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ANALYSIS OF TRITIUM AND HEAT EXCESS IN ELECTROCHEMICAL CELLS WITH Pd CATHODES

L. Bertalot, L. Bettinali, F. De Marco, V. Violante
Associazione EURATOM-ENEA sulla Fusione, Centro Ricerche Energia Frascati, C.P. 65 -00044 Frascati, Rome, Italy

P. De Logu, T. Dikonimos Makris, A. La Barbera
ENEA, Dipartimento INN-PCM, Centro Ricerche Energia Casaccia, Rome, Italy

INTRODUCTION

The origin of the excess heat [1,2] developed during the electrolysis of heavy water in "Cold Fusion" cells is up to now open to question. The necessary presence of deuterium suggests that fusion reactions can be partially or totally responsible for the generation of excess heat.

Experience has shown neutron emission to be sporadic and very weak; on the other hand tritium was found in small but detectable amounts [3,4]. Moreover if tritium accumulates in the solution it can be comfortably measured postmortem.

Two experimental campaigns were performed:

The first one in Frascati having as main objective the detection of tritium excess. Particular care was exerted to avoid any tritium and hydrogen contamination.

The second one at the Texas A & M University in the framework of a scientific collaboration, having as objective the excess of heat and tritium measurement.

EXPERIMENTAL

Electrochemical cells

Two type of cells were used.

The first one was used in Frascati for nine tests (named C1 to C9) and is shown in Fig.1a. The vessel is made of glass and the lid of teflon. The lid is screwed on the top of the cell. The connector for the Pd cathode is a nickel tube containing a thermocouple to detect the cathode head temperature. The tube is insulated from the solution by means of a glass tube sealed with araldite. Different anodes and dimensions were used. Some details are reported in Table I.

The second type of cells was used at TAMU for three experiments (named C10 to C12) and it is shown in Fig 1b. It was made of stainless steel with a teflon lid. The lid is screwed on the top of the cell and it has two connectors and a valve to permit a free gas evolution. The connector for the Pd wire is a Pt wire spot welded and insulated from the solution by using a teflon tape wrapped around it.

All the Pd cathodes were annealed under vacuum before use. In the Frascati experiments they were treated at 1000 °C for 10 h. In the calorimetric tests the cathodes were treated at 950 °C for 1 h. In every case the Pd cathodes were washed in ethanol, rinsed in water and in heavy water just before the cell assembling. Pd wires from Engelhard 99.95% were used for the cells C1 to C4, from Johnson & Matthey 99.9997% for the cells C5 to C9 and from Alpha Product 99.997% for the cells C10 to C12. Platinum and Nickel from Carlo Erba 99.5% were used as anodes for the cells C1 to C9 and platinum from Alpha Product 99.9995% for the cells C10 to C12. Heavy water from Fluorochem Limited 99.9% atomic in deuterium for the cells C1 to C9 and from Aldrich with 99.8% atomic in deuterium for the cells C10 to C12 was used. Both had similar activity of about 185 dpm/ml. Lithium from Carlo Erba 99.9% for the cells C1 to C9 and from Aldrich 99.9% for the cells C10 to C12 was used. Deionized water for the cell C11 and Sodium deuteroxide from MSD Isotopic 99.8% atomic in deuterium for the cell C12 were used.

