# Power Excess Production in Electrolysis Experiments at ENEA Frascati

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## Abstract

Continuing the research activity on heat excess detection during the electrolysis of heavy water with palladium (Pd) cathodes, previously reported at ICCF3 and ICCF4, new experiments have been performed with success. In one of them it was also possible to correlate the power excess production with other parameters of the experiment: its description will be the subject of this communication.

## 1. Introduction

Many types of experiments are enlisted under the name of "Cold Fusion" (CF), following the first one performed by Fleischmann and Pons (1). Among them, the measurement of the production of heat in excess during the electrolysis of heavy water with a palladium (Pd) cathode has been more extensively investigated, and a substantial progress has been produced.

In the past years we have performed two campaigns of measurements of this type, which have produced positive results: i.e., they have allowed us to detect heat in excess during extended periods of time (up to tens of hours) with values largely above the sensitivity of the apparatus (by 1 to 2 orders of magnitude). We have chosen a particular geometry, in which the cathode is a flat Pd electrode of circular shape, in contact on one side with the electrolytic solution, and on the other side with a vacuum-tight ambient, in which the pressure of the deuterium gas permeating through the metal could be measured: in this way we have also been able to get information helpful to the comprehension of the dynamics of D in Pd during the electrolysis (2). The evaluation of the D/Pd ratio with resistivity measurements was not possible with this apparatus, because of its unfavourable geometry. We have thus decided to perform a new experiment, aimed to learning how to measure the D/Pd ratio through the resistivity of the cathode. In order to do so, we have changed the geometry of the electrolytic cell, by using a cathode in the form of a thin Pd cylinder

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and the anode in the shape of a Pd hollow cylinder, surrounding the cathode.

In the first attempt the aim of our experiment was not reached. On the other side, the experiment was particularly successful as far as the production of heat in excess is concerned, and for the possibility of correlating the heat production with other parameters of the experiment, noticeably the difference of potential between anode and cathode (which in the following we will call the voltage V): this correlation can in our opinion help understanding the phenomena at the basis of the heat excess production.

## 2. The experiment

The current in the electrolytic cell was started on March 21, 1994, and was shut down on May 9, after 50 days. In this period heat excess was observed in three occasions, each one lasting more than one day. In this chapter we will describe, in the order: the cell, the calorimetry, and the results.

## 2a. The cell

The cell, with the exception of the shape of the electrodes, is of the same type described in reference (2). Anyway, we will outline here its main features (see Fig.1). It is made out of Pyrex glass, with a substantially tight Teflon cap: it contains $\approx 250$ cm$^3$ of high purity heavy water. The electrolyte used is LiOD, and the molarity has been changed during the experiment from 0.1 M to 0.5 M. The cathode is a Pd solid cylinder, 2 mm in diameter, with a useful length (the length facing the anode) of 2 cm. The anode is a Pd hollow cylinder, 2 cm high, 0.5 mm thick and 8mm inner diameter. The electrolytic current is fed with a constant-current power supply, and both the current and the voltage are continuously monitored: since the voltage is subjected to abrupt changes due to the production and detachment of gas bubbles at the surface of the electrodes, its signal is recorded across an RC circuit, with a constant time of $\approx 10$ s, long with respect to the characteristic times of the quoted changes, short with respect to the characteristic times of the heat transfer processes. The electrodes are connected to the external circuit by spot-welding to them nickel conductors. The gases evolved at the electrodes (O$_2$ and D$_2$) are conveyed through a Teflon pipe outside of the cell, and the gas flow is measured
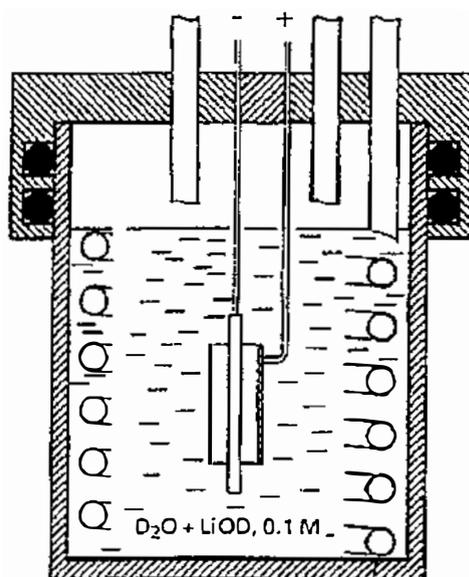


