MULTICELL EXPERIMENTS FOR SEARCHING TIME-RELATED EVENTS IN COLD FUSION

D. Gozzi, P.L. Cignini* and M. Tomellini*

Dipartimento di Chimica, Università “La Sapienza”
P.le Aldo Moro 5, 00185 - Roma, Italy

S. Frullani, F. Garibaldi, F. Ghio, M. Jodice and G.M. Urciuoli

Laboratorio di Fisica, Istituto Superiore di Sanità and sezione INFN-Sanità
V.le Regina Margherita 299, 00161 Roma, Italy

Abstract

A new ten-electrochemical cell experiment has been carried out in order to confirm the previous results and try to understand the key role of some experimental parameters in triggering the cold fusion events. The experiment was designed to detect: a) excess heat; b) loading factor by in situ measurement of the cathode displacement; c) nuclear products: neutrons, tritium in the electrolytic solution and in the recombined heavy water, γ-ray; d) effect of the palladium electrode preparation. To measure the excess heat, a calibration curve of the input power vs. temperature of the LiOD + D₂O solution was obtained for cells equal in shape, materials and operating in the same experimental condition in which the experiment was actually performed. The unique difference was on the cathode. The cathode used in the calibration measurements was made of palladium rod gold-plated by electrochemical deposition. Neutron detector is a 3He proportional counter, the same used in the previous experiments, but the data acquisition is now implemented by a fast pulse-shape storage and off-line discrimination for a very accurate counting. The findings of the experiment, lasted about 50 days, are: i) dependent on the type of the cathode, specific excess power values up to 96 W/cm² was found; ii) specific excess power showed linear dependence from the current density with a threshold at around 150 mA/cm²; iii) the cathode swelling was dependent from the type of the cathode and in the case of rods it increased with the current density; iv) no evidence of nuclear products statistically significant was detected.

+CNR- Centro di Termodinamica Chimica alle Alte Temperature, c/o Dipartimento di Chimica, Università "La Sapienza", Roma
*Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma II "Tor Vergata", 00100 Roma

In this paper the texts of the separate communications given by S. Frullani and D. Gozzi at the 2nd Annual Conference on Cold Fusion are jointly reported.
1. Introduction

The aim of the present paper is to report recent results obtained in a new ten-electrochemical cell experiment carried out in order to confirm the previous results (1-2) and try to understand the key role of some experimental parameters, if any, in triggering the cold fusion events.

Our approach to the cold fusion experimentation was and still is to search time-correlation among independent measured parameters, both to give a stronger evidence that we are not dealing with instrumental artifacts and to obtain useful information on the related mechanisms. Due to a permanent skepticism of a part of the scientific community, we believe useful that the people still working on this field must continue to show that a big amount of reliable experimental data give results which are not explained with conventional theoretical approaches and therefore we are concerned in a new frontier of the scientific knowledge.

The experiment was designed to detect: a) excess heat; b) loading factor by in situ measurement of the cathode displacement; c) nuclear products: neutrons, tritium in the electrolytic solution and in the recombined heavy water, γ-ray; d) effect of the palladium electrode preparation. The main difference between the present experiment and the previous one (2), is constituted by excess heat measurements, a more efficient neutron counting system based on the pulse shape discrimination and in situ measurement of the cathode swelling due to the absorption of the electrochemically generated deuterium.

2. Experimental

We shall only report those parts of the our experimental set-up and procedures which have been added with respect to the previous experiments which can be found in the literature (2). Just to facilitate the understanding, we can summarize the features of the experiment as follows:

- Ten equal cells connected in series operating in galvanostatic conditions;
- The only difference among them is in the preparation and/or shape and/or dimensions of the Pd cathode;
- All the cells are placed in a torus-shaped thermostated bath at (24.5 ± 0.1) °C. They are symmetrically located in the bath. Five K-type thermocouples are placed along the torus. Room temperature is kept constant at (20 ±1) °C;
- Before to fill the cells with the solution, a D₂ stream was maintained for some time;
- All the cells have a separate gas recombiner for tritium (T) monitoring in the gases;
All the cells are provided with a device to maintain a constant level of solution by adding D$_2$O when consumed;

Each cell is monitored for:
- Temperature of the cathode
- Temperature of the solution
- Voltage of the cell
- T in solution and in gas phase externally recombined

Two cells out of ten have a displacement transducer to monitor the cathode swelling during D-loading;

One $^3$He proportional counter for neutron detection is placed in the centre of the torus and two $\gamma$-ray detectors (NaI and HPGe) are properly located around the bath.

### 2.1 Excess heat Measurements

Because our torus-shaped multicell apparatus is not a calorimeter, but it is an isothermal device, accurately thermostated, which allows to keep at constant temperature the external wall of each of the ten electrochemical cells, the variation cell to cell of the heat flux crossing each glass tube only depends from the temperature of the electrolyte solution since all the parameters influencing the heat transport (electrolytic solution and its volume, geometry of the cell and materials by which it is made of, exchange surface area, etc.) are equal for all the cells. Thus, at a fixed input power imposed to the cell, a stationary thermal gradient will be established between the inner solution and the thermostated bath. If the stationary values of the temperature of the electrolyte solution are reported as a function of the respective input power applied to the cell, we have a calibration curve which provides the excess heat data when well-defined deviations from it occur during the real experiment.

