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PRODUCTION OF EXCESS ENTHALPY IN THE ELECTROLYSIS OF D₂O ON Pd CATHODES

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1. INTRODUCTION

We report the preliminary results of an experiment aimed at detecting the simultaneous production of excess heat and ⁴He in Palladium cathodes loaded with Deuterium up to a stoichiometric ratio $x=D/Pd$ larger than 1.

In a different presentation to this Conference [1] the dynamics of the loading has been discussed.

When x rises above 0.7, deuterons enter into a coherent state [2], described by a unique wave function, whose phase includes any externally applied electric potential as stated by quantum physics. Thus, by applying an electric potential $-V$ to a one-dimensional cathode, we are able to lower the D chemical potential by an amount:

$$\delta\mu = -Z^*eV \quad (1)$$

where Z^*e is the screened charge of a D nucleus in the Pd lattice.

Lowering the barrier which normally prevents the further loading of Palladium beyond the β -phase is an effective method to reach the critical threshold $x=1$ above which the “anomalies” of the enthalpy and Helium production start.

2. EXPERIMENTAL LAY-OUT

We have compared the loading of a Pd sample with and without the application of a longitudinal electric potential. Thin films are the best candidates to study highly loaded systems since their loading is approximately linear in time up to the β phase and the time of loading is considerably reduced with respect to massive samples. However a thin Pd deposit, a few cm^2 wide and 1 or 2 microns thick to be used as a cathode in electrolytic experiments, has an electric resistance of a few tenths of Ohms. Thus the application of a large voltage drop across such a deposit will produce a current flow that will induce a large Joule heating. Such a temperature increase can in principle destroy the coherence; to reduce this counter effect the electrical resistance of the cathode should be made as large as possible. The best solution is a one-dimensional cathode, having a great length and a narrow cross-section. At ICCF8 we reported a series of experiments carried out with cathodes with a suitable geometry. [3] The preliminary measurements have shown that the D/Pd loading was 30-40% higher than that for a sheet cathode and this loading has been also achieved in a much shorter time. However such cathodes had very severe limits since their mechanical fragility limited the duration of the experiments to a few hours at best. Moreover the deposits did not survive excess heat production. We have devoted our main effort to the production of deposits with a better adhesion to the substrate in order to sustain the mechanical stress induced by Hydrogen or Deuterium loading. New cathodes with the same geometry as in the previous experiments have been obtained by sputtering Pd on an inert substrate (Alumina, Sapphire or crystal Silicon); different kinds of buffer layer have been tested in order to have a good adhesion and special care has been devoted to the mask alignment and in the pattern etching that have turned out to be critical since the presence of under etching (i.e. corrosion of the metal-substrate interface) decreases the contact surface between the film and the substrate. These structures have a total length of about 1 m, 54 μm wide and 2 μm thick their typical electrical resistance is about 2500 Ohms.

Electrolysis was performed in a small (8.5 cm^3 volume) electrolytic cell filled with 5.5 ml 10-4M LiOD solution whose conductivity was $104 \pm 1 \text{ } \square\text{S/cm}$; a Pt sheet parallel to the cathode has been used as the anode (anode-cathode separation is 5 mm).

The Hydrogen (Deuterium) loading is estimated by measuring the ratio of the electrical resistances R/R_0 (where R_0 is the resistance of the empty palladium matrix) which is a known function of the loading, valid for an homogeneously loaded sample. However it is quite difficult to measure the cathode resistance independently of interference by the electrolytic current. Actually, part of the cell current flows into the cathode and eventually adds up (with its sign) to the current used to measure the resistance. An AC measurement by a lock-in amplifier can be used when the cathode resistance is in the range of hundreds Ohms which is the maximum load that a wave generator can withstand. In order to perform a DC measurement, independently of the load, a switch that excludes the electrolytic current during the DC resistance measurement must be used.

The cell voltage does not drop to zero sharply when the switch is opened. If the switching time is short enough (180 ms in our case), the cell voltage is not allowed to decrease below the thermoneutral potential (1.54 V), so that the loading process is not interrupted. During such a time a DC current is allowed to flow into the cathode to measure the resistance (see fig.1).

