ti by air exposure), which might not be easily removed after cathodic polarization. The surface treatment of Pd consisted of dipping for 10 min in 5 M HCl; the acid probably dissolves any metal trace (Fe, Cr, etc.) residual of Pd cold working. Such traces acting as hydrogen recombination centres may partially hinder Pd deuteride formation.

During electrolyses, D_2 and O_2 gases were conveyed through the lid of the cell to a bubbler containing paraffin which, as well as insulating the system from the atmosphere, acted as a trap condensing D_2O vapour; significant vaporization from the cells generally occurred only when the current applied was ≥ 1.0 A. The gases from the bubbler were then taken to recombine (Pd catalyst) and collected as D_2O.

Electrolyses with currents up to 1 A were carried out using a Model 551 Amel (Milan, Italy) galvanostat: higher currents were obtained with a dc constant-voltage generator.

TRITIUM DETECTION

Procedure and instrumentation

Tritium in both the electrolyte and D_2O from recombined gas was determined by counting the β-decay of solutions with a LSC by the procedure and instrumentation already described [1]. With respect to our previous conditions, the β-energy window of the spectrometer was reduced; although this compromise decreased the background fluctuations, efficiency fell from 40 to 11.5%.

As a consequence of nuclear reactions (or for other reasons) ^3H might be present in the bulk of the metal electrode. However, looking for ^3H inside the metal is not strictly necessary as the metal hydride during the electrochemical loading does not behave as a "fixed" compound but rather as a "dynamic" state involving continuous bulk–surface hydrogen exchanges. This situation was recently pointed out by the experiments of Storms and Talcott [5], whereby ^3H pre-loaded Pd electrodes were seen to undergo easy ^3H unloading after cathodic polarization in D_2O.

Results of experiments

Ti rod (1), Ni cell

This experiment was carried out from 18 October to 7 December 1990 using the first 10-cm^2 Ti rod cathode. The cell was filled with 45 cm^3 5 M NaOD prepared

from the D_2O stock at lower ^3H content: this volume was then kept constant by compensating any loss (electrolytic, evaporation or sampling), with periodical refilling. Electrolysis was performed with a constant potential difference between cathode and anode so as to have currents ranging from 50 to 750 mA cm^{-2}. Electrolysis was stopped twice: the electrode was temporarily removed from the cell, its surface was cleaned mechanically from scale and then activated chemically before re-starting electrolysis.

The results of tritium determinations, systematically performed during the experiment, are illustrated in Fig. 1a: the content in the electrolyte is shown at the top of the figure and that of gas just below; the lower part of the figure shows the current program applied.

Since the ordinate represents net count s^{-1}, cleaned of ^3H content in D_2O, two facts were observed: (1) no electrolytic ^3H separation between liquid and gas apparently operates; (2) ^3H tested in both phases is mostly above the background level. Although the excess determined in a single sample may be within statistical error limits, the general trend is definitely positive: therefore an integral ^3H excess above 2×10^{11} atoms could be estimated for the gas.

Ti rod (2), Ni cell

This run was started on 21 December 1990 and stopped on 25 January 1991. Conditions were the same as above but for a new Ti rod electrode of the same dimensions/quality and a new D_2O stock at higher ^3H content.

Figure 1b shows that some ^3H separation did occur during this run: the liquid was seen to be enriched progressively at the gas cost (see side above and below the 0 background line).

In this figure the open circles plot the theoretical curves provided by an electrolytic separation factor of $S = 2$ on the basis of the current program applied (see bottom of figure) [1]. It appears that for both phases experimental ^3H determinations are below the theoretical curves; in other words, the overall ^3H balance is negative despite some fluctuations. Indeed, the D_2O vapour condensed in the bubbler was lost due to an explosion and was thus withdrawn from the overall ^3H balance.