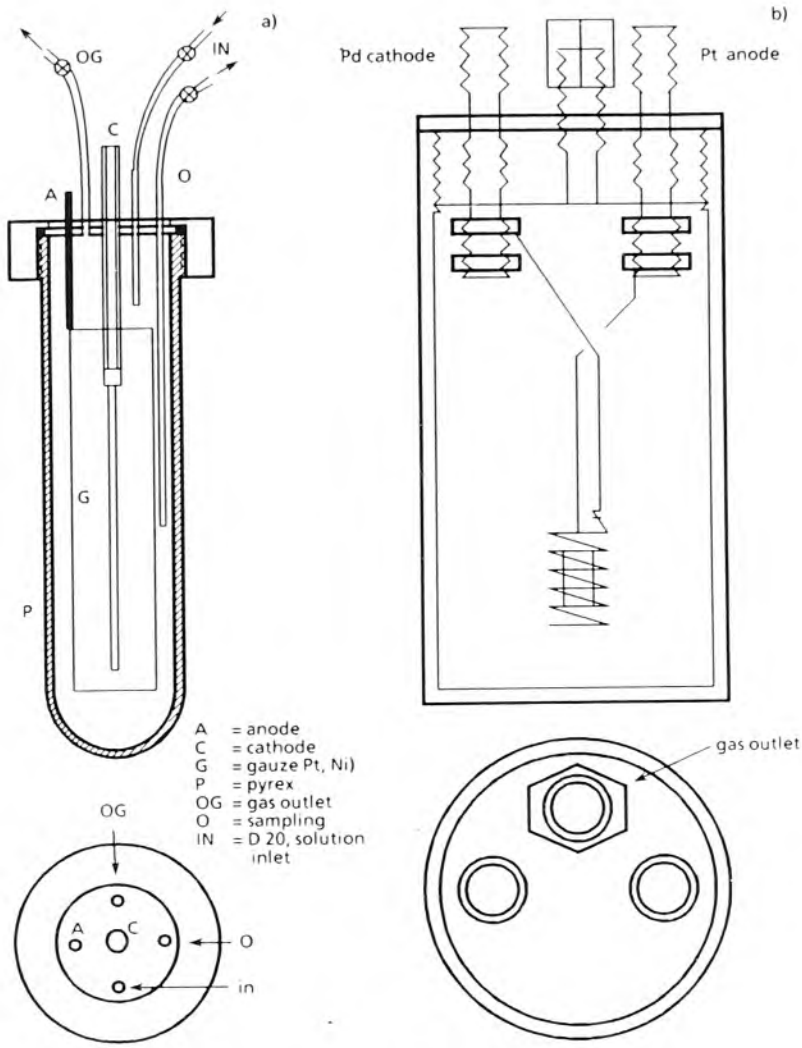

Fig. 1a - Frascati cell **Fig. 1b - TAMU cell**

Diagnostics

The neutron detection equipment consists of three ^{3}He neutron counters and a BF_3 counter, all embedded in polyethylene. One of the ^{3}He detectors is used to monitor the noise/background signal. The overall efficiency of the counters are in the order of 5 10^{-5}-10^{-4} cts/n. The minimum detectable neutron emission rate is 30 n/s at the source. No significant neutron emission rate above the minimum detectable rate has been observed in all the experiments.

The tritium measurements, within $\pm 3\%$ error, have been carried out by means of a BETA counter 2560 XL Packard, having a 33% efficiency for tritium. The background level was 4 CPM. The tritium measurements have been performed by taking into account the radiation energy spectrum emitted by the liquid scintillator.

Chemical and microstructural characterization of the cathodes was performed by using an high resolution scanning Auger spectrometer Perkin Elmer model 600.

Calorimetry

A commercial available 4 cells Hart Scientific Model 8244 heat conduction calorimeter was used to measure the heat output from the electrochemical cells. It was possible to operate with 4 cells at the same time in a power range up to 2 W

Table I - Synopsis of the Cells.

Cells	Anodes	Cathodes Pd wire (mm)	Current density (mA/cm^2)	Time (day)
C1	Pt[a]	1×37[d]	100-700	46
C2	Ni[a]	0.5×82[d]	100-700	36
C3	Ni[a]	as C2[d]	100-700	34
C4	Ni[a]	as C2[d]	100-1200	33
C5	Ni[a]	tube = 6.3[e] ×82×0.15	100	16
C6	Pt[b]	as C5[e]	60	84
C7	Pt[b]	as C2[e]	100-650	66
C8	Pt[b]	as C2[e]	100-650	82
C9	Pt[b]	as C2[e]	100-650	82
C10	Pt[c]	0.5×10[f]	500-950	62
C11	Pt[c]	as C10[f]	600-800	60
C12	Pt[c]	as C10[f]	600	48

[a] Gauze and [b] Coil from Carlo Erba. [c] Coil and [f] from Alpha Product. [d] from Engelhard [e] from Johnson and Matthey