The electrolytic current itself produces the voltage drop along the cathode and allows the sudden decrease of the Pd/D chemical potential as soon as the system undergoes a spontaneous (without any change in the electrical parameters) β - α phase transition due to the threshold achievement as in fig.2. The effect is also induced by increasing the current and thus the potential over a threshold value, driving the system to the transition.

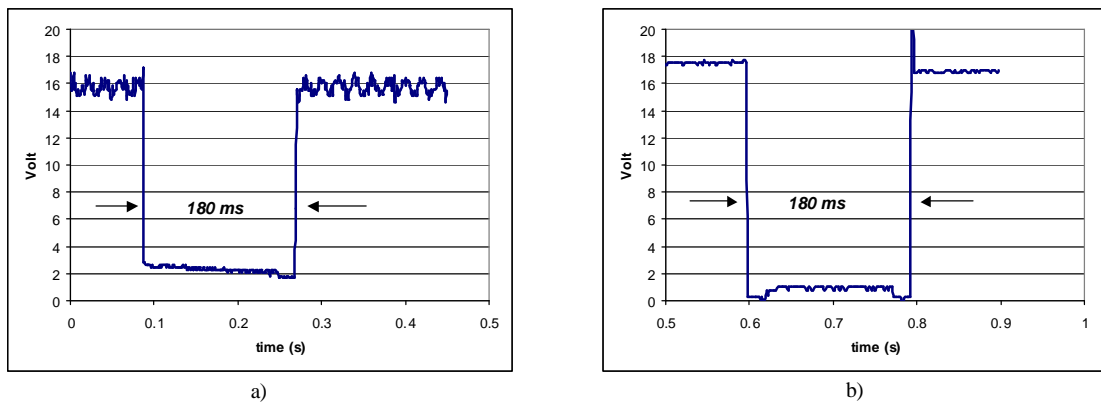


Fig.1 a) Residual voltage between electrodes during the measurement of the resistance R ; b) voltage across the cathode in the same period.

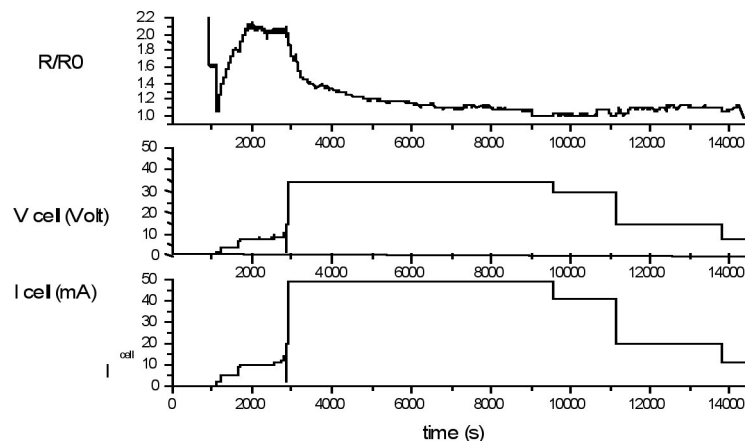


Fig. 2 Cell current I_{cell} , voltage across the cathode, $V_{cathode}$, and normalized resistance R/R_0 vs. time. The I_{cell} and the related $V_{cathode}$ increase induce a sudden drop in R/R_0 corresponding to an increase of loading from $x=0.7$ to $x > 1$ within a few seconds.

Obviously, an increase in the cell current produces a linear increase of $V_{cathode}$ but such current densities (20 to 100 mA/cm²) are not effective in obtaining similar results on plates or massive depositions in such a short time.

It is worthwhile to note that films suitably realized can show a very satisfactory behaviour in terms of adhesion to the substrate during several cycles of loading and de-loading. We did not observe detachment from the substrate or breaking of the cathode structure even after many cycles. We have checked the Pd

lattice structural parameters after several cycles and we have found that even if the lattice parameter and the crystallite size do not change significantly, the micro strain shows that an average plastic deformation has occurred to the Pd bulk (see table I).