Pd tube, Ni and Ti plate, Pt cells

These cells were run together (18 February–3 April and 19 February–19 March 1991) inside the cavity of the n-spectrometer; D_2O from the same stock at higher ^3H content was used, and the electrolysis current field on the cathode was asymmetric in both cells.

The ends of the 1.6-cm^2 Pd tube cathode were sealed by electric soldering: although the Ni coil anode surrounded the tube symmetrically, a deuterium diffusion gradient was predicted inside the metal during electrolysis (in fact, we expected the tube to explode). The cell was filled with 40 ml 0.1 M LiOD solution and fed galvanostatically with current from 0.125 to 1.000 A cm^{-2}.

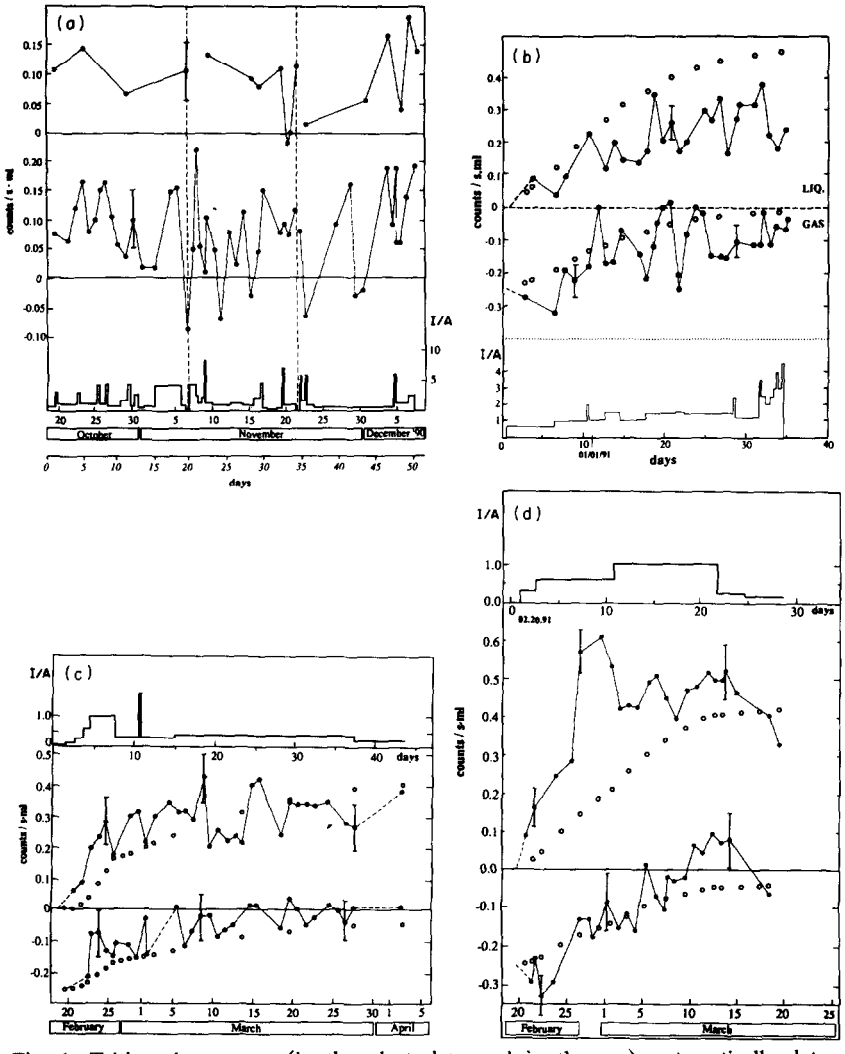

Fig. 1. Tritium increments (in the electrolyte and in the gas) systematically determined during electrolysis. (a) Ti rod (1)–Ni cell; this run was interrupted twice (see vertical lines) for cleaning the cathode; (b) Ti rod (2)–Ni cell; the empty dots plot the theoretical curves provided by an electrolytic separation factor of $S = 2$; (c) Pd tube–Ni cell; (d) Ti plate–Pt cell.