#### 2.1.1 Calibration procedure

Few points are necessary to explain the procedure we adopted in making the calibration curves:

- Two cells (by dimensions, shape, materials, etc.) equal to those used in the experiment have been calibrated in the same experimental arrangement previously described;
- Two types of calibration for each cell were carried out both in LiOD + D$_2$O solution:
  - Thermal (by an electric heater);
  - Electrochemical (as in the experiment) by using gold plated Pd cathodes. Each electrode was carefully controlled by SEM microprobe mapping of Pd to be sure that Pd was not detected;
- In both the cases each stationary temperature of LiOD solution at fixed input power was kept as a point of the respective calibration curve;
It can be shown that the stationary temperature at constant input power does not depend on
the electrode mass. This can influence the time constant only. Thus, the calibration curve
obtained is valid throughout our system.

The choice of this procedure was based on the fundamental concept that, in absence of
processes other than the D₂O electrolysis, the two calibration curves must be found
superimposed due to equality:

\[ |V| \times I_h = (|V| - V^\circ) \times I_e , \]  

where \(|V|, I\) and \(V^\circ\) are, respectively, the voltage at Joule heater or electrode leads, the current
crossing the respective systems and the thermoneutral voltage given by \(-\Delta H^\circ_f(D₂O, l)/2F\)
being \(\Delta H^\circ_f(D₂O, l)\) and \(F\), respectively, the enthalpy of formation of liquid D₂O and the
Faraday's constant. \(V^\circ\) has been taken equal to 1.5367 V(3). The subscripts \(h\) and \(e\) stand for,
respectively, by-heater and electrochemical calibrations. Furthermore, we used as blank for
the calibrations heavy water solutions and Pd gold-plated cathodes because we believe that
both these conditions allow to be closer to the real experimental situation. In fact, the use of
light water solution instead of the heavy water solution as blank, though so widely adopted to
guarantee the reliability of the cold fusion findings, is quite imprecise from the calorimetric
point of view because heat capacity and thermal conductivity of the solution, enthalpy of
vaporization of D₂O as well as thermal conductivity of H₂ and D₂ are all appreciably
different. The gold-plating of Pd cathode avoids the process:

\[ D_{ads} \rightarrow D_{bulk} (Pd) \]  

while the processes

\[ D_{ads} + D_{ads} \rightarrow D_2(g) \]  

and/or

\[ D_{ads} + D_2O + 2e(Au/Pd) \rightarrow 2 OD^- + 1/2 D_2(g) \]

remain the same as in the case of Pd only. The ads subscript stands for the chemisorbed
status of the deuterium atom onto the cathode surface. Obviously, if the process 2 is
completely forbidden, we can be sure that neither cold fusion phenomena nor chemical
process occur.

Figure 1 shows some stationary steps used to build the calibration curves by making
use of both an electric heater (Fig. 1A and 1B) and the electrolysis (Fig. 1C and 1D). Figures
1B and 1D display a portion corresponding to a single step of the respective A and C curves.
2.1.2 Electrodes and cells

Gold-plated Pd cathodes were prepared starting from Johnson & Mattey 6 mm diameter rod, cut in 25 mm long pieces, machined at one end for encasing the thermocouple and then accurately polished before the electrochemical plating. The gold layer thickness was about 4 μm. To improve the electrical contact also the shield of the all K-type thermocouples used in this experiment was gold plated. Since the shields are electrically insulated from the inner thermoelements, they also work as current leads for the cathodes. To obtain this, the shields were soldered on the top of each cathode. The space around the junction cathode/thermocouple were filled with epoxy resin and then covered by a piece of thermoplastic tube to avoid the direct contact with the alkaline solution. All the materials used were tested for long time to be inert in LiOD alkaline solutions.

Anode and cell geometry and dimensions were given elsewhere (2). Here it is just sufficient to mention the characteristic of the heater. This was a 50 W resistor obtained by winding Kantal wire on a capillary alumina tube. The whole diameter was 3.2 mm. It was placed in a NMR-type test tube filled with silicon oil and inserted in the proper hole of the cell teflon cap.

2.2 Further details on the electrolytic cells

2.2.1 Cathode swelling measurement

Two cells out of ten were modified in the bottom part to allow the insertion of a LVDT (Linear Voltage Displacement Transducer) by Penny+Gilles, U.K. mod.1354. This kind of
transducers have an infinite resolution and the sensitivity is given better than 1 mV/μm practically depending on both the electronics of the d.c. power supply and voltmeter used for the readings. By our apparatuses, we can measure displacements greater than 0.1 μm and up to 5 mm in both the directions. The LVDT was placed in a teflon cylinder fitted to the bottom of the glass cell. To seal the LVDT from the alkaline solution and to allow the spring loaded probe to move free, a very thin plastic membrane was used. Due to the type of assembly, we can measure the electrode swelling only in the z-axis (major dimension) direction. The voltages were read by two of the 60 analogic input channels of the data logger and directly converted in μm according to the linear calibration curves previously found. LVDT data as well as the other ones coming from the entire apparatus are transferred through the data logger to a Macintosh II fx running on a home-made acquisition program written on LabVIEW 2.1 (National Instruments, Austin, TX).

2.2.2 Cathodes

The ten Pd cathodes used were prepared in different ways as reported in Table I below. The cathode and thermocouple assembly was done by the same procedure as reported in section 2.1.2.