TABLE I

	As received	After cycles
Lattice Parameter (Å)	3.8805 ± 0.0025	3.8826 ± 0.00024
Crystallite size (Å)	357 ± 78	367 ± 26
Micro strain	9.253 E-4 ± 3.76 E-5	4.8 E-3 ± 2E-3

3. CALORIMETRY OF COHERENT NUCLEAR REACTIONS

Calorimetry of nuclear reactions in vacuo is usually done by stopping all the nuclear fragments and measuring the energy released to the stopping medium. In the case of nuclear reactions in condensed matter the heat released in the material (i.e. into the Pd cathode) is only a fraction of the total amount of the energy produced. Because of the high temperature and erratically fluctuating reactions an important amount of energy is emitted in form of IR radiation and can thermalize far from the cathode thereby escaping calorimetric detection. The most reliable calorimetry is then reached by collecting all the reaction products, here ⁴He atoms. Local measurement of heat can therefore only give a lower bound of the energy produced or in the limit simply serve as a watchdog of the reaction.

Our experiment has been designed to allow both heat and ⁴He measurement on line so allowing us to have a qualitative and quantitative comparison between the data. In a further paper submitted to this Conference[4] the details of ⁴He measurement that is now being implemented are discussed.

Gases evolving from the cell, after being thoroughly purified of all the non-noble species, are analysed so that we get the fraction of the noble gases (He, Ar, Ne) present in the specimen. It is thus possible to gain a calibration in terms of the natural relative abundances in the atmosphere; in terms of this calibration we can get a baseline for ⁴He, measurements of ⁴He above this baseline must be attributed to a source within the cell.

Excess heat has been measured using a commercial Peltier element in good thermal contact with the cathode substrate. A linear relation can be found between the power dissipated into the cell and the voltage displayed by the Peltier element.

The overall outcome of the experiments so far now is the following :

1. Excess heat appears rapidly when $R/R_0 \leq 1.4$, namely when $x \geq 1$ (within the time constant of the calorimeter 160 sec);
2. in all the experiments the heat measured by the calorimeter is at the level of about 20 mW, corresponding to an unitary rate of 0.2 kW/cm³ (see fig.3);
3. in one experiment a section of the cathode (corresponding to the section with the most negative potential and, thus, with the highest loading according to the Preparata effect) suddenly melted, in spite of the calorimetric measurement of an excess of only 20 mW. The molten section accounted for the 5% of the total volume (see fig.4). One could hardly observe the melting of the stripe unless the system is driven from nucleate to film boiling.[7] Taking the conventional view that this transition occurs at 60 W/cm² this would require in our case a specific excess energy of 600 KW/cm³. Since the heat of melting of Pd is 17.66 KJoule/mole the time required for melting at the above rate of excess power production is about 3 ms in agreement with the observed phenomenology.

This last result suggests that our thermal calorimetry is unable to detect the production of excess heat above a quite low level.

A possible interpretation is that when the rate of fusion increases, the instantaneous temperature of the "hot spots" reaches the level where the bulk of the dissipated heat escapes through the Stefan-Boltzmann radiation channel. The amount of the energy irradiated away is proportional to T^4 , whereas the peak energy, when $T < 1900^\circ\text{K}$, is in the infrared region of the spectrum. Since the volume of our cells is very small, the Peltier sensor occupies only a fraction of the full solid angle and the cell walls are quite transparent to the

radiation. It is therefore conceivable that, at high T, a large fraction of the irradiated heat is lost, whereas on the contrary the thermodynamics of melting provide more reliable estimates.

Further missing parts of the missing energy are the fractions invested into possible nuclear transmutations or in the production of X rays.

