

Study of Deuterium Charging in Palladium by the Electrolysis of Heavy Water: Heat Excess Production.

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Summary. — An experiment based on the electrolysis of heavy water with a palladium cathode is reported. The production of excess power during the electrolysis has been measured with the help of a quite accurate and reliable calorimeter. The correlation of the detected power excess with some meaningful parameters of the experiment is investigated. Some of the features of the experiment permit to investigate the dynamics of deuterium in the palladium lattice, which is thought of as the basic phenomenon for excess power production.

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1. — Introduction.

In the last four years many experiments have been performed in the field conventionally known as «cold fusion», with results that are not easily reproduced and that are not easily explainable in the light of established knowledge, both in solid state and in nuclear sciences. A thorough review of the experiments, both positive and negative, and of the proposed theories has been published quite recently by Storms [1].

There have been numerous reports of excess power production over power input during the electrolysis of heavy water with a palladium cathode. This type of experiment was first performed by Fleischmann and Pons in 1989 [2]. One of the few features that have become clear in these years is the relation between the power excess production and the amount of deuterium absorbed by the cathode, called in the following D/Pd ratio (atomic): no effects are seen if the D/Pd ratio is lower than 0.8. This suggests that a new class of phenomena might take place in the palladium lattice when the amount of absorbed deuterium exceeds this value.

The experiment described here had as a primary goal the testing of the production of excess heat: this task has been accomplished with positive results. Furthermore, we devised for the electrolysis a novel approach, which seems a very promising method for investigating the mechanism regulating the transport of deuterium in the palladium lattice, which, in our opinion, is at the core of this class of phenomena. This allowed us to demonstrate the correlation between excess power and some parameters of the physical system, presumably related to the D/Pd ratio.

A model, proposed by two of us (ADN and VV), successfully interprets the results of the experiment in terms of deuterium motion in the palladium lattice: it will be presented for publication.

Preliminary reports on both the experiment and the model have been presented at a specialized conference [3].

2. - The electrolysis.

A peculiarity of this class of experiments, designed to detect power excess, is the high level of current densities: hundreds of mA/cm² are passed through the cell, which is one to two orders of magnitude higher than in the electrolysis used normally to study the kinetics of hydrogen-electrode reactions. Besides this, three main features characterize this experiment.

A group from Osaka University has claimed that higher D/Pd ratios can be obtained if low-current periods are alternated with high-current ones of the same time duration («hi-lo» technique): a semi-period of 6 hours was used [4]. We have adopted this technique, and have investigated the influence of the period on the power excess production.

A particular geometry was adopted: the cathode is immersed on one side in the electrolytic solution, while the other side faces a vacuum-tight region into which gaseous D₂ (or H₂) is introduced. Measuring the pressure variation of the gas in this region, at constant volume and temperature, provides information on its permeation through the cathode, thought of as a membrane.

Experiments designed to detect power excess normally have long durations, up to weeks, or even months. For such long times, a typical feature that can influence the experiment is the poisoning of the cathode surface, due to the continuous deposition, through electrolysis, of substances contained in the solution, or dissolved from the cell walls, or even the metal constituting the anode (usually platinum): this renders the absorption of deuterium in the cathode more and more inefficient, preventing high D/Pd ratios, and thus eventually «shutting down» the phenomenon under observation. In order to overcome this problem, a palladium anode has been used. The palladium anode is slowly but continuously dissolved in the electrolyte, and conversely palladium is deposited on the cathode surface, thus regenerating it, creating new active sites for the absorption of deuterium.

A schematic drawing of the electrolytic cell is shown in fig. 1. In order to minimize poisoning effects, the only materials in contact with the electrolyte are Pyrex glass and Teflon. An L-shaped glass pipe is immersed in the liquid and ends with the cathode, which is held in its position through a vacuum-tight connection obtained with the help of an O-ring and a teflon support; in this way one side of the cathode is