<table>
<thead>
<tr>
<th>#</th>
<th>Type</th>
<th>Treatment</th>
<th>Dimensions (mm)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>rod</td>
<td>HVLHT</td>
<td>Ø 6x25</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>powder sponge</td>
<td>pressed</td>
<td>5.3x4.3x25.7</td>
<td>300 MPa</td>
</tr>
<tr>
<td>3</td>
<td>rod</td>
<td>as received</td>
<td>Ø 6 x 25</td>
<td>LVDT</td>
</tr>
<tr>
<td>4</td>
<td>powder sponge</td>
<td>HVSS</td>
<td>5.2x4.4x25</td>
<td>LVDT</td>
</tr>
<tr>
<td>5</td>
<td>rod</td>
<td>as received</td>
<td>Ø 6 x 25</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>rod</td>
<td>RFHQ</td>
<td>Ø 6 x 25</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>amorphous lamina</td>
<td>as received</td>
<td>Ø 4.1x16</td>
<td>Teflon supported*</td>
</tr>
<tr>
<td>8</td>
<td>31 wires</td>
<td>CSD</td>
<td>Ø 0.5x22</td>
<td>Au welded one end</td>
</tr>
<tr>
<td>9</td>
<td>rod</td>
<td>RFHQ</td>
<td>Ø 3x22</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>powder sponge</td>
<td>HVLS</td>
<td>4.7x3.9x23</td>
<td></td>
</tr>
</tbody>
</table>

HVLHT = High Vacuum Long Heat Treatment (10 h at 1250°C and cooled at 6°C/h)
RFHQ = Radio Frequency Heated at 1350 °C for 10 min under Ar and Quenched in LN2
HVSS = High Vacuum Short Sintering (5 min at 1250 °C)
CSD = Cold Screw Dislocated
HVLS = High Vacuum Long Sintering (10 h at 1250°C and cooled at 6°C/h)
* The Pd content was 32.35% in weight. The lamina thickness was 0.05 mm.
Amorphous lamina samples were supplied by Prof. P.H. Fang, Institute for Space Research, Boston College, MA
2.2.3 Electrolytic solution

It was a 0.2 M LiOD solution prepared in the usual way by using D₂O (Fluorochem Ltd., England) at 99.91 wt% in the isotopic content. The nominal T activity was 60 nCi/kg corresponding to 147 dpm/ml. In the first part of the experiment D₂O at higher T content (254 dpm/ml) was used.

The Li concentration in the electrolytic solution of each cell was systematically analysed during the experiment by plasma absorption spectroscopy. If the Li concentration was found less than the initial value, this was restored by a proper addition of a more concentrated LiOD solution. Li concentration generally decreases much more at high current densities due to the increased action of the evolving gases in carrying microbubbles of solution out of the cell and, as it will show in the results section, it decreases also because of the absorption by the Pd cathode.

2.3 Nuclear measurements

2.3.1 Neutron detection

With respect to the previous experiments (1-2), we improved our counting system by storing the analog signals from ³He proportional counter and off-line discrimination based on the characteristic pulse shape produced by a thermalized neutron interacting with ³He gas.

According to the scheme reported in Fig. 2, the logic signal from the neutron counter, through the look-at-me channel of the data logger, drew the computer to read the digitized pulse shape produced by the oscilloscope in 1024 byte string. The minimum interval of time between two acquired shapes was determined by the time resolution of the look-at-me channel which was 2 ms. Each stored shape was written together the event date in the format dd-mm-yy:hh-mm-ss.sss. The whole stored file of each run was constituted by an appended binary text file which can be segmented and converted in the voltage vs time original curves by a suitable home-made LabVIEW program.
The pulse shape associated to a thermalized neutron displays a negative voltage value without any positive component all along its length (see Fig. 3A of ref.2) while a pulse produced by spurious electromagnetic signals picked-up by the counter shows both positive and negative values (see Fig. 3B of ref.2). Due to the characteristics of the signals, a suitable filter has been put in the off-line analysis. The program labels as neutrons only the events that go through the filter. Further check of the reliability of the adopted procedure was done. We calculated by integration of each filtered pulse the corresponding collected charge and, for each run, a spectrum was obtained (see Fig.3) which was always in agreement with the spectrum obtained by the calibration with an Am-Be source.
For each run the total counting and the counting rate were given only by filtered signals. The dating of the signals allowed to perform the counting choosing the proper time gate.

The signals which did not pass through the filter were stored in a separate file for further analyses. In fact, there are scattered evidences (2,4) that the electrochemical system itself could be source of electromagnetic signals. We are looking for some correlations, for instance, between the frequency of those spurious signals and applied current density.

2.3.2 Tritium measurements

The sampling for the tritium analysis both in the solution and in recombined gases was done at fixed values of the electrical charge passed through the cells. This is necessary to facilitate the control of the tritium mass balance. The external catalytic recombiner is constituted by porous Pt supported on alumina tube and heated at 400 °C. The D₂O recombined vapours are condensed on a water-cooled glass surface.

The tritium measurements were carried out by the procedure already reported (2).

