

Tritium and neutron emission in conventional and contact glow discharge electrolyses of D₂O at Pd and Ti cathodes *

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We recently found that the level of ³H in D₂O / 0.1 M LiOD solutions electrolyzed at Pd sheet cathodes increased, although sporadically (<20%), till a order of magnitude over background, we indeed used D₂O with very low background ¹.

The surface of a Pd sheet cathode (1 x 1x 0.05 cm³) which gave apparent generation of ³H had developed localized swelling with deep pitting underneath; if this phenomenon was relating with ³H, the latter was likely formed by means of a near-surface process, which might be easier to reproduce if electrodes of relatively larger dimensions are utilized.

The experimental design adopted for the four conventional electrolytic runs hereafter described was mostly in agreement with the above consideration.

We are also reporting on contact glow discharge electrolyses (CGDE) aimed at inducing critical conditions at/in the metal deuteride cathode.

Detection of nuclear particles

Tritium in both the electrolyte and D₂O from recombined gas was determined by counting the β-decay of solutions with LSC by the procedure and instrumentation already described <1>.

With respect to our previous conditions the β-energy windows of the spectrometer was reduced: although this compromise decreased the background fluctuations, efficiency fell from 40 to 11.5%.

A neutron spectrometer based on a NE 213 liquid scintillator was developed at the Dept. of Physics the University of Padova. The detector basically consists of 4500 cm³ scintillator

* Work performed in collaboration with ENEA - Frascati

¹ G. Mengoli, M. Fabrizio, C. Manduchi, G. Zannoni, L. Riccardi, F. Veronesi, A. Buffa, J. Electroanal. Chem., 304 (1991) 279.

The upper end of the cylinder is sealed to a stainless steel container (internal $\phi = 10$ cm, $h = 12$ cm) which composed the cavity for placing 1-2 electrolytic cells. The scintillator is seen by three XP 2020 photo-multipliers through optical contact with 3 windows at the bottom of the cylinder. Threefold coincidence is required with resolving time of less than 10 ns.

The usual technique of pulse shape discrimination was adopted to reduce γ -ray contamination: in one set of runs (normal electrolyses) a high energy threshold (1.7 MeV) was set to the proton recoil spectra and thus γ -ray contribution can be estimated at about 5%; conversely, in a subsequent set of runs (C.G.D.E.), the energy threshold was lowered to 0.75 MeV but a much more severe n / γ temporal discrimination was adopted.

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.

According to one acquisition line, the neutron frequency of pulses and the corresponding pulse amplitude distribution (proton recoil energy spectra) were stored in a Labview program in a Macintosh II PC linked to the detector by 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 other parallel acquisition line was operated directly from the detector with a multichannel scaling analyzer with 6 or 2 s time steps for 16384 channels. In this way the proper frequency could be determined for each pulse with a temporal resolution of $1\mu\text{s}$, as against $25\mu\text{s}$ of the Labview system.