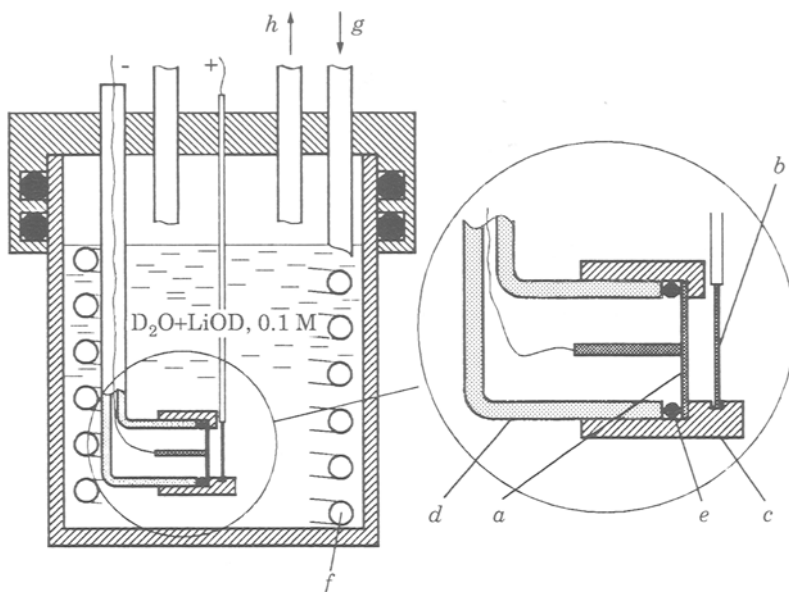


Fig. 1. - Schematic drawing of the apparatus. The electrolytic cell consists of the cathode (a) and the anode (b), rigidly held by the Teflon support (c), which also allows a vacuum-tight connection of the cathode to the glass pipe (d) through the O-ring (e). In the glass coil (f), with inlet (g) and outlet (h), water at constant temperature and constant flow is circulated. The measurement of ΔT between g and h permits to evaluate the power excess produced.

immersed in the electrolyte, while the other one faces the inside of the glass pipe. The latter can be filled with deuterium gas at a selected pressure, and then the pressure can be monitored at constant volume and temperature, procuring in this way a measurement of the deuterium permeation through the cathode in both directions. The anode, of palladium as well, is rigidly held parallel to the cathode, at a distance of 3 mm, by the same Teflon support holding the cathode. In the experiments reported here circular plane electrodes were used, with size of 1 and 2 cm² and thickness of, respectively, 0.25 and 0.5 mm. For the electrical connections, nickel wires, coated by Teflon, were used. A solution of LiOD (0.1 M) in heavy water was the electrolyte; for the control experiment, it was LiOH (0.1 M) in light water.

The electrodes [5] were subjected to a pretreatment before operation: they were heated at a temperature of 900 °C, still far from annealing, and then rapidly quenched at liquid-nitrogen temperature. All these operations, and the mounting of the electrodes in the cell were performed in a controlled atmosphere of argon in a glove-box. Samples of palladium observed with an electron microscope before the electrolysis showed a structure in grains, with the average linear dimension of grains of about 20 μm .

The electric current was fed by a constant current generator. Due to the high values of the current used in the experiments, bubbles of gas (D₂ and O₂) are continuously formed, producing oscillations in the applied voltage. The measurement of the voltage, necessary for the calorimetric evaluations, was performed through an integrating RC circuit, with a time constant of ≈ 20 s,

a time long with respect to the dynamics of bubbles in the liquid, and short with respect to the thermal equilibrium time of the thermodynamic system.

3. - Calorimetry.

Calorimetry consists in comparing the power input with the power output in a thermodynamic system: an excess power is detected when the latter is higher than the former. The power produced in the electrolytic cell, due both to the imposed power input (electrolysis) or to any other cause inside the cell, produces a temperature increase of the cell. The measurement of the temperature rise permits to evaluate the power output. In order to obtain a linear response of the system, in this experiment we chose parameters and procedures such as to minimize the temperature difference between the cell and the environment, while maintaining high calorimeter sensitivity. The main feature consists of the «flow» configuration of the calorimeter. A glass pipe shaped as a coil is immersed in the cell (see fig. 1) and water at constant temperature (25 ± 0.1)°C and constant mass flow (less than $1 \text{ cm}^3/\text{s}$) is passed through it, extracting heat from the electrolyte. Note that the symmetry of the heat exchanger guarantees that heat is extracted independently of the point at which it is produced. Moreover, by using an appropriate mass flow, it is possible to obtain a quite small rise of the cell temperature (in our case 1 W corresponds to ≈ 0.15 °C). The temperature difference between water inlet and outlet is proportional to the power output, and is measured by a thermocouple used in differential mode: this assures for the measurement a substantial independence from the temperature fluctuations of flowing water. In order to minimize the heat losses to the environment, the cell was thermally insulated from the room, with a 20 cm thick polyethylene layer, and the room temperature was kept constant at (25 ± 1) °C.