2.3.3 γ measurements

Seven energy windows of the HPGe γ detector spectrum spanning between 350 keV and 2.8 MeV were monitored during the experiment. Lower energy windows were centered in the region where the emissions from the Pd nuclei levels occur due to the Coulomb excitation induced by 3.0 MeV protons generated in the d + d reaction. Energy window around 2.204 MeV was used to monitor the natural background due to 214Bi. A window around 2.224 MeV was used to monitor the γ emitted in the radiative capture of neutron by proton.
Seven energy windows of the NaI $\gamma$ detector spectrum spanning between 2.1 and 27.0 MeV were at the same time monitored. The lower energy window was again used to detect the radiative capture reaction, an energy window around 2.6 MeV was set to measure the natural background, an energy window around 23.8 MeV to monitor the d(d,$\gamma$) $^4$He reaction.

3. RESULTS and DISCUSSION

3.1 Excess heat

3.1.1 Calibration curves

Figure 4 shows sequences of steady-states of the solution temperature when the heating occurred by the heater (h) or electrolysis (e) mode. The input power values, $I_p$, were calculated in both the cases according to the left and right side, respectively, of Eqn. 1. The calibrations were made at the same time on two identical cells containing, as shown before, gold-plated cathodes likely prepared in the same way. After each calibration the LiOD solution was analysed for the Li content and replaced in the cells by a fresh one having same volume and concentration. Figure 4 clearly shows that the calibration curve obtained in the electrolysis mode on cell #2 is quite anomalous with respect to the other calibrations which are satisfactorily represented by the best fitting line:

$$T_s = (25.3 \pm 0.1) + (0.477 \pm 0.002) I_p$$

which was then assumed to evaluate the behaviour of all the cells during the ten-cells experiment.

To try for an explanation, at the end of the calibration measurements, we examined by SEM microprobe mapping the surfaces of both the cathodes to check the status of the gold layer. In the cathode of cell #2, we found two zones along the lateral surface of the cylinder clearly not covered by gold. The molar Li concentration, [Li], was found 0.184 and 0.075, respectively, for the cells labeled #1 and #2. If we compare these values with the initial value of 0.187 (equal for both the cells), changes are found in the Li concentration equal to -1.6\% and -59.9\%, respectively. Assuming that all the Li concentration change, $\Delta$[Li] depends on the reduction and bulk-diffusion into the cathode, the final composition of the cathode has to be considered equal to $\Delta$[Li]V0Mpd/1000Wc = 0.05, i.e., PdLi$_{0.05}$, being V$_0$ = volume of LiOD solution = 35 ml, M$_{pd}$ = atomic weight of Pd and W$_c$ = weight of the cathode of cell #2 = 8.55 g. Therefore, the decrease of [Li] is consistent both with the surface microprobe analysis and with the well-known fact that at high current densities, that is, high cathodic overvoltages, alkaline metals can be reduced in aqueous solution, even if, in an unstable state, except for in the case where a concurrent process does exist.
By interstitial diffusion and a favourable chemical potential gradient, as in the case of hydrogen and its isotopes, Li penetrates into the Pd bulk producing solid solutions without going back into the aqueous solution because of the reaction with water. The difference observed in the case of cell #2 roughly means that the solution can be, for instance, heated at 40 °C by using an input power equal to \(-11\%\) of that one necessary if the Pd cathode did not absorb deuterium (cell #1). In terms of specific excess power, this means 10 W/cm\(^3\) about if we consider all the volume of the cathode #2 subjected to deuterium absorption.

If we consider the right term of eqn.1, we realize that this is representative of a particular aspect of a more general treatment. In fact, only one electrochemical process was there considered (D\(_2\)O electrolysis) and no chemical process. In general, we would have to write the eqn. 1 in the form:

\[
[IV \times I]_h = [(IV - \Sigma V_i \circ) \times I]_e - \Sigma \Delta H_i \circ v_i
\]  

(5)

where the summations run over all possible electrochemical and chemical processes. In eqn. 5, \(v_i\) is the reaction rate of the \(i\)-th chemical reaction which could be also current dependent. Obviously, if the input power axis of the calibration plot is recalculated by taking into account the right-side of eqn. 5, the slope of the curve can change and, in principle, the equality with the left-side term should be satisfied. All the tentatives made so far to lower, through eqn. 5, the slope of the electrochemical calibration curve of cell #2, plotted on Fig. 4, were unsuccessful. Work is still in progress to improve this calculation.
3.1.2 Ten-cell experiment

Concerning the experiment which started on May 6, 1991 and lasted 50 days approximately, we show on Figure 5 two quite different trends of the excess heat as recorded throughout the experiment.

![Figure 5. Specific heat power excess for cells #1 and #9 and applied current profile throughout the experiment](image)

To compare correctly the excess heat data for all the electrodes, we used to normalize the excess heat power with respect to the cathode weight instead of its volume being this, for certain electrodes, difficult to measure due to their irregular shape. The applied current (all the cells are connected in series) is reported on the right ordinate of fig. 5. We can see that cell #1 does not show throughout the experiment appreciable excess heat values and they are not current dependent. A very different behaviour is shown by cell #9 where the excess heat has been found above any reasonable experimental error and the correlation with the current seems to be very close.