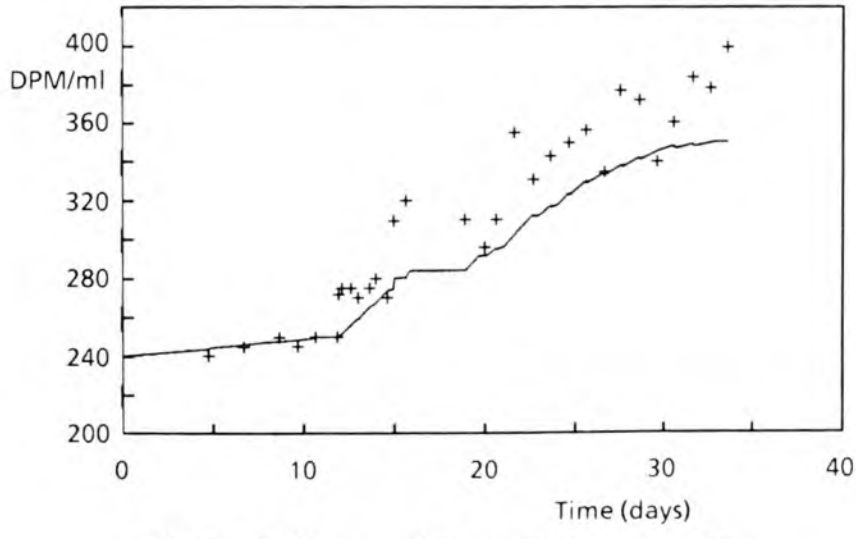

Fig.2 - Tritium enrichment vs time in C3

per cell. The calorimeter is based on the Seebeck effect. A potential proportional to a difference of temperature is generated. Such a potential is then directly proportional to the heat flow coming from the cell. . All the four cells have a twin cell. The system is mounted in a large aluminum block that is submerged in a

