DEUTERIUM GAS LOADING OF PALLADIUM USING A SOLID STATE ELECTROLYTE

Jean-Paul Biberian and Georges Lonchampt[*]

CRMC2-CNRS, Faculté des Sciences de Luminy, 138, Avenue de Luminy, 13288 Marseille cedex 9, France
[*] 31, chemin Malanot, 38700 Corenc, France

ABSTRACT

A palladium foil cathode, 50 mm in diameter, 100 µm thick is placed between two anodic palladium foils of same dimensions. A proton conductor layer (poly-ethyleneoxide) (PEO) and phosphoric acid) is deposited between the cathode and the two anodes. The system is placed in a chamber filled with deuterium gas, at a temperature of 75°C. At first, deuterium fills the two anodes up to D/Pd = 0.48 measured by pressure decrease. Then a voltage is applied between cathode and anodes, and the cathode gets loaded by D^+ electrochemical migration through the solid state electrolyte. Correspondingly, the pressure decreases. Loadings of up to 0.73 have been obtained. When voltages are reversed, the cathode deloads, and the pressure in the chamber increases. This method is well suited to measure over-potentials and absolute loadings. The input power is very low, since the production of D+ ions entering the cathode is close to 100% whereas in liquid electrolyte cells, a small fraction of the ions produced is absorbed by the cathode. Therefore excess heat measurement is easily detected.

1 INTRODUCTION

It has been established by several authors that excess heat observed in Cold Fusion experiments is highly dependent on deuterium loading. According to McKubre et al [1], an average value of D/Pd larger than 0.85 to 0.9 needs to be achieved in order for the nuclear reaction to occur. A major difficulty that is the source of the irreproducibility of Cold Fusion experiments is how to achieve such a   high loadings, and secondly how to measure it. The resistance measurement has been extensively used by many authors, but it is not an absolute measurement. Also high loading is hard to achieve, because as loading increases, the equivalent deuterium pressure in the sample increases dramatically. In their original paper, Fleischmann and Pons (2) correlate over-potential to an equivalent astronomical pressure of deuterium. The relation between over-potential and deuterium pressure is given by the Nernst law

$$\eta = -\frac{RT}{nF} Log \frac{P_1}{P_2} \qquad (1)$$

where:

η	Over-voltage in volts,
R	Perfect gas constant : 8.32 Jmol^{-1}K^{-1}
T	Temperature in Kelvin,
n	Number of electrons involved during the reaction 2D$^+$ + 2e $\rightarrow$ D2 (here n=2)
F	Faraday constant(96500)
P_1, P_2	Deuterium pressure

In an electrochemical cell if an over-potential of 1 Volt is reached, then this corresponds to loading with an external pressure of deuterium gas of 10^{33} atmospheres! The over-potential is of complex origin, and difficult

to measure. So far most Cold Fusion experiments have been performed with a water electrolyte, and atomic deuterium at the cathode is produced by dissociation of heavy water. A fraction of which dissolves in the palladium cathode. Therefore a large quantity of power is wasted, and makes excess heat measurements less reliable, since the total enthalpy measured is the sum of the input power and the anomalous heat produced. A large input power decreases the precision of excess heat measurement.

2. EXPERIMENTAL SET UP

Figure 1 gives a description of the experimental set up. A palladium foil cathode 50 mm in diameter 100 μm thick is positioned between two anodes of similar dimensions. A solid state electrolyte is placed between the anodes and the cathode. The electrolyte is poly (ethylene oxide) (PEO) containing deuteriated phosphoric acid. It is a deuteron conductor.
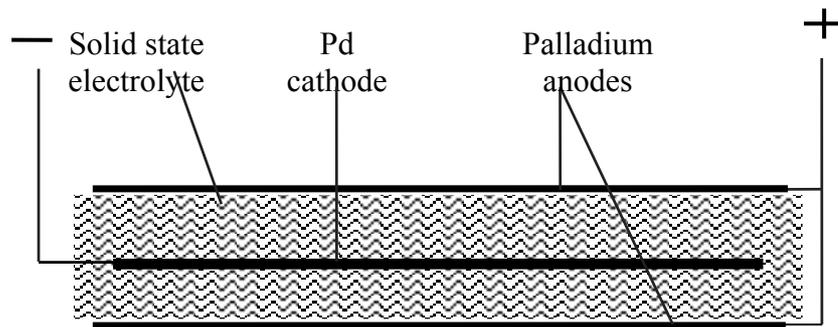
Figure 1