Figure 6 gives a bird-view, for all the cells, of the specific excess power results as function of the applied current density. We divided the curves of figure 6 in three categories chosen according to the preparation of the cathodes, as reported in Table I. We can focus our attention to some points emerging from inspection of fig. 6. These are:

- Except for cells #1, #3 and, for opposite reasons (see below), #8, all the cells show a threshold in the current density which is located around 100 mA/cm²;
- While cell #1 and #3, as already mentioned, did not give any excess heat whichever was the current density, cell #8 started to produce excess heat at a lower current density value, below 50 mA/cm². This could be consistent with the fact that the whole cathodic surface area was not equal to the calculated value, given by \( n\pi\delta(h + \delta/4) \), but, reasonably, it was less than that value because of the partial shielding of the innermost wires toward the
electrolytic solution, caused by the outermost wires. $n$, $\Omega$ and $h$ are, respectively, the number of the wires, their diameter and length (see Table I). A similar reasoning could be done for cell #7 due to a

![Power Excess vs Current Density Graph]

Figure 6. Trend of the specific excess power vs current density as found for the ten cells. Cell #3 has not be reported because its trend is very similar to cell #1 (see Table II)

possible not precise evaluation of the whole cathodic surface area;
- The cathodes, in categories SINTERED and $\Omega$ 6mm RODS, can be considered sufficiently comparable among them since at least the shape, dimensions and starting materials are in common for the cathodes belonging to the same category;
- By comparing the categories, it clearly appears that the cathodes made of 6 mm diameter rods show the lowest power excess but there is not a significant difference between as received and quenched cathodes;
- On going from the cathode #1 to cathode #8, we pass from a practically undislocated material to highly dislocated one, whereas, in the SINTERED category, the concentration and distribution of dislocations probably remains unaffected by the type of preparation. In fact, it is reasonable that the cathodes maintain the same properties of the grains of the starting powder of the Pd sponge which is highly dislocated, as expected by itself nature;
- It is interesting to observe the very unlike behaviour between the two RFHQ cathodes (#6 and #9) which were different only by diameter. We believe that this has to be connected to the dynamics of the high compressive stress which is established in the rod in the direction from the surface toward the bulk when fast cooling occurs. Because the rate at which cooling proceeds into the bulk, all the other conditions fixed, depends on the diameter, the
magnitude of the compressive stress, which can dislocate the rod in an ordered way, becomes consequently a function of the diameter.

In Table II below it is reported the specific integral excess heat as calculated for all the cells.

<table>
<thead>
<tr>
<th>Cell #</th>
<th>Category</th>
<th>Weight (g)</th>
<th>Specific Integral Excess heat (MJ/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.2954</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ø6 mm RODS</td>
<td>8.3403</td>
<td>0.02</td>
</tr>
<tr>
<td>5</td>
<td>8.1150</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>8.5263</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4.2158</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>SINTERED</td>
<td>3.5654</td>
<td>3.7</td>
</tr>
<tr>
<td>4</td>
<td>3.8545</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>MISCELLANY</td>
<td>3.3124</td>
<td>3.9</td>
</tr>
<tr>
<td>9</td>
<td>2.0283</td>
<td>9.5</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.6182</td>
<td>11.6</td>
<td></td>
</tr>
</tbody>
</table>

Figure 7 shows the comparison with the F.&P. (5) data and those of cell #8, for instance, concerning the specific power excess dependency from the current density.

Figure 7. Specific power excess dependence on the current density compared with data in Ref. 5
Though our slope is less steep than the slope found by F.&P., it is important to observe that both the trends are linear and the difference in the slope and intercept can be reasonably attributed to the nature of the cathode.

### 3.2 Cathode swelling measurements

Before to show some preliminary results of cathode swelling measurements, performed in order to obtain in situ the loading factor \([D/Pd]\), let us consider briefly some basic points related to this kind of measurements. According to the literature (6-7), in an unstrained Pd specimen, D₂ absorption produces a relative swelling, \(\Delta V/V\), given by:

\[
\Delta V/V = 3 \Delta L/L = (0.20 \pm 0.01)[D/Pd] \tag{6}
\]

Due to the fcc structure of Pd, the swelling is an isotropic process producing the same relative elongation, \(\Delta L/L\), along each of the x,y,z axis. Probably, only cathode #1 is in this quite-ideal situation due to the particular heat treatment that allowed it to loose all the internal stresses of the material reaching the state of internal thermodynamic equilibrium. In a cold-drawn rod having diameter \(\Omega\):

\[
\Delta V/V = (\Delta x/x) + (\Delta y/y) + (\Delta z/z) = 2(\Delta \Omega/\Omega) + (\Delta z/z) \tag{7}
\]

due to the fact that there is a tensile strain along z-axis and compressive strain on the x,y plane. In this case, we cannot use the above relationship 6 for determining \([D/Pd]\). In a sintered specimen, eqn. 6 is still approximately satisfied but it is necessary to consider that the expected expansion, due to the deuterium absorption, occurs for a certain fraction, \(\delta\), in the free volume, \(V_p\), of the pores. Thus, the eqn. 6 becomes:

\[
(\Delta V - \delta V_p)/V = 3 \Delta L_{meas}/L \tag{8}
\]

where \(V_p = W_s(\rho_{Pd} - \rho_s)/\rho_s \rho_{Pd}\). \(W_s\) and \(\rho_s\) are, respectively, the weight and density of the sample s. In this case, the measured expansion, \(\Delta L_{meas}\), allows to measure \(\delta\) by eqn. 8 through eqn. 6 as:

\[
\delta = (0.20 [D/Pd] - 3 \Delta L_{meas}/L)[1/(1 - f)] \tag{9}
\]

if at least one \([D/Pd]\) value is known and \(f = \rho_s / \rho_{Pd}\).