Under these conditions a calibration of the calorimeter was performed, either producing Joule dissipation in an electric heater immersed in the electrolyte, or passing a current through a control electrolyte. The linearity of the calibration curve, expressing the measured ΔT as a function of the power input W , confirmed that all the above conditions were satisfied: the linearity was satisfactory up to 25 W, which

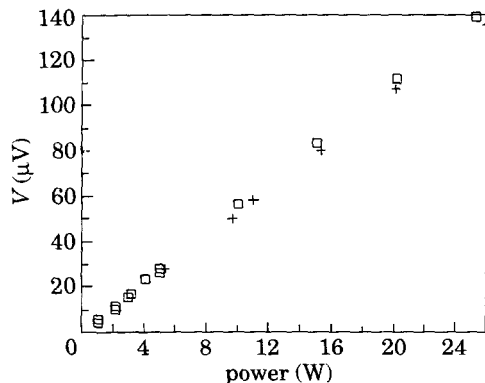


Fig. 2. - The calibration curve of the calorimeter. The voltage V reported is the output of the differential thermocouple, and thus gives ΔT , the difference in temperature between points h and g (see fig. 1). Squares represent measurements in light water, crosses in heavy water: 1°C corresponds to $39 \mu\text{V}$.

is much higher than the power reached in the experiments, and is shown in fig. 2. The error in the power measurement was of ± 50 mW, mostly due to the accuracy of the thermocouples.

Two additional checks were made. The temperature difference between a point in the cell and the water inlet temperature was monitored, and showed values in agreement with the main ΔT measurement. An electric heater was placed in the cell, not far from the electrodes, and was used during the electrolysis, from time to time, to check, by producing an additional power inlet, that the calorimeter was working correctly.

The power inlet due to electrolysis was calculated by multiplying the current by the voltage across the cell decreased by 1.54 V, thus taking into account the work done by the current to dissociate the heavy-water molecule. A flowmeter confirmed that the amount of gas evolving from the cell was consistent with the electric charge passed.

The temperatures were measured by thermocouples, whose reading was monitored by nanovoltmeters, connected to a PC-based data acquisition system. The pressure on the gas side of the cathode was measured with a strain gauge device and then recorded. The voltage across the cell was measured across an RC circuit, as mentioned above, and also recorded.

4. - Results.

The experiment consisted in four runs, each lasting more than 10 days: three with heavy water, and one (control) with light water. In all three runs with heavy water we detected the production of excess power. No excess power was measured in the control light-water run. Run no. 1 served also to test the various technical aspects of the measurement: thus, experimental procedures were changed while running it. For this reason, we will not refer to it in the following, even though we were able to detect the production of excess power. During the three positive runs we tried to correlate the excess power with meaningful parameters of the experiment, as discussed below. In doing this, it happened that for extended periods of time no excess power was produced, while in other extended periods a significant amount of excess power could be detected. In both conditions we systematically checked the behaviour of the calorimeter, by adding extra power to the cell and measuring the corresponding increase in temperature. These results seem to us very convincing proof of the reliability of the experimental system. The maximum excess power measured amounted to ≈ 3 W (60 W/cm³) for both low and high currents: this corresponds to ≈ 10 times the power input at low currents, and to doubling of the power input at high currents.

We tried to study the dependence of the excess power produced on the following parameters:

- a) the period of the hi-lo sequence,
- b) the voltage across the cell,
- c) the pressure variation on the gas side.

(We found no correlation between current density and excess power.) The results were as follows.