This electrolyte is used in lithium batteries, and operate between 70 °C and 120 °C. The PEO solvates the phosphoric acid making the D^+ ions mobile.

$$O - CH_2 - CH_2 - O - CH_2 - CH_2 - O - CH_2 - CH_2 - O - CH_2 - CH_2 -\ldots\ldots\ldots$$

$$D_3^+ - PO_4^- \qquad D_3^+ - PO_4^- \qquad D_3^+ - PO_4^- \qquad D_3^+ - PO_4^- \cdots\cdots\cdots$$

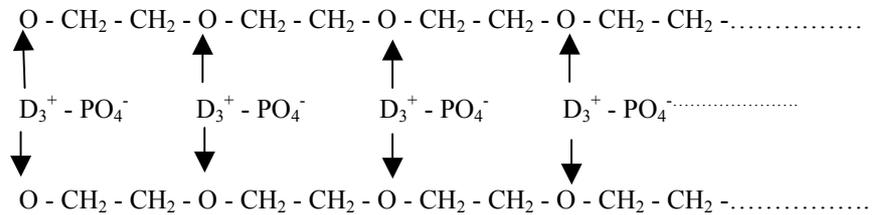$$O - CH_2 - CH_2 - O - CH_2 - CH_2 - O - CH_2 - CH_2 - O - CH_2 - CH_2 -\ldots\ldots\ldots$$

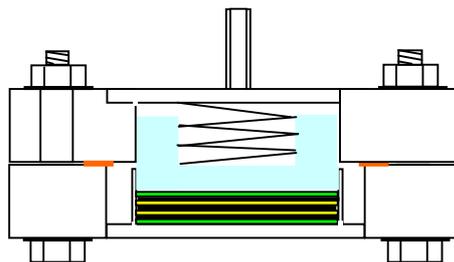Figure 2 shows a schematic of the electrolytic cell, it is

Figure 2

Figure 3 shows the calorimeter set up. The cell is placed in a 100x60x60 cm³ insulated box.. The temperature inside the box is maintained constant by a water heated radiator placed inside the box. The room in which the experiment is placed is regulated within +/- 0.5 K. The cell is at the center of a 40x40x40 cm3 box filled with polystyrene insulator. Temperatures are measured with calibrated thermistors at the top and bottom of the cell, and at the top and bottom of the insulating box.

Calibrations have been made with a resistor, and the calibration is 20 K/W. A temperature rise of 0.02 K corresponds therefore to an input power in the cell of 1 mW. This is the actual precision of the calorimeter.
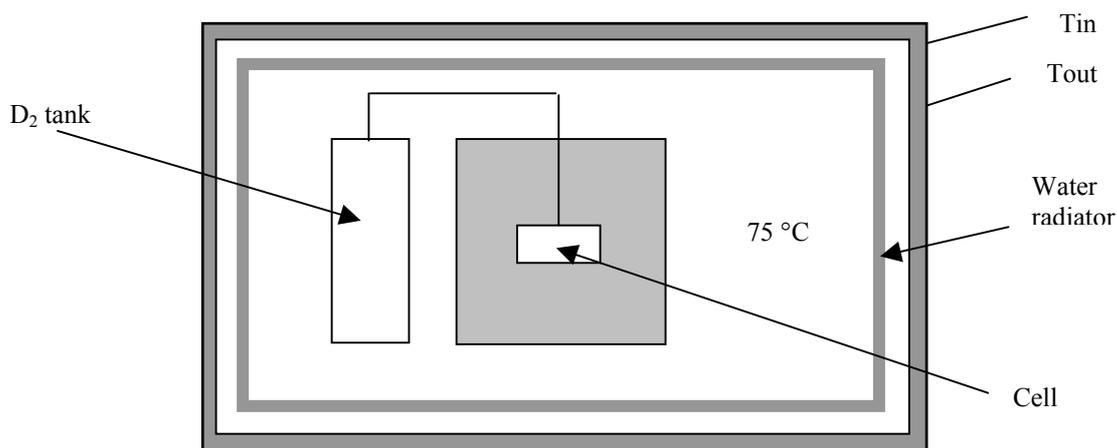

Figure 3

3 EXPERIMENTAL

The principle of operation is the following:

- At the anodes: the D_2 gas diffuses in the anodic palladium as D, at the interface with PEO D$\rightarrow$ D$^+$ + e$^-$

- Inside the PEO electrolyte, the D$^+$ ions migrate under the action of the electric field

- At the cathode, D$^+$ + e$^-$ $\rightarrow$ D, and diffuses inside the cathodic palladium.