In our experiment, we measure the expansion along the major axis of the cathode, that is, \(\Delta L_{meas}/L\) (#4-sintered) and \(\Delta z/z\) (#3-\(\Omega\)6mm rod as received). In figure 8, we report the
recordings of the cathode swelling and the electrode temperature for the two cells equipped with the LVDT at the beginning of the experiment when, before to fill the cells with the electrolyte solution, a stream of D2(g) was allowed to circulate in the cells for conditioning the Pd cathodes. As it was already found (2,8), the response to the D2(g) exposure of the sintered cathode was completely different with respect to the rod and, as it will be shown, this difference will continue throughout the experiment.

![Figure 8](image)

Figure 8. Behaviour of the cathodes monitored by the LVDTs when exposed both to D2 stream, at atmospheric pressure, and D2 electrochemically generated. Temperature of the cathodes is also shown.

As shown in fig. 8, in the same experimental conditions, the swelling of the sintered cathode #4 was about 70 times greater than the swelling of the cathode #3. This could be easily explained by considering the respective porosity of the two materials which allows to the gas, in the case of the sintered cathode, to be in contact with a larger surface. Thermogravimetric measurements (9), carried out on sintered specimens, like #4, showed that at 101.3 kPa of D2(g) and at room temperature, the weight gain was such that an equilibrium [D/Pd] value of 0.67, as expected, was reached in a time interval of about 20 min which is comparable with that reported on fig. 8. Therefore, we can associate the $\Delta L_{\text{meas}}/L$ to [D/Pd] and, through eqn. 9, we can calculate $\delta = 0.114$. This means that at least 11% of the expected swelling does not
contribute to expand the cathode, provided that its density is assumed isotropic. Due to the unidirectional pressing applied in the preparation and subsequent short sintering, the density could be higher along the z-direction increasing $f$ in the eqn. 9 and, accordingly, the value of $\delta$. Previous calculations (8) made on the integration of the temperature vs time curve were and still are in satisfactory agreement with the heat expected to be produced by the exothermic reaction which yields $[D/Pd] = 0.67$ producing.

In fig. 8 the behaviour of the cathode just after the beginning of the electrolysis at 10 mA/cm$^2$ is also reported. The LVDT of cathode #4 did not detect any appreciable variation while cathode #3 LVDT showed a well-defined increasing trend which continued as shown in figure 9 below.

![Figure 9. Behaviour of cathodes #3 and #4 observed in a long step-changing current density profile](image)

If we take into account the different $\Delta L$ ordinates of the two plots above, we realize that the cathode #4 swelling was practically independent from the current density, maintaining quite constant the value which was reached during the exposure to $D_2(g)$ stream. For cathode #3, $\Delta L$ was found to be strictly current density dependent. We observed that to maintain a certain swelling value it was necessary to continue to increase the current density otherwise a contraction of the cathode occurred.

Though the dilatation measurements did not allow us to obtain an absolute value of $[D/Pd]$, we believe the relative changes with respect to the current density are very interesting, when compared with the very low changes observed, simultaneously, on the sintered
cathode. In fact, these findings go in the direction of our precedent work (10), based on the assumption that [D/Pd] values out far from the thermodynamic equilibrium can be achieved if some structural and morphological conditions are present in the material. Particular structured domains, where the continuity of the chemical potential does exist, could be sites where high [D/Pd] values might be reached because of the effect of high local current densities on the low-ionic conductor PdD_x. This effect, as shown in literature (10), increases with the ionic transport number. To make this phenomenon macroscopically evident, it is necessary to have in the material a high concentration of large ionic-conductor domains satisfying particular structural arrangements able to set, locally, very high current densities. Due to the above considerations, we can only evaluate the lowest values of [D/Pd] for both the cathodes #3 and #4 which are, respectively, 0.26 (if eqn. 6 is calculated at the maximum measured value of ΔL, see Fig. 9) and 0.67. In this context, the respective excess heat data of Table II could be considered consistent.

3.3 Nuclear Measurements
3.3.1 Tritium measurements

As mentioned in the experimental section, we carried out systematically (roughly at fixed electrical charge passed through the ten-cell system) tritium measurements by 1 ml sampling both in each cell and in the respective catalytic recombinator. In figure 10, the trends
vs the integral charge passed both for tritium in solution and in recombined heavy water are
given. The plots reported are considered typical and they refer to cells #1, #10 and #8,
respectively, one for each category of cathodes. Detailed information on the procedure used to
evaluate the tritium mass balance is reported elsewhere (2). Here it is sufficient to point out
that the shape of the trends is due to the mixing, at the point marked by the arrow, of a new
heavy water feed, at lower T content, [T]°f, with the solution at higher T content, [T]°i. In
fact, the final T enrichment was always within the expected enrichments from = 2[T]°f to =
2[T]°i, roughly. As a consequence of this, the trends for the recombined gases were
influenced accordingly. However, no significant evidence of T excess was found throughout
the experiment in any of the ten cells.

From data like those reported in fig. 10, it is possible to calculate the enrichment factor
defined as the ratio, at a certain charge passed, between the tritium concentration in the
solution and tritium concentration in the gas phase, i.e., \( \alpha_E = \frac{[T]_{\text{sol}}}{[T]_{\text{gas}}} \). The knowledge
of this term is important to evaluate, after prolonged electrolysis, the final content of T, \([T]_f\),
in a D2O electrolytic solution having an initial concentration of tritium \([T]°\). In fact, as it can
be shown (11), \([T]_f = \alpha_E [T]°\).