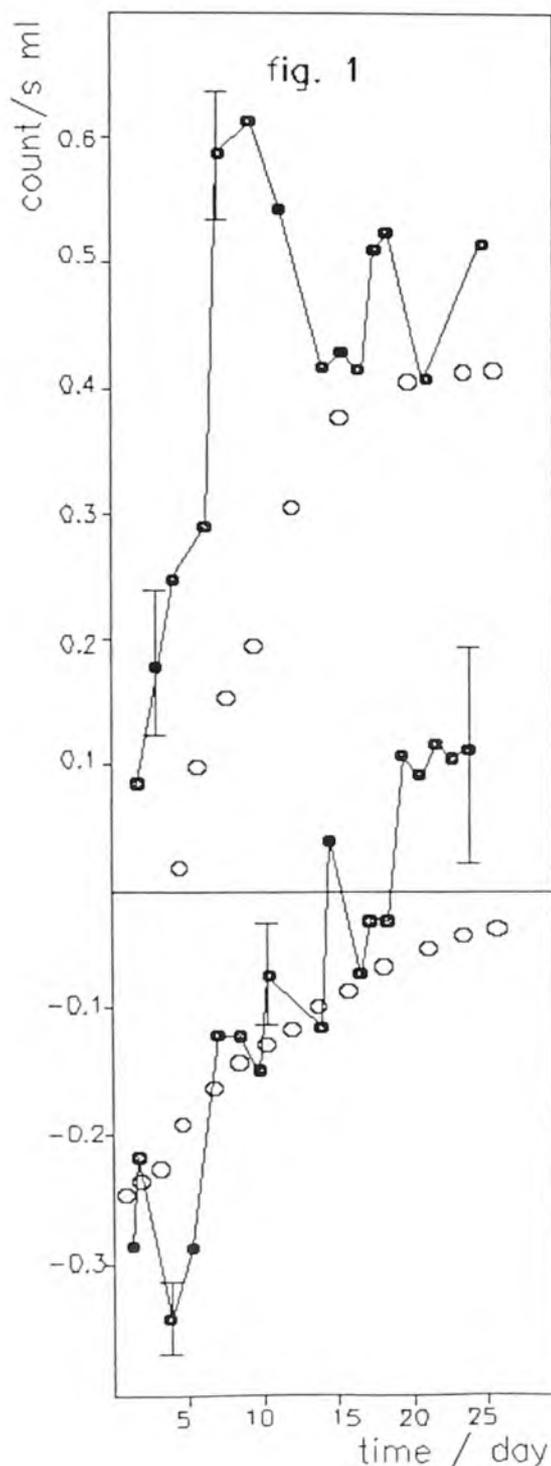
Conventional electrolyses

The electrolytic cells were assembled using centrifuge tubes having internal dimensions $\phi = 3.3$ cm, $h = 11$ cm. The cathodes were: Ti rod (cells 1 and 2), $\phi = 1$ cm, $h = 3.5$ cm, area = 10 cm^2 ; Pd sealed tube (cell 3), $\phi = 0.2$ cm, $h = 2.5$ cm, thickness = 0.02 cm, area = 1.6 cm^2 ; Ti plate (cell 4) $3 \times 2.5 \times 0.1\text{ cm}^3$. The anodes were: Ni coil (cells 1-3) spiral-wound around the cathode; Pt sheet (cell 4) $3 \times 2 \times 0.01\text{ cm}^3$ facing the cathode.

Current till 1 A were supplied by an AMEL mod. 551 galvanostat; higher intensities were obtained by a dc constant voltage generator. The experiment of cell 1 was carried out using

D₂O with ³H background = 88 ± 25 dpm ml⁻¹, whereas D₂O used for the other experiments had ³H background = 260 ± 25 dpm ml⁻¹. During electrolyses the volume of solution was kept constant by periodical refilling; D₂ and O₂ gases were conveyed through the lid of the cell to a trap condensing D₂O vapour and taken to recombine as D₂O (Pd catalyst).

1 Tritium results



Cell 1 containing 45 ml of 5 M NaOD in D₂O was fed with $i = 0.05-0.75 \text{ A cm}^{-2}$ from 18/10/90 to 7/12/90. Systematic ³H assays outlined that: no electrolytic separation between liquid and gas took place; ³H tested in both phases was mostly above the background level. Although the excess in a single sample may be within statistical error (σ) limits, the general trend was definitely positive.

Cell 2 was running from 21/12/90 to 25/1/91 at about the same conditions of cell 1, but for D₂O which had higher ³H content. Electrolytic ³H separation did occur, as the liquid was here seen to be progressively enriched at the gas cost, but the overall ³H balance was negative. The apparent loss of ³H must be imputed to evaporation as a negligible D₂O / TDO separation is likely to occur in the vapour phase.

Cell 4, containing 40 ml of 1M Li₂SO₄, was running from 19/2/91 to 19/3/91. A sharp increase of ³H level in the electrolyte did

occur after the first week; see figure 1 where experiment (full dots) is compared with theoretical prevision $S = 2$ (empty dots), the upper part refers to electrolyte, the lower to the gas. The major ^3H increase occurred within 1-2 days with $i = 0.6 \text{ A}$; the subsequent decline was probably caused by the rise of the current to 1 A, whereby ^3H production apparently ceased and more frequent refillings of D_2O (at low ^3H) were necessary also to compensate significant evaporation loss. We note that figure 1 cannot be explained by any separation factor.

2 Neutron results

Neutron data were collected in continuous from November 90 to the end of March 91: periods during which the electrolytic cells were working inside the detector alternated with periods of blank determinations.

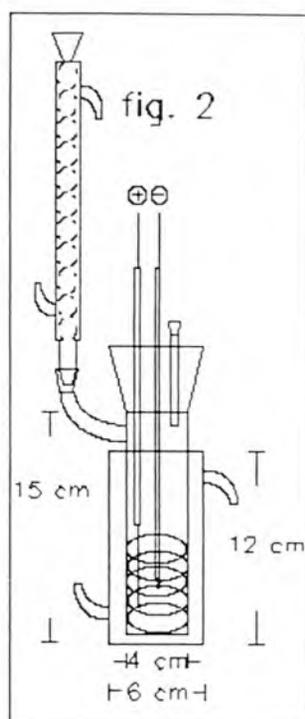
The background frequency corrected for the efficiency was above $100 \text{ neutron s}^{-1} \pm 15\%$. In these conditions, although the frequency during the electrolytic runs was something higher, any attempt of determining a net neutron flux based on subtraction of background measured in different periods can be questioned.