Therefore as a result, during electrolysis, the deuterium is transferred from the external tank inside the palladium cathode. The operation is performed at constant voltage. As the cathode loads up, its potential increases, and the current decreases. Ideally, if there is no deuterium recombination at the cathode surface, the current should drop to zero when the electrochemical potential of the cathode equals the applied voltage. As the cathode gets loaded a double layer forms near the cathodic surfaces.

Figure 4 shows a potential diagram of the voltage between anodes and cathode when an external voltage of 1 Volt is applied. The vertical section of the potential curve corresponds to the double layer at the cathode formed by D+ ions at the surface of the palladium and electrons inside the palladium. The inclined lines are produced by the Ohmic resistance of the electrolyte.
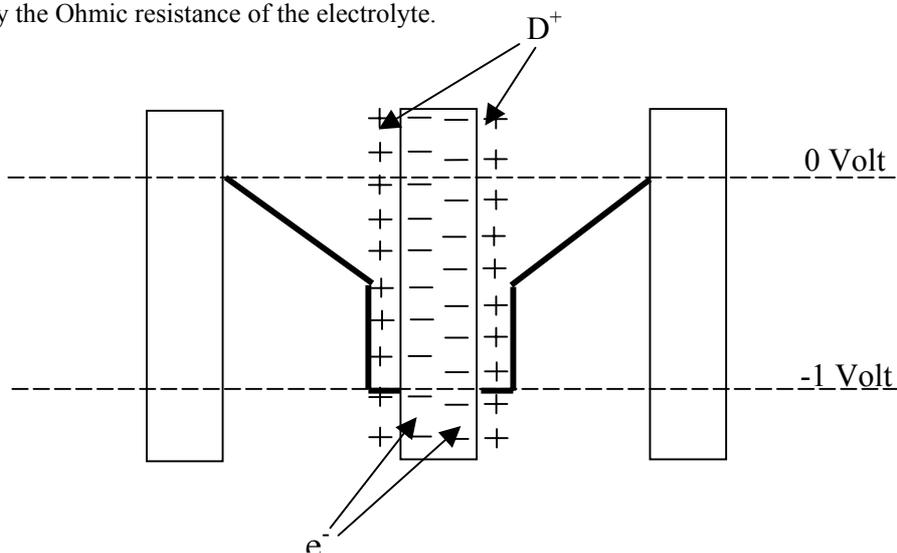

Figure 4

4 EXPERIMENTAL RESULTS

4.1 LOADING

The experiment described here has been conducted at a temperature of 75°C. The proton conductor thickness being 400 µm. Figure 5 shows the pressure variation versus time, as well as the temperature increase at the top of the cell.. One observes two sections: a fast pressure drop from 786 to 618 Torr corresponding to the absorption of deuterium in the anodes, and a slower pressure decrease, corresponding to absorption in the anodes and the cathode. Part of the pressure drop in this second section is due to the absorption of deuterium gas directly in the cathode, and part due to the electrical loading This indicates that the PEO is not completely sealed, and that some deuterium molecules pass through the PEO and are absorbed by the cathode. At maximum loading D/Pd = 0.48 in the anodes, and D/Pd = 0.73 in the cathode.

4.2 HEAT OF ABSORPTION

Our heat calibration: 20 K/Watt is applied to calculate the heat of absorption of deuterium in palladium by integration of the temperature curve during the first stage of loading. The calculated value is 9500 +/- 500 cal/mole D_2. This value is slightly larger than the literature one, 8100 +/- 150 cal/mole D_2 measured on powdered palladium. The difference might be due to the fact than on metal particles a surface effect decreases the absorption energy.