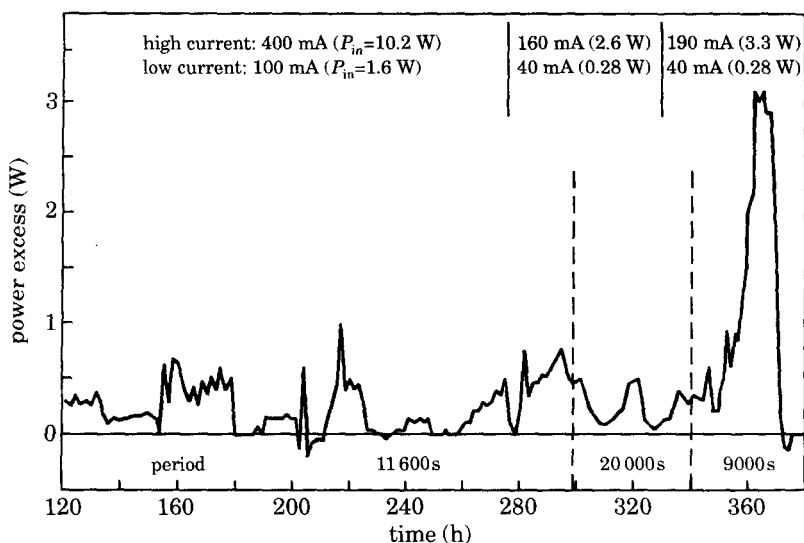


Fig. 3. – The power excess measured during run no. 2 as a function of time. The influence of the period of the hi-lo procedure is investigated. The peak shown at the end of the graph is the maximum power excess measured, *i.e.* 3 W (the same for low-current and high-current modes), which lasted almost 20 hours.

a) Dependence on the period. The range investigated was 5000–20 000 s: the lower limit was imposed by the thermal relaxation time of the system, about 20 min. In fig. 3, referring to run no. 2, which lasted more than 500 hours, the excess power is reported as a function of time, for a large part of the run. In the first 120 hours, not shown in the figure, the period was of 20 000 s, and no excess power was detected. In the last 150 hours, also not shown in the figure, the period was 9000 s and no excess power was detected. After the run, we found that the anode showed macroscopic holes in its body, which altered the electric-field configuration in the cell: this presumably produced the «shutting-down» of the observed phenomenon in the last part of the run. The observed holes are attributed to the continuous transfer of palladium from anode to cathode during the electrolysis. Even though it is difficult to establish a quantitative correlation between the period and the excess power, it seems reasonable to infer from the data presented here that shorter periods are more effective in producing the phenomenon.

The last peak shown in the figure is the maximum excess power measured, quoted above: note that it lasted about 20 hours.

b) Dependence on the voltage. An accurate determination of the electrolysis' parameters would require the measurement of the cathode's potential, *i.e.* the potential measured with respect to a reference electrode. We did not have a reference electrode, and thus we could only measure the difference of potential between the two electrodes (which in the following we will call «the potential»), while a constant current was passing through the system. In fig. 4 data from run no. 3 are reported. In this run we purposely changed the current intensity by steps, and the values of the difference of potential between the electrodes are shown in fig. 4a) and b), respectively for the high-current mode and the low-current one, as a function of time. Note that in the first half of the run we increased the current in four steps, and then we decreased

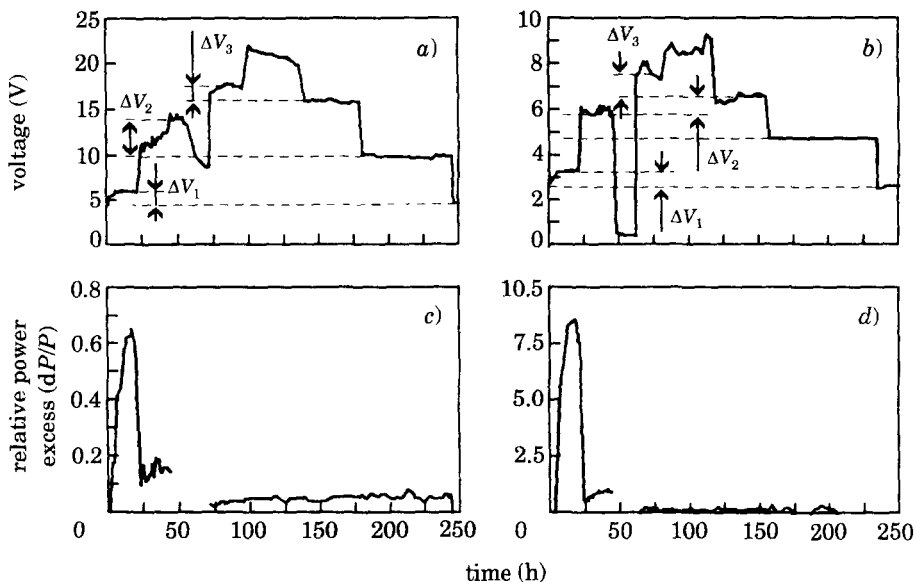


Fig. 4. - Run no. 3. During the run the current has been increased in four steps, and then decreased in the same four steps. The values were (a) and c) refer to the high-current mode, b) and d) to the low-current one): 7-50, 50-200, 150-350, 200-600 mA/cm². In a) and b) the voltage across the cell is plotted vs. time. In c) and d) the corresponding relative power excess is shown. The ΔV 's represent the difference between the voltage during the stepping up and that during the stepping down of current, the latter with a substantial absence of power excess: this quantity in the text has been called by convention «the overpotential».