However statistical analysis of neutron frequency distribution as obtained from the multichannel scaler analyzer, revealed some significant differences between blank and experiments. Thus the rate of pulse frequency measured during a background period outlines about a Gauss curve; in other words, a Poisson distribution of the frequency can be predicted. Such distribution does not hold any longer for pulses recorded during the electrolytic runs. It appears that during electrolysis the background was overlapped by a phenomenon of higher frequency.

Contact glow discharge electrolysis

In conventional electrolysis performed with two electrodes of different sizes, conditions may be attained whereby the lines of current converging on the smaller electrode cause local vaporization of the solvent, creating a gas sheath around it. If the applied voltage is increased enough, normal electrolysis is then converted to contact glow discharge electrolysis: a bright steady discharge takes place between electrode and solution through ions forming in the

gaseous sheath.



Our experimental design consisted of: one Pd rod cathode, $\phi = 0.1$ cm $h = 0.5 - 0.7$ cm; one Pt coil anode, $\phi = 0.05$ cm $l = 20$ cm, wound around the cathode at 1 cm distance; and 42 ml of $1.5 \cdot 10^{-2}$ M LiOD (or 10^{-2} M Li_2SO_4) solution. The gas exit of the cell was equipped with a cooler which refluxed vaporizing D_2O in the cell (figure 2).

The Pd electrode was generally charged for 2-3 days at 50-100 mA cm^{-2} , then potential current characteristics were varied to induce CGDE. The cell was operated inside the cavity of the n-spectrometer: particular care was taken to see the discharges did not induce electric noise in the

detector. Oscillating currents, sparks and lightning are generated when trying to achieve the much more stable conditions of a steady-glow discharge.

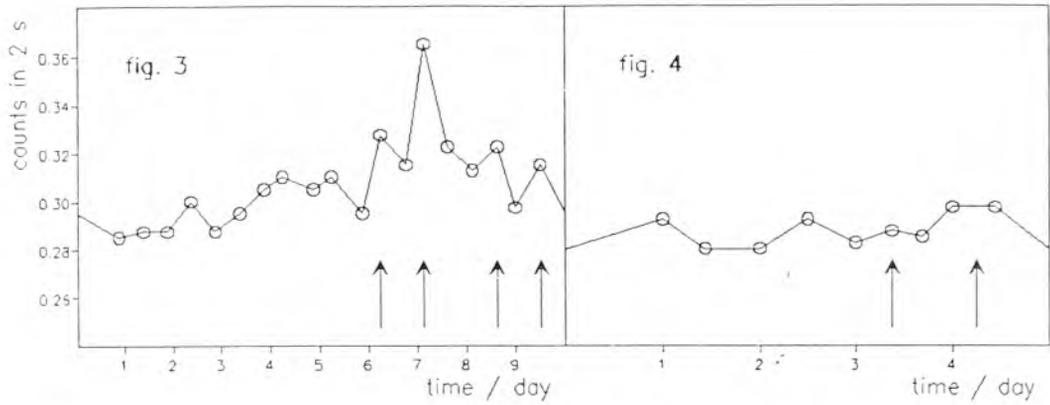
To avoid possible electronic artefacts, we adopted the following:

- when setting up the right conditions, the electronics of the n-spectrometer were disconnected from the recorder. The operation required from a few to some tens of seconds before attaining a smooth discharge with 350 V applied and ≤ 0.1 A of current flow;
- an oscilloscope continuously monitored the signal and the occurrence of noise could be detected at any time;
- some control experiments were carried out in light water in the same CGDE conditions.

Results

Figure 3 shows how the pulse frequency increased remarkably over the background during the periods of CGDE (see the arrows). At this electrode the phenomenon could be reproduced over a few days, although with decreasing intensity, and eventually ceased. A maximum of 50 s^{-1} excess over the background can be estimated.

Figure 4 shows histograms recorded under CGDE with two different electrodes for the same conditions but using light water. No increase over background frequency was observed.



The results presented so far are preliminary and need to be studied further. We have programmed more conclusive experiments by using thicker electrodes, a dc generator of higher power, and careful shielding of the electronics.

We also note that, with CGDE, the most critical non-equilibrium conditions are created at/in the metal deuteride:

- many types of positive ions including deuterons and possibly charged D_2O clusters occur in the discharge;
- the temperature may reach the melting point of the metal.