Also, the pressure decrease versus time is in agreement with a diffusion coefficient in the 10^{-7} cm^2 s^{-1} range.
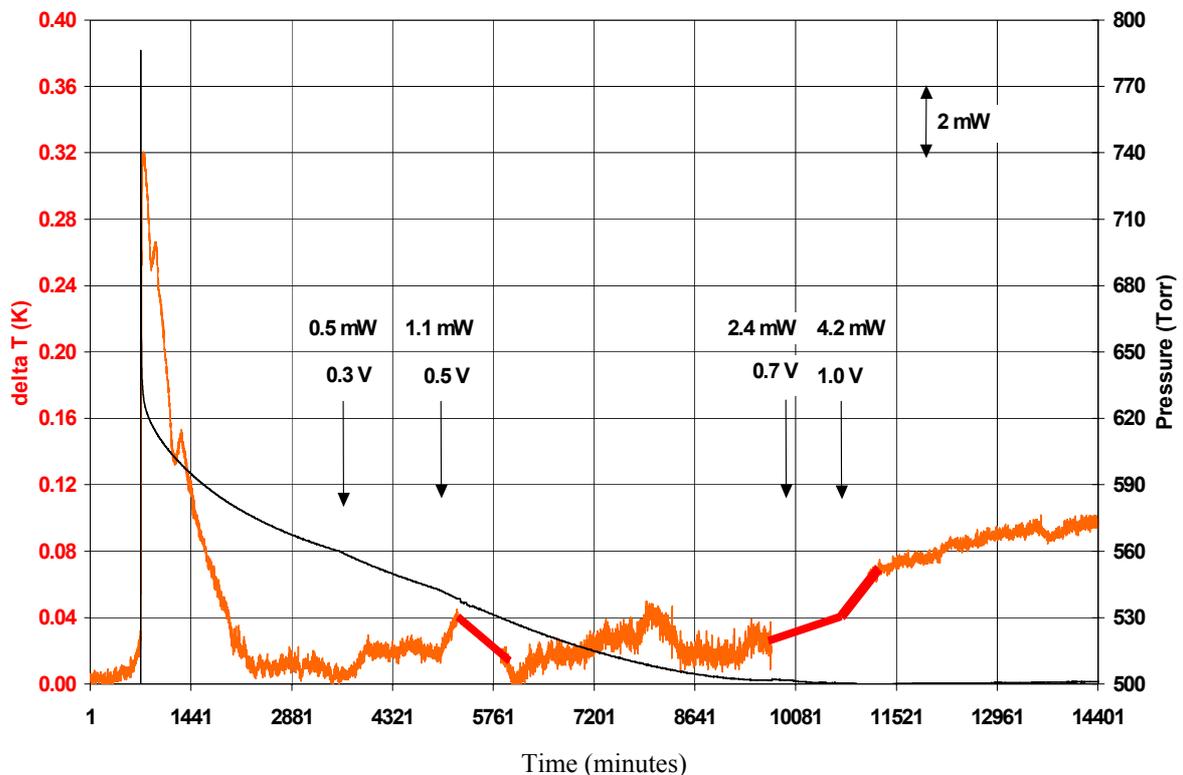

Figure 5

4.4 – DOUBLE LAYER

At 1 Volt potential, we have measured the resistivity by adding an AC voltage to the DC current, The resistivity varies from 500 Ω at 10 Hz to 214 Ω at 20 kHz. We can deduce from this that the circuit is equivalent to a resistor **R** in series with a capacitor **C**, with the following values:

$$R = 210 \ \Omega \quad \text{and} \quad C = 27 \ \mu F$$

The DC current being 2.32 mA at 1 Volt, we can deduce that the over-voltage

$$\eta = 510 \ mV$$

This calculation of η is in agreement with the open-circuit voltage 400 mV measured on an oscilloscope when the circuit is suddenly opened.

If we consider the double layer as a capacitor **C**, with charge **Q** and a voltage η, we can deduce:

$$Q = 1.4 \ 10^{-5} \ C, \text{ and } 1.3 \ 10^{13} \ D+/cm^2$$

4.5 – DELOADING

When voltages are reversed, the cathode becomes anodic and deloads. On several occasions we have been able to repeat the cycles several times. This is another method for measuring the D/Pd ratio in the cathode.

4.6 – EXCESS HEAT

So far we have not observed any excess heat. However in previous experiments with a much less accurate calorimeter we have observed temperature anomalies that we wish to confirm with this new system.

5- CONCLUSION

We have developed a new technique for loading deuterium in palladium. Using a proton conductor, it is possible to measure with precision deuterium loading in the cathode. Our calorimetry has a sensitivity of 1 mW, and therefore is capable of measuring even small excess heat production. We have determined the heat of absorption of deuterium in palladium 9500 +/- 500 cal/mole D_2. We are now presently working in improving the system to detect any anomalous excess heat production.

ACKNOWLEDGMENTS

REFERENCES

[1] M.C.H. McKubre, S. Crouch-Baker, F. Tanzella, M. Williams and S. Wings, Proceedings of ICCF6, October 13-18, 1996, Japan, pages, 75-82.

[2]- M. Fleischmann and S. Pons, J. Electronal. Chem. (1989) 301-308.