Fig.1 Schematic view of the apparatus: cathode and anode of the electrolytic cell are shown. In the coil presented in section water flows for calorimetry.

every few hours, in order to check it against the value of the cell current, thus confirming the efficiency of the electrolysis: values between 95% (at low currents) and 100% (at high currents) are always obtained. At intervals, depending on the current intensity, fresh heavy water must be added in order to compensate for the electrolysed water. Before starting the experiment, both the electrodes have been cleaned with organic solvents, and then degassed by bringing them to the temperature of $\approx$ 200°C under vacuum for about an hour. Assembling and charging heavy water has been performed in an inert atmosphere of argon.

## 2b. Calorimetry

Also the calorimetry is in principle the same as in reference (2); anyway, it will be described here. The cell, contained in a glass dewar, is placed inside a large styrofoam box, in which the temperature is kept constant to better than 0.5°C with the help of a source of heat (an electric bulb) and a source of cold (a coil in which water from the tap is circulated): the latter is substantially at constant temperature, while the bulb is activated by a thermoregulator led by a thermometer placed in the box. A fan assures that the maximum temperature difference inside the box is lower than 0.5°C. The main feature of the calorimeter is a Pyrex glass coil immersed in the cell, as shown in Fig.1, in which water is circulated. The heat exchange between the circulating water and the liquid in the cell acts in such a way as to extract most of the power produced in the cell, in the following called the output power. We evaluate that a large percentage (of the order of 95%) of the power produced is extracted in this way, the remaining fraction being dissipated (mostly by convection in the liquid to its free surface and then by conduction/convection and by radiation) to the outside world. Care is taken that the water enters always at the same temperature (within 0.1°C) and is circulated with a constant flow. The former feature is obtained by using a thermoregulated water source, while the latter is pursued by having the water circulated by free fall from an upper container to a lower one: then, it is sent back to the upper container by a pump. The water flow rate is however checked every few hours and it results constant within 1% along the whole experiment. Two thermocouples are placed at the inlet and at the outlet of the circulating water to the cell, and are connected in a differential mode (by short-circuiting two leads together, and measuring the difference of potential between the two remaining leads). This circuit gives directly the difference of temperature between these two points ($\Delta T$), which is a monotonous function of the power output, and by calibration is found to be substantially linear for powers lower than 30 W. Note that the use of a water-circulating coil extended to all the height of the cell guarantees that the measured value of the power output is averaged on the whole volume of the cell. The calorimeter is calibrated by producing a known power in the cell and measuring the $\Delta T$. This has been done by using an electrical resistor immersed in the same position in which the cathode will be placed, and dissipating in it a known Joule power. The calibration has been made at different starting temperatures, between 20° and 50°C, for different molarities of the solution, and for powers ranging up to 50 W.

In order to calculate the power excess, the power input is subtracted from the power produced in the cell, i.e., the power output. The former is obtained by the formula:

$$P_{in} = (V - 1.54) \, I \text{ watts}$$

with V in volts and I in amperes (the constant 1.54 volts takes into account the energy spent by the current to electrolyse the water). The power output is obtained, as said before, through the measurement of the temperature difference T between the

inlet and the outlet of the circulating water in the cell, with the help of the calibration curves obtained previously. We evaluated the overall error in the measurement of the excess power to be well within 100 mW, at all power output levels.