Figure 11 shows a typical trend of the enrichment factor for cell #9 throughout the
experiment.

![Figure 11](image-url)

Figure 11. Typical trend of the enrichment factor. Here cell #9 is reported

It is important to observe that throughout this long experiment, \( \alpha_E \) was found
practically constant. Some authors reported (13) different results and explained the variations
of the enrichment factor as due to co-deposition onto the cathode surface of impurities which
change the nature of the electrode/electrolyte interface and, consequently, the relative rate of
the charge transfer of the hydrogen isotopes.
The sensitivity of our measurements to detect an anomalous tritium content on the sample can be estimated to be of the order of 100 dpm/ml (effective value was 30 dpm/ml) that means a content of tritium of $10^9$ atoms in one milliliter. By analysing the excess heat reported in table II, we can compute that all the cathodes, except to #1 and #3, have shown an integral excess heat of the order of 10 MJ. If this excess heat is to be attributed only to fusion reactions having tritium as final product, the number of reactions needed is of the order of $10^{19}$. Even considering that the process lasted for all the length of the experiment (50 days) one would expect in the solution + gas phase a production of $\approx 10^{17}$ tritium atoms every day and, by taking into account the volume of the solution, $10^{15}-10^{16}$ atoms of tritium would have been in 1 ml solution sampled. This number is $10^6-10^7$ higher than the level of sensitivity of our measurements and it is hard to think an artifact responsible for a negative result.

3.3.2. Neutron measurements

The frequency of neutron counting was analysed using variable time integration intervals. In figure 12 the frequency as counts per hour is reported for all the runs. No evidence of any neutron signal different from background was found.

![Figure 12. Average neutron counts per hour measured in all the acquisition runs](image)

The analysis has been repeated for each run with several choices of time integration intervals (from 10 minutes to 1 hour) by comparing each of the obtained distributions with the relative Poisson distribution expected according to the measured count mean value. In figure 13 the result of this analysis is shown for one particular run which is representative of the results obtained in all the runs. The experimental data are shown as well as the expected
values. These are reported with an error bar indicating their possible variability when the mean value of the Poisson distribution is changed within the measured value of the standard deviation. In all the cases the mean value is compatible with the background value and the count distributions follow the statistics expected proving, in this way, the background nature of the neutrons detected.

![Graph showing observed and expected values](image)

Figure 13. Frequency count of neutrons as observed in 542 intervals of ten minutes acquisitions and as expected in a Poisson distribution. The variability of the expected values obtained allowing the measured mean value to vary between $\mu - \sigma = 0.32$ and $\mu + \sigma = 0.37$ counts/10 min. is also reported.

Being one cell (#3) operated for a certain time with pulsed current, a special test has been made by analysing the time sequence of neutron counts with respect to the current value. No correlation has been found, being the count distributions during the $I=I_{\text{Max}}$ and $I=0$ time intervals described by the same Poisson distribution with an acceptable statistical significance.

According to the discussion at the end of the previous section 3.3.1 on the comparison between excess heat and nuclear products, a number of $10^{19}$ reactions is needed again to explain the heat found with the only fusion reaction having neutron and $^3$He as final products.

Under the same assumptions already made and taking into account the efficiency of the neutron counter a counting rate greater than $10^{10}$ times the normal background would have been detected.

3.3.3 $\gamma$ measurements

Gamma spectra from HPGe and NaI (Tl) counters, respectively, in the energy ranges of 0.30 - 2.83 MeV and 2.0 - 27.0 MeV, were sequentially acquired for living time intervals
of eight minutes. For each measurement the integral count of selected energy windows reported in tables III and IV were stored. For the spectra of both counters an energy window was reserved to monitor natural background, being the e channel of the Ge counter centered on the energy of a γ emitted by the $^{214}\text{Bi}$ (a daughter radioisotope of $^{238}\text{U}$) and the b channel of the NaI counter centered on the energy of γ emitted by $^{208}\text{Tl}$ (a daughter radioisotope of $^{232}\text{Th}$).

**TABLE III**

<table>
<thead>
<tr>
<th>channel</th>
<th>window energy (keV)</th>
<th>motivation</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>349.9 - 450.7</td>
<td>de-excitation of Pd isotopes</td>
</tr>
<tr>
<td>b</td>
<td>475.9 - 561.7</td>
<td>de-excitation of Pd isotopes</td>
</tr>
<tr>
<td>c</td>
<td>986.9 - 1074.4</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>2194.9 - 2211.5</td>
<td>radiative capture</td>
</tr>
<tr>
<td>e</td>
<td>2216.9 - 2230.8</td>
<td>$^{214}\text{Bi}$ (natural background) (U-238 daughter)</td>
</tr>
<tr>
<td>f</td>
<td>2605.6 - 2622.1</td>
<td>$^{208}\text{Tl}$ (natural background) (Th-232 daughter)</td>
</tr>
<tr>
<td>g</td>
<td>2770.6 - 2825.7</td>
<td></td>
</tr>
</tbody>
</table>