Figure 1c compares ^3H experimentally found (solid points) with theoretical prediction (open circle) for an electrolytic separation factor $S = 2$ (the currents are shown at the top of the figure).

Electrolytic separation very likely occurred, but the overall tritium balance was positive (above statistical level) during the first 1–2 weeks of electrolysis; fluctuating ^3H increases were simultaneously seen in both gas and liquid.

The Ti plate–Pt cell was charged with 40 ml 1 M Li_2SO_4 solution; the geometry of this cell (parallel plate electrodes) induced an asymmetric current field on the cathode, thus probably causing steady diffusion gradients in the metal; galvanostatic currents from 0.05 to 0.17 A cm^{-2} were applied (based on one side of the plate).

According to the data shown in Fig. 1d, the ^3H trend tested was qualitatively similar to the previous one except for a more significant ^3H production which occurred after 1 week of electrolysis. The overall ^3H balance was positive for at least 3 weeks. After 25 days of electrolysis the resistance of this cell increased sharply (soldering between the Ni and Ti electrodes failed, as was tested at the end of the experiment), so that only currents ≤ 0.20 A could be supplied by the galvanostat. With 0.15 A applied the cell indeed overheated and periodical D_2O refillings (above the electrolytic consumption) were necessary to compensate the evaporation loss. In these conditions ^3H levels of both solution and gas declined (see Fig. 1d): however, an ^3H level near, within the statistical error, to that of the solution was tested for D_2O condensed in the trap.

NEUTRON DETECTION

Spectrometer

In order to have a sensitive instrument which could give neutron energy spectra a detector based on an NE 213 liquid scintillator was developed at the Department of Physics of the University of Padova and assembled in a suitable room at IPELP. This room, specially devoted to this investigation, has a temperature control of ± 1°C, the importance of which must not be underestimated. The detector consists basically of a 4500-cm^3 scintillator enclosed in an Al cylinder (inside diameter 20 cm, $h = 18$ cm) with a highly reflective internal surface. The upper end of the cylinder is sealed to a stainless steel container (internal diameter 10 cm, $h = 12$ cm) which composed the cavity for 1–2 electrolytic cells, thus practically covering a 4π angle. The scintillator is seen by three XP 2020 photomultipliers through optical contact with three windows at the bottom of the cylinder. A schematic view of the detector is given in Fig. 2. Threefold coincidence is required with a resolving time of less than 10 ns. Special attention was paid to light collection factors, scintillation stability and oxygen removal facilities.

The usual technique of pulse shape discrimination was adopted to reduce γ-ray contamination: in the set of blank and electrolytic experiments a high energy threshold (1.7 MeV) was set to the proton recoil spectra and thus the γ-ray contribution can be estimated at about 5%.

With these arrangements the spectrometer was set at an effective n-efficiency in the range 0.3–0.35%, as determined by a weak ^{252}Cf source.

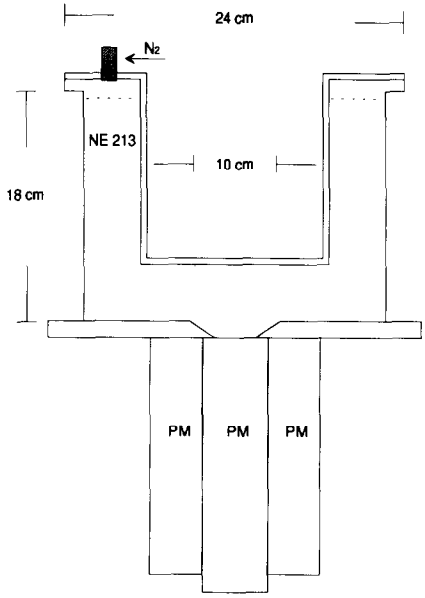

Fig. 2. Cross-section of the NE 213 neutron detector.