## 2c. The results

Fig.2 shows a summary of the results, expressed as the time evolution of the experiment: only the last, most relevant, 22 days are shown. Two quantities are reported: the excess power P, measured as described before and expressed in watts (scale on the left), and the voltage V, measured in volts (scale on the right). The abscissa is the time t, measured in days, from 28, corresponding to April 18, to 50, corresponding to May 9. The basic temperature chosen for the experiment was 30°C. The molarity was increased on the 10th day from the initial 0.1 M to 0.5 M. The maximum current of 2 A was applied on the 30th day, the previous value being 1.2 A.

The first episode of power excess production started on the 30th day, and was hardly noticeable: the power excess grows very slowly, reaching the value of about 200 mW on the 32nd day, when the addition of heavy water in the cell shuts the excess power down. But another productive period starts soon after, lasting 5 days, with power excess increasing up to about 700 mW, ending on the 37th day, when another refilling - this time not with pure water, but with a 0.5 M solution preheated at the cell temperature - destroys it again. No heat excess is produced in the following 5 days. In order to "stimulate" the system, on the 43rd day we invert the current in the cell for 30 seconds, interchanging cathode and anode in the circuit. After 1.5 days another period of excess power production is initiated: this time it will
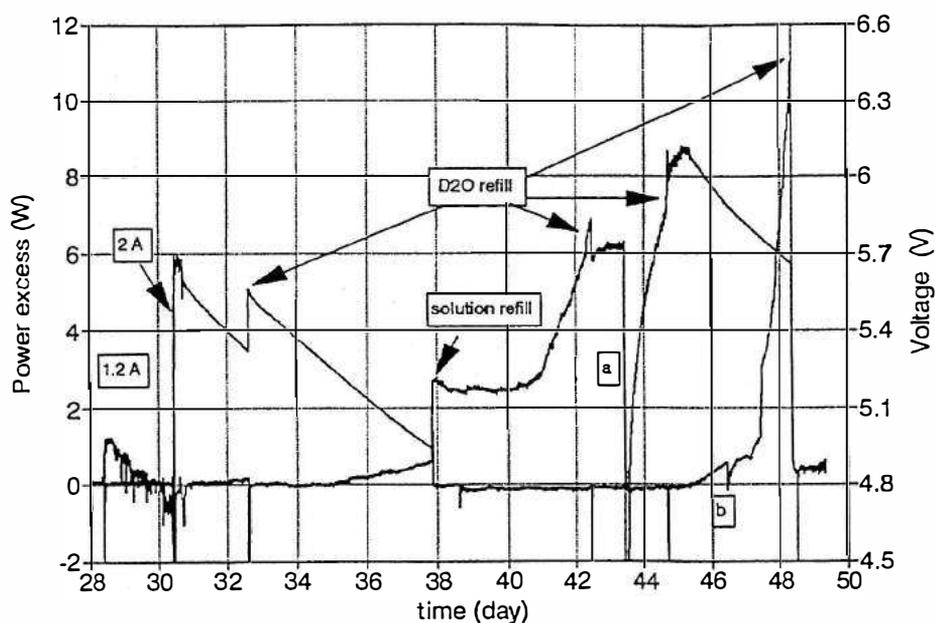


Fig.2 The rsults obtained during the last 22 days of the experiment. Letter a refers to the inversion of current described in the text. Letter b refers to the 10-s short-circuit produced on the 46th day.

last about 3 days, the excess power will grow almost exponentially, eventually reaching the value of 11 W. Note that the power input at that moment was 8 W. Once more the undelayable addition of heavy water shuts the cell down, and this time forever.

On the 46th day, while doing a check on the circuit, we unwillingly short-circuited the cell for about 10 seconds. This is not visible on the voltage, but had a quite dramatic effect on the power production: it looks as if the system is less efficient in producing heat for about one day, then goes back rapidly to the previous trend. Without this episode, one could claim that the increase in power excess production was a real exponential as a function of time. Anyway, we think that this episode is quite instructive, and we will go back to it when commenting the results.