it, running along the same steps. In fig. 4c) and d) the corresponding values of the power excess are reported on the same time scale. In this experiment a large power excess was measured in the first part of the run; then, a failure of the low-current generator had the effect of strongly decreasing the power excess, which never came back to the previous value. The dashed lines drawn on fig. 4a) and b) show that in the first part of the run, when excess power was detected, the potential across the cell, for the same current, was higher than in the second part, when no excess power was detected. The difference between the two measurements, that we define the «overpotential», ranges from about 10% to about 50% of the value measured in the absence of power excess. Thus, it is possible to state that there is a clear connection between the overpotential and the production of power excess.

c) Dependence on pressure variation in the gas. In fig. 5 we report data from run no. 3, the same run as fig. 4. In order to investigate the flow of deuterium gas through the cathode, the pressure in the gas volume behind the cathode is continuously monitored, keeping both volume and temperature substantially constant. The flow can then be easily evaluated using the ideal gas law. In fig. 5 the time derivative of the pressure, expressed as the number of deuterium atoms crossing the cathode surface per unit time, is plotted as a function of time: the negative sign of the flow indicates that deuterium gas is flowing into the cathode. Two characteristic regions of the run are shown: in fig. 5a) at the beginning of the run, and in fig. 5b) at the end of it. In the same graphs the corresponding power excess is shown. The correlation between power excess and permeation of deuterium

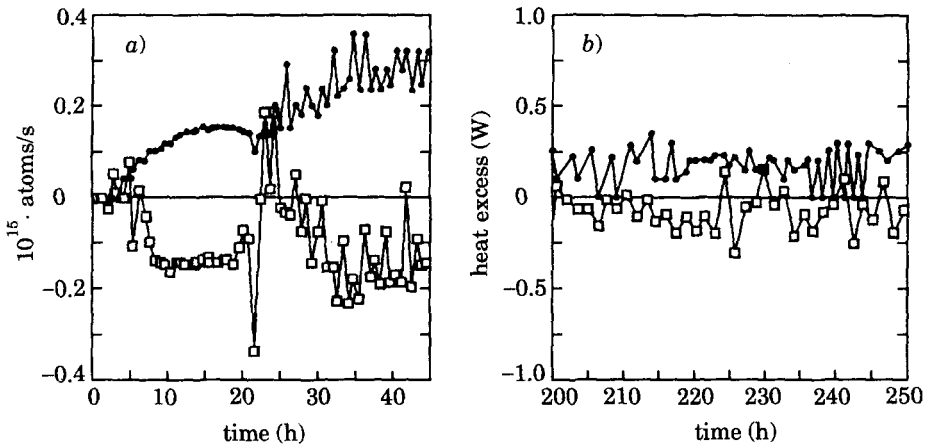


Fig. 5. - Run no. 3 again. The first 50 hours (a) and the last ones (b) are reported. The time derivative of the pressure is shown as a function of time, and is expressed as the number of atoms per second crossing the cathode (squares): the negative sign means that deuterium is entering the cathode from the gas side. On the same graphs the power excess is reported (dots). The two graphs show a very different behaviour in the two instances: in the presence of a significant power excess (a) and when power excess is absent (b).

gas into the cathode is clear: when power excess is produced, there is a clearly measurable flow of deuterium into the cathode.

5. - Conclusions.

The experiment described here has confirmed the production of heat excess in an electrolytic cell with heavy water and a palladium cathode, using an accurate and reliable calorimetric measurement. The geometry used in the cell, in particular the possibility of measuring the permeation of deuterium gas through the cathode during the electrolysis, represents a step forward in the study of this class of phenomena. It permits to investigate the dynamics of deuterium atoms in the palladium lattice, which seems to be a promising means for understanding the physics of high-concentration metal hydrides.

Two of us (ADN and VV) have developed a model, designed to interpret the movement of deuterium atoms in the palladium lattice as matter waves, and studied superposition and interference phenomena of the waves. The model yields results that fit quite well some of the features of the experiment. A paper on this subject will be submitted for publication.

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