Signal analysis

Two lines simultaneously operated the acquisition, storage and processing of the signals from the detector.

According to one line, the frequency of pulses and the corresponding pulse amplitude distribution (proton recoil energy spectra) were stored by a Labview program in a Macintosh II PC linked to the detector through a Crate-Camac interface. Thus the computer at any given moment sampled a set of 100 pulses, providing its neutron average frequency and pulse energy distribution.

The following were supplied by data processing: (1) frequency histogram (each referring to one 100-pulse set) as a function of recording time (24 h); (2) pulse frequency averaged in 24 h; and (3) integral distribution over 24 h of pulse energy (i.e. proton recoil energy spectrum in time).

The other parallel acquisition line was operated directly from the detector with a multichannel scaling analyzer with 6 s time step for 16384 channels. In this way the proper frequency could be determined for each pulse with a temporal resolution of 1 μs, as against 25 μs of the Labview system. However, no information could be obtained on pulse amplitude distribution.

Results of experiments

Figure 3 summarizes the data collected from November 1990 to the end of March 1991. Each point represents the daily count frequency (Labview system);

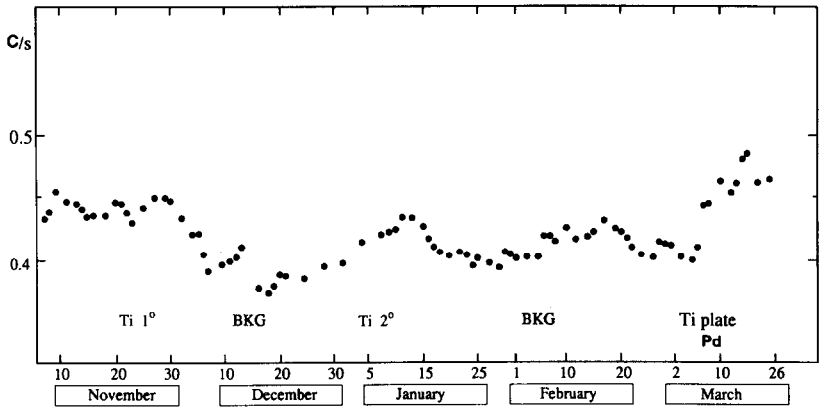

Fig. 3. Histogram reporting the frequency of pulses averaged during each day from November 1990 to March 1991. Electrolytic experiments (white periods) are alternated with dummy cells in the cavity of the spectrometer (gray periods).

periods during which the electrolytic cells were working inside the detector alternated with periods of pure background determinations (in the latter case, a dummy cell containing 40 ml D_2O was placed in the spectrometer cavity).

Although count frequency during the electrolytic runs appears higher than in blank experiments, the histogram of Fig. 3 mainly follows the background fluctuations. In fact, no conclusive or contradictory effects were observed on count frequency when a running electrolytic cell was temporarily removed from the spectrometer. Also, for the experiment showing the most significant ^3H excess, no relationship was observed between ^3H observation and possible neutron emission. This fact is hardly surprising considering that: (1) our background, taking detector efficiency into account, is well above 100 events s^{-1}; (2) no shield against external radiation was arranged around the experiments and thus fluctuations of $\pm 15\%$ were often observed; and (3) neutron emission, if any, from electrolytic experiments is mostly (according to refs. 6 and 7), 1–2 orders of magnitude below our actual background.

However, statistical analysis of neutron frequency distribution, as obtained from the multiscaler analyzer, revealed some significant differences between data collected in blank experiments and during electrolysis.

Thus Fig. 4a–b shows that the rates of pulse frequency averaged in the entire period of each background measurement outline a roughly symmetrical Gauss curve; in other words, an almost Poisson distribution can be predicted for the background.