The exam of the voltage behavior is quite interesting in this experiment. In particular, we notice an apparent "change of mode" exhibited by the voltage whenever a power excess production is in course. The signal, that in the absence of power excess is rather noisy, with oscillations within about 0.03 volt, becomes abruptly quiet, and takes on a very regular trend, consisting in a decrease of the voltage as a function of time. The passage from the noisy to the quiet mode can be seen twice: on the 30th day and on the 45th day. The latter is shown with an expanded scale in Fig.3. In next chapter a possible interpretation of this phenomenon will be presented.

The end of the experiment was determined by the enormous increase of V produced after the last refilling on the 48th day: the value went up to about 13 volts. We interpret this as a consequence of the substantial destruction of the anode, consumed by 50 days of electrolysis (which was confirmed by the inspection of the electrolytic cell performed at the end of the experiment).

## 3. Comments on the results

### 3a. Is there a phase transition?

In the description of the results we have shown that there seems to be a correlation between the appearance of heat excess and the "mode" of the voltage V as a function of time. The first mode that we envisage is characterised by a random oscillation of the voltage, within about 0.03 volt, and a general trend in time, increasing and decreasing, the latter not always clearly correlated to the various operations performed on the apparatus: this has been the mode of the first 30 days, and of the 7 days between the 38th and the 45th. In the second mode, quoted before, present when heat in excess is produced, the noise is strongly reduced and the general trend of the voltage is a regular decrease: this can be explained, also quantitatively, by the consumption of water, at constant amount of electrolyte, and thus with increasing molarity, produced by the electrolysis.

The extended graph of the voltage as a function of time in the vicinity of the change of mode (Fig.3) emphasizes the noise reduction: it reminds visually the occurrence of a phase transition, mostly for the abruptness of the commutation between the two modes. We have tried to imagine an empirical and qualitative explanation of what happens. We imagine that during the electrolysis, once the deuterium has been charged in the cathode, gaseous $D_2$ is formed on its surface. What one would expect is that the molecules so formed organise themselves in tiny bubbles of gas, which grow slowly, still remaining attached to the surface, until they reach a convenient size, such that the buoyant force due to the Archimedes principle exceeds the sticking force of the bubble to the surface: then, the bubble detaches itself and moves to the surface of the liquid. During the growing phase, the bubble
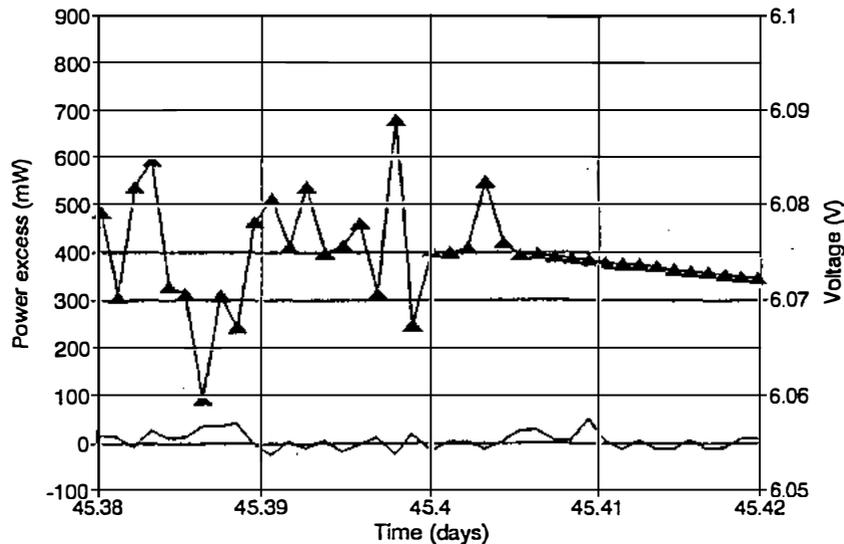
Fig.3 An enlarged detail of Fig.2, showing the change of mode of the voltage V on the 45th day.