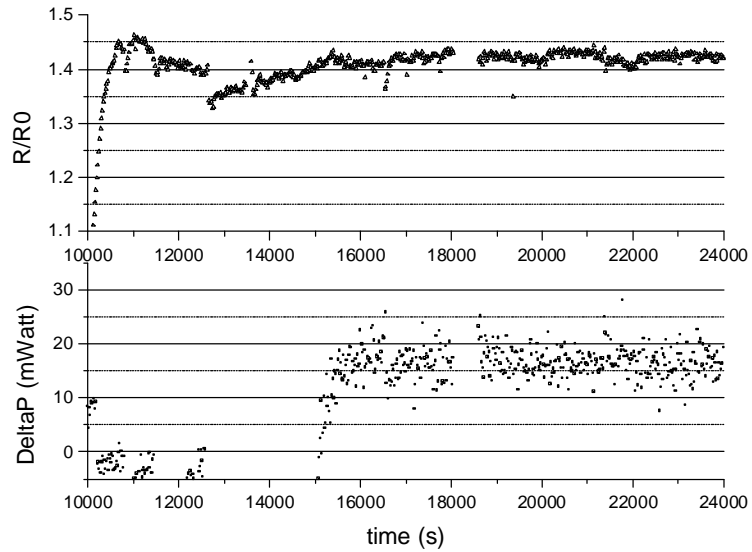


Fig.3 As soon as the threshold $x=1$ ($R/R_0 = 1.4$) is reached a tiny but clear excess heat appears.

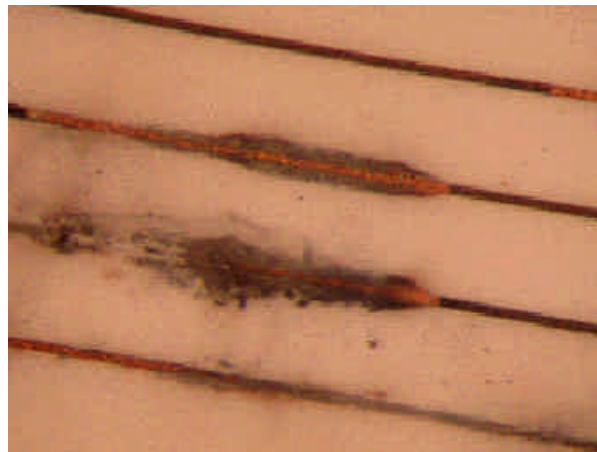


Fig.4 Section of a cathode burned during electrolysis. During the event the I_{cell} was 4 mA and $V_{cathode}$ was 30 Volt (supplied by an added generator), the extended damage is seen in several separated subsections so that the melting cannot be attributed to Joule heating

4. CONCLUSIONS

The Preparata effect is a very efficient and reproducible mechanism to obtain a 30% -40% gain in D loading. The existence of this effect proves that D nuclei in the Pd lattice are in a coherent state. The effect is easily obtained through the voltage drop across the one-dimensional cathode induced by the electrolytic current. The most suitable geometry of the cathode to give good control of the parameters ($V_{cathode}$, loading ratio, excess heat) during the experiment is the “bustrophedic” pattern on a thin film. Pd thin films show, however, a very high mechanical instability during Hydrogen or Deuterium loading because of the elongation of the lattice parameter. To solve this problem it is necessary to find an appropriate buffer layer between Pd and the substrate and to obtain a sharp profile of the pattern. We have found that thin deposits on Alumina are able to sustain several load-deload cycles and very high loadings ($x > 1$) have always been obtained.

Using such a peculiar loading it is possible to reach reproducible heat excesses from heavy water electrolysis with Pd thin films cathodes.

The peculiarity of the coherent nuclear reaction in a solid shows that the calorimetric data must be interpreted with some reservations: because of the high local temperature of the reaction, a considerable part of the energy is released as IR radiation and can, therefore, be absorbed far from the temperature transducer. Conventional calorimetry, based on the measurement of the thermal constant of the calorimeter, can give misleading results because, during erratic high temperature events, such a thermal constant can change. Both Martin Fleischmann[5] and Giuliano Preparata[6] have discussed this topic extensively in the past years suggesting isoperibolic calorimetry as a solution: in this case the thermal constant is evaluated as a function of time by supplying small amounts of heat to the calorimeter and measuring the time constant of the temperature rise. However this method implies a quite heavy mathematical analysis and could be inaccurate when there are noisy temperature signals due to thermal instabilities or turbulence in the cell.

The most reliable calorimetry then turns out to be the nuclear product measurement. According to the prediction of QED the measurement of ^4He can give a reliable account of the energy produced during the reaction according to the figure $1 \text{ Joule} = 2.6 \cdot 10^{11}$ atoms of ^4He . Experiments aimed to measure ^4He atoms in real time during the electrolysis are in progress in our laboratory in Frascati.

5. ACKNOWLEDGMENTS

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