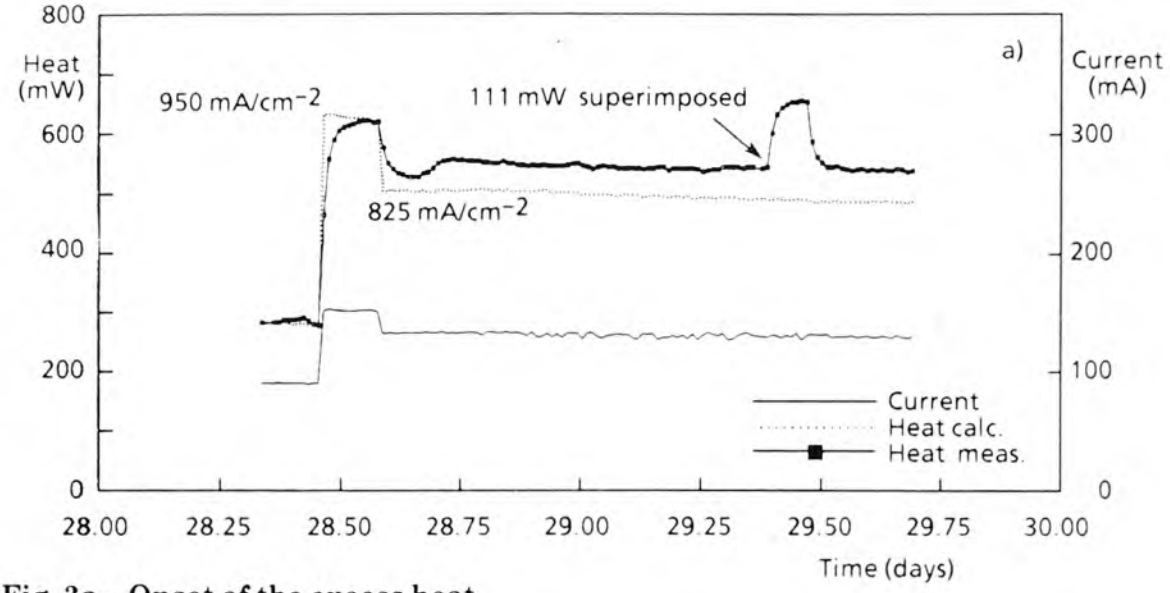

Fig. 3a - Onset of the excess heat

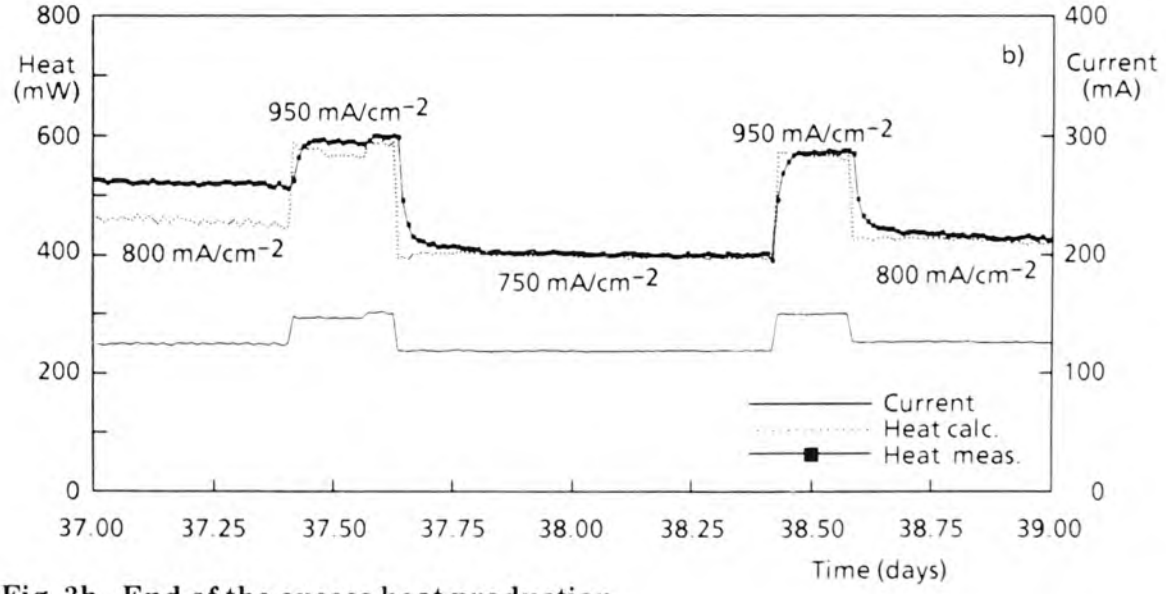

Fig. 3b - End of the excess heat production

constant temperature water bath. When a temperature change occurs in the working cell, a potential is generated and registered. The twin cell design has the advantage of canceling external thermic effect. The signals of the twin cells are connected in a differential way. This connection results in a long-term stability and reproducibility of the base line. The system can easily be calibrated by means of internal resistors and 5 mW is the maximum error estimated.

RESULTS AND DISCUSSION

Tritium measurement

The tritium measurement relative to the cell C3 is shown in Fig. 2. The continuous line shows the isotopic tritium enrichment by assuming 2 as separation factor. The content of tritium in all the experiments is in agreement

with the expected isotopic enrichment even if the behaviour of the single cells is different on a day to day basis. In two of them sharp, short ($\leq$ 12h) increases occurred a few times, that can be fitted with a separation factor larger than 5.

Heat Measurement

One cell out of three gave an excess of heat (cell C10). In Fig.3a and 3b two diagrams relative to heat versus time are shown. The cell was first operated for about 23 days by imposing different current densities and applying current pulses up to 1.4 A/cm^2 (for a maximum time of 30 min). During the following five days the cell was maintained at 600 mA/cm^2. Then the current density was enhanced up to 950 mA/cm^2 for three hours (i.e. the relaxation time of the calorimeter) and then decreased at 850 mA/cm^2. After three hours an excess of heat generation rate of about 50 mW was detected.

To verify if the system were working well 111 mW were superimposed by means of the internal resistor and after three hours exactly 111 mW more were measured (see Fig. 3a). The excess of heat generation rate lasted about 10 days, at that moment the current density was again increased up to 950 mA/cm^2 for a time and then decreased at 750 mA/cm^2: the excess of heat generation rate disappeared (see Fig. 3b). During the 10 days such an excess ranged between 50 and 80 mW, that means 12-20% of the power input. The total energy produced was about 57 kJ ($>$200 MJ/molPd). During the last three days of excess of heat generation rate, the gas evolution was several times measured by means of a flow meter to verify if any recombination took place. The result was 100% $\pm$ 5% of the expected flow rate. To produce an excess of heat of about 50-80 mW a recombination of 25-40% should be considered, which is rather far from the gas evolution measured.

Auger analysis

Semiquantitative Auger analysis performed on cathodes has shown a thick scale of about 200-300 Å mainly constituted of Oxygen, Iron and Calcium and lesser quantity of Copper, Platinum, Silicon and Carbon. Similar contaminants have been found on cathodes used at TAMU and at Frascati.

CONCLUSIONS

- Nine cells were set up in Frascati aimed to detect tritium as the indicator for D-D fusion trying to avoid contaminations.
- No tritium above the electrochemical isotopic enrichment was found.
- Three cells were set up at Appleby's laboratory at TAMU inside a commercial calorimeter.
- One cell gave an excess power ranging between 12 and 20% (25-40 W/cm^3) for about 10 days producing about 57 kJ.
- Post mortem Auger analysis on cathodes revealed similar contaminants.

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