represents an increasing electrical impedance to the current: thus, at constant current, this means that the applied voltage has to continuously increase. When the bubble detaches itself from the cathode and flies to the surface, there is an abrupt decrease of the electrical impedance of the cell, and thus a decrease of the voltage. Each bubble, thus, produces in time a tiny saw-tooth shaped variation of the voltage. What we see on the left side of Fig.3 is presumably the average effect of many bubbles which are growing and eventually detaching themselves from the cathode surface: the use of an RC filter on the V-measuring circuit has only the effect of reducing the voltage changes produced by this phenomenon. In order to explain why, on the right side of Fig.3, the oscillation disappears, we can imagine that, for some unknown reason, the bubbles are no more allowed to grow, and the gas is leaving the surface of the cathode with much smaller bubbles. Since the buoyant force cannot be altered, the only explanation is that the sticking force is much smaller. This could be due to some disturbance coming from the inside of the cathode, which alters it. The fact that this passage from one mode to the other is so abrupt as shown in Fig.3 substantiates the hypothesis that we could be dealing with a phase transition in the $PdD_x$ lattice, characterised by the set up of some kind of field (phonons?) within the lattice.

We have been looking into our previous experiments (2), to see whether this change of mode accompanied the appearance of heat excess production, and we had a confirmation, even though less dramatic. Anyway, we must remember that in the previous experiments, as quoted above, we used a planar geometry for the electrodes. The contribution of the cathode potential to the build-up of the voltage V is much more relevant in a cylindrical geometry with a thin inner electrode (the cathode), as that used in the present experiment, than in a planar geometry. Thus, it is to be expected that the phenomenon is more evident in the present configuration.

## 3b. Surface or bulk?

Since the first days of CF the question of whether the observed phenomena, whatever they were, were taking place on the surface or in the bulk of the system has been put and extensively discussed. For the heat excess phenomena, their depend-

ence on the D/Pd ratio is a clear indication that the bulk of the $PdD_x$ system is involved. Nevertheless, the relevance of the surface, for example to the D-charging, is out of discussion. The argument is not a straightforward one, and more research is required to address it, and give it an answer, provided that a simple answer does exist.

However, in our experiment there are two episodes, already quoted in chapter 2, that could contribute to this discussion, and we want to point them out. On the 43th day (see Fig.2) we inverted for 30 seconds the current in the electrolytic cell. The effect was much more dramatic than expected. It took almost one day for the voltage to go back to the original value. The second episode took place on the 46th day, while producing excess power. We short-circuited the cell for 10 seconds, and, if we accept the hypothesis of the exponential growth of the power excess, again it took one day to resume its original trend, with a dramatic recovery at the end of the day, consisting in the increase of 2 W in half an hour. Keeping in mind the order of magnitude of the coefficient of diffusion, even at the high levels expected at high D/Pd ratios, such short perturbations should affect only the first few monolayers of the system, and this is enough to produce a big change in its behaviour. This seems to indicate the relevant role that the first layers of the charged cathode have on the observed phenomena.

## 4. Conclusions

It seems to us that the experiment reported here constitutes a strong confirmation of the reality of CF, at least for what concerns the production of heat in electrolytic cells with heavy water and Pd cathode. Many open problems remain, such as the nature of the energy produced, the existence of a phase transition, whether the phenomenon takes place in the bulk or on the surface of the cathode, and so on: we have tried to outline some of them in Chapter 3. They will be addressed in our next experiments, starting with the measurement of the D/Pd ratio in real time. Other implementations to our experiment will be realised, the most important of which consists in analysing the gases evolving from the cell, mostly $D_2$ and $O_2$, in order to check for the presence of the helium isotopes, that would provide an evidence for the nuclear nature of the heat. A field that should be thoroughly investigated concerns the material science properties of the $PdD_x$ system, with the aim of evaluating the meaningful parameters for a reproducible charging of D in Pd at high D/Pd ratios.

## Acknowledgements

## References

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