Table IV

<table>
<thead>
<tr>
<th>channel</th>
<th>window energy (keV)</th>
<th>motivation</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>2124 - 2328.2</td>
<td>radiative capture</td>
</tr>
<tr>
<td>b</td>
<td>2455.1 - 2750.8</td>
<td>$^{208}\text{Tl}$ (natural background) (Th-232 daughter)</td>
</tr>
<tr>
<td>c</td>
<td>18007.1 - 19929.5</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>20013.6 - 21998.9</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>22010.1 - 23998.4</td>
<td>$d + d \rightarrow ^4\text{He} + \gamma (23.8 \text{MeV})$</td>
</tr>
<tr>
<td>f</td>
<td>24019.6 - 27004.6</td>
<td></td>
</tr>
</tbody>
</table>

For each run the analysis of the measurements was made by checking the fluctuation of the ratio of the counts in a given channel against that of the background channel. In figures 14 and 15 we report an example of measurements with Ge and NaI counters, respectively. The
counting ratios fluctuate around the mean value. The upper dotted lines indicate the deviations from the mean of three times the maximum value of the error of the ratio on a single integration interval within the run. These levels can be considered as the threshold that indicates a statistically significant deviation. In all the measurements no significant deviation from background has been detected.

Figure 14. Ratio of the counts of different energy windows over natural background. Ge detector. \(a, b, c, \text{etc.}\) are the energy windows (see table III)

The sensitivity of the different channels to detect a possible fusion reaction is very different due to the several factors that affect the possibility to detect gammas of given energy coming from a fusion channel. Gammas of low energy 0.35 - 0.55 MeV are expected to be a signal of the reaction chain:

\[
d+d \rightarrow {}^{3}\text{H}+p \quad , \quad p+\text{Pd} \rightarrow p+\text{Pd}^{*} \quad , \quad \text{Pd}^{*} \rightarrow \gamma+\text{Pd}
\]

Taking into account the reaction yield and the counter efficiency the threshold sensitivity was about \(10^{17}\) fusion reaction in \( {}^{3}\text{H}+p \) channel in the time integration of eight minutes.
Photons coming from the radiative capture of neutrons by protons of materials containing hydrogen are expected in the energy window centered around 2.22 MeV.

Figure 15. Ratio of the counts of different energy windows over natural background. NaI detector. a, b, c, etc. are the energy windows (see table IV)

This spectrum channel is a monitor of the reaction chain

\[ d+d \rightarrow ^3\text{He}+n \], \[ n+p \rightarrow d+\gamma \]

The threshold sensitivity both for Ge and NaI counters was about \(10^6\) fusion reactions in the \(^3\text{He}+n\) channel in a time interval of eight minutes.

From the results shown in figure 6, by computing the power excess of different cathodes and taking into account the palladium mass, a maximum value of about 13 W is found. Considering fusion reactions in the two classical channels (p + T and n + \(^3\text{He}\)) as
source of the power excess measured, a number of $10^{12}$ reactions per second are needed, that is $5 \times 10^{14}$ if we consider that the phenomena lasted along all the eight minutes of the time interval integration. By comparing this value with the sensitivity threshold, we conclude that in the low energy window the sensitivity was not sufficient to detect the p + T channel through the $\gamma$ measurements. On the contrary, in the windows selected to monitor the $\gamma$ emitted by the radiative capture, the expected signal from n + $^3$He reaction was $10^8$ times higher than the sensitivity.

Gammas in the upper windows of the NaI spectrum would monitor the fusion channel

$$d+d \to ^4\text{He}+\gamma (23.8 \text{ MeV})$$

This reaction, on the contrary to the case in which the energy (and not only the momentum) is absorbed by the crystal lattice, does not release locally heat and should not give contribution to an observed excess heat generated in the cathode. The threshold sensitivity for this fusion channel was about $10^7$ fusion reactions in the used integration time. To explain the heat excess measured in this experiment as generated by nuclear phenomena, a reaction not monitored by our instrumentation (for instance the $^4$He production with the energy absorbed locally by the lattice) must be called.

4. Conclusions

The following conclusions can be drawn:
- Excess heat and cathode swelling were found strongly dependent from the preparation of the Pd cathodes;
- Sintered and bulk cathodes behave in different way with respect to the absorption of deuterium as shown by the displacement measurements. In the case of bulk cathode, the D/Pd ratio seems to be greatly influenced by the applied current density showing a real non-equilibrium condition. The sintered cathode absorbs deuterium without any correlation with the current density like in a state of thermodynamic equilibrium;
- The highest specific excess heat and power were found to be, respectively, 130 MJ/cm$^3$ and 96 W/cm$^3$;
- Specific power excess displays a linear dependence on the applied current density with a possible threshold effect according to the literature;
- From the double calibration procedure adopted (thermal and electrochemical) an intriguing evidence arises which is, by itself, the most important feature of the cold fusion nature to which a clear answer is still lacking;
- Though neutron, tritium and gamma measurements were taken throughout the experiment, no statistically significant evidence of release of these nuclear products was found;
- Evaluation of the sensitivity of the respective nuclear measurements gives confidence that if the energy were released through channels involving the generation of the monitored nuclear products they would be detected at a statistically significant level;
- To explain the heat excess measured in this experiment as generated by nuclear phenomena, a reaction not monitored by our instrumentation (for instance the $^4\text{He}$ production with the energy absorbed locally by the lattice) must be called;
- Also the findings here reported go into the direction of the scattered results still coming from cold fusion experiments which even more require a complete set of independent parameters to be controlled and nuclear products to be measured ($^4\text{He}$ for instance) both to exclude the chemical nature of the heat generated and possible other sources of error.

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6. References

8. D. Gozzi et al., unpublished results