This distribution does not hold for pulses recorded during electrolytic runs, although these measurements were averaged for times longer than before (Fig. 5a–c). It appears that during electrolysis the background is overlapped by a neutron flux of higher frequency. Moreover, the shift from the background distribution is: (1) higher for Ti (1) than Ti (2): the former in fact had a net positive

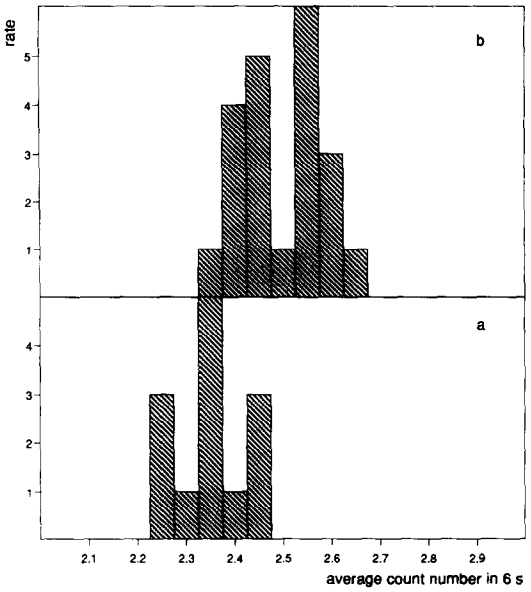

Fig. 4. Statistical analysis of pulse frequency distribution during the blank experiments. (a) December 1990; (b) February 1991.

balance for ^3H; and (2) more evident when two cells (Pd–Ni and Ti plate–Pt) were run together in the spectrometer cavity.

DISCUSSION

Tritium enrichment in the electrolyte due to electrolytic separation seems to be related to the characteristics of the D_2O used (either its initial ^3H content or catalytic impurities). Notwithstanding the possible occurrence of this effect, three cells out of four, at least for some periods (mostly the first few weeks), showed an apparent generation of ^3H above the statistical error; for the cell in Fig. 1d the tritium increase cannot be accounted for by a separation factor of $S = \infty$, being near the levels ($\approx 10^{11}$ atoms) reported in our preliminary paper [1]. In this case the major ^3H increase occurred within 1–2 days, with no relationship to the current density applied. On the contrary, when the total current was changed from 0.6 to 1.0 A, ^3H generation apparently ceased: this fact and the frequent refilling of D_2O (at low ^3H) to compensate also the increased evaporation, account for the peculiar peak shape of ^3H curve (Fig. 1d).

With respect to the Ti rod (2) experiment, the negative ^3H balance might be accounted for by unmeasured evaporation losses (see above). If T/D separation by evaporation is lower than the electrolytic one, tritium enrichment in solution below that provided by the gas impoverishment is expected (as indeed shown in Fig. 1b). Separation by evaporation may well occur with a factor given by the root of mass

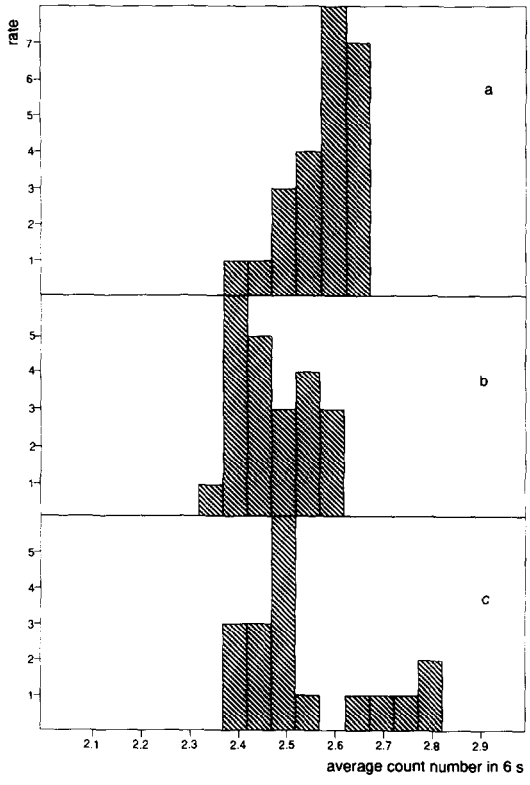

Fig. 5. Statistical analysis of pulse frequency distribution during the electrolytic runs. (a) Ti rod (1)–Ni cell; (b) Ti rod (2)–Ni cell; (c) Pd tube–Ni, Ti plate–Pt cells.

ratio, and in fact an ^3H level near that of the electrolyte was systematically observed in the condensed steam from Pd tube and Ti plate cells. However, this explanation might not account for all the ^3H lacking.

We note that our choice in the Ti experiments of either 5 M NaOD or 1 M Li_2SO_4 electrolytes conformed to two previous (positive) reports [2,8]: however, our present ^3H findings (Ti plate cell) confirm only those by Sanchez et al. [8]. The choice of the electrolyte is not a trivial matter: at high pH the formation of Ti deuterides requires very negative potentials and the compounds may be unstable, whereas much more favourable synthesis conditions are realized, on thermodynamic grounds [9], in neutral and slightly acidic electrolytes. According to the literature [10,11] electrolytic deuteration of Ti penetrates only a few micrometers underneath the metal surface, and the locus of possible nuclear reactions is probably within such thickness: the sharp ^3H increase in the solution (not in the gas) tested in the Ti plate cell agrees with a surface or near-surface generation, whereby mainly energetic ionic ^3H leave the electrode [5].

Figure 3, reporting the daily count frequency of the neutron detector during several months of blank and electrolytic experiments, emphasizes the difficulty of a quantitative determination of neutron emission, if any, from the cells. In fact, in our conditions any attempt at determining a net neutron flux based on subtraction of background measured in different periods, appears to be totally arbitrary.

The pulses constituting the background are mainly due to: (1) ambient radioactivity; (2) noise from electronics and/or liquid scintillator; and (3) cosmic radiation.

A Poisson distribution of pulse frequency is predicted for either low radioactivity level or instrumental noise. Cosmic events may conversely occur by bursts: however, their average frequency is around 10^{-2} n s^{-1} cm^{-2} and thus the cosmic-neutron contribution to the background measured by means of our detector (active area 300 cm^2; efficiency 0.3–0.35%) is only a few per cent, which results in the overall Poisson distribution observed in the blank experiments.

What about the non-Poisson pulse frequency distribution tested during the electrolytic runs? It is not impossible that intense cosmic-neutron bursts were just occurring during the periods of electrolysis, but one must admit that an emission from the cells seems more likely.

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REFERENCES

1 G. Mengoli, M. Fabrizio, C. Manduchi, G. Zannoni, L. Riccardi, F. Veronesi and A. Buffa, J. Electroanal. Chem., 304 (1991) 279.
2 P.K. Iyengar and M. Srinivasan, Overview of Barc Studies in Cold Fusion, First Annual Conference on Cold Fusion, Salt Lake City, UT, 28–31 March 1990.
3 Y. Arata and Y.C. Zhang, Fusion Technol., 18 (1990) 95.
4 A. Takahashi, T. Iida, F. Maekawa, H. Sugimoto and S. Yoshida, Fusion Technol., 19 (1991) 380.
5 E. Storms and C. Talcott-Storms, Fusion Technol., 20 (1991) 246.
6 I. Bockris and D. Hodko, Chem. Ind. (1990) 668.
7 M. Srinivasan, Curr. Sci. (1991) 1.
8 C. Sanchez, J. Saevilla, B. Escapizo, F.J. Fernandez and J. Canizares, Solid State Commun., 71 (1989) 1039.
9 G.H. Keisall and D.J. Robbins, J. Electroanal. Chem., 283 (1990) 135.
10 I.I. Phillips, P. Poole and L.L. Shreir, Corr. Sci., 12 (1972) 855.
11 P. Millenbach and M. Givon, J. Less-Common Met., 87 (1982) 179.