LABORATORI NAZIONALI DI FRASCATI
SIS – Pubblicazioni

LNF–98/007 (P)
16 Marzo 1998

A preliminary D/Pd loading study: anomalous resistivity transition effect

F.Celani, A.Spallone, P.Tripodi, D. Di Gioacchino, G.A. Selvaggi (1), P.Marini, V. Di Stefano (2), S.Pace (3), A.Mancini (4)

(1) Istituto Nazionale di Fisica Nucleare – L.N.F., via E.Fermi 40, 00044 Frascati.
(2) EURESYS, via Lero 40, 00144 Roma
(3) INFM – Dipartimento di Fisica, Università di Salerno, 84081 Salerno, Italy.
(4) ORIM S.r.L., via Concordia 65, 62100 Macerata, Italy

Abstract

Several tests has been performed trying to over–load (D/Pd> 0.8) a Pd wire with Deuterium by mean of electrolytic procedures.

A proper elicoidal electrodes geometry has been adopted to provide opportune electric fields during the electrolysis and several picks up has been located along the wires to obtain a profile of wire Deuterium concentration by mean the resistivity.

Tests operated with high electric current (up to 1 A) flowing along the wire and low electrolytic voltage showed a D/Pd loading of 0.75 at maximum.

Tests operated with high voltage (from 50 to 100 V) have showed in some cases an overcoming of D/Pd= 0.95. In these cases an anomalous effect of cyclical loading/deloading has been newly observed by this group.

No average anomalous heat in excess (more than 15%) has been observed during these tests.

PACS.: 72.15.–v; 82.30.Nr
Key words: Deuterium, Palladium, Resistivity Transition

Presented at the
III Workshop on Cold Fusion, November 27–29, (1987), Asti, Italy

1 – INTRODUCTION

It is common opinion, according many Researchers working on "Cold Fusion" experiments, that to observe heat in excess or anomalous nuclear products it is necessary to saturate a metal matrix (as Pd) by Hydrogen isotopes (as Deuterium) [1)].

A peculiar study is in progress to determinate a reproducible procedure to reach this goal, trying to produce high D/Pd loading values using long thin Pd wires by mean of electrolysis.

It is possible to determinate the D/Pd concentration of a sample from the known resistivity vs concentration curve (R/Ro vs D/Pd) [2,3)] and observing the loading or deloading process trend on the time. Looking at this curve, the peak value (D/Pd=0.75 at R/Ro=2) must be largely overcome if we wish to observe "Cold Fusion" phenomena. In addition, if we want to know (from the resistance measurement), in which side it is the peak of the sample concentration, we need to leave the electrode deloading and observe its resistivity derivative on the time.

Because in normal condition (NTP) a Pd sample absorbs D up to a D/Pd=0.67, it is necessary to force the loading or operating at very high pressure (millions of Pa) or applying on the electrode surface an electric field density as strong as to avoid deuterons to be outgoing.

An other effect, well known as Coehn effect [4)], to achieve extra high loading is to apply a high voltage gradient along the Pd electrode, moving most inner deuterons to cumulate on the most cathodic (MC) point of the wire (electromigration effect). Some Researchers [5)] claim that, as peculiar issue of this effect, high electric currents inducted through the wire, should be able to increase the loading value at the MC point as well as producing a wall effect to the desorbing deuterons (confinement effect).

This ideas are been the motivation of the following tests performed.

2 – APPARATUS SET–UP

A peculiar version of a electrolytic cooling flow calorimeter was projected and mounted by the group at Frascati Laboratory (named Twin project: similar devices are working at INFN Frascati Lab, made since 1996 and NHE Sapporo Lab made since 1997).

A schematically view of the experimental apparatus is drawn in fig.1 and fig. 2; it is essentially composed by an electrolytic cell immersed in a vessel filled by water cooled by an external water constant flow circuit. The vessel is thermally insulated. The electrolytic cell is composed by a glass beaker filled of electrolytic solution (diluted $LiOD+D_2O$ 0.25 mM/l solution) in which is immersed a teflon cylinder and around it two wires (Pd of 160 cm and Pt of 200 cm, diameter of both of 100 mm) are, in parallel way (2 cm separated), elicoidally turned; a further Pt wire is turned between the anode and cathode wires and used as reference electrode and for thermal and electrolytic calibrations. Each wire is partitioned in several sectors (4 sectors into the solution and 1 in air) by 6 picks up read by a multimeter for resistance measurement. Temperature sensors (8 sensors of which 2 at the input/output vessel cooling flow) are located inside and outside the vessel for calorimetric measurement.

The calorimetry efficiency is ranging from 79 to 92 % depending by the cooling flow (from 1.2 to 6.8 ml/s). The calorimetry sensitivity is better of 0.5 W (at low flow).

3 – LOADING TESTS

All the following tests have been performed operating at high cooling flow (6.5 ml/s) in order to get loading measurements at about the same isothermal conditions (cell bath and room temperature are included between 18 and 22 °C).

After each test, the Pd wire is left to desorb spontaneously up to return to the initial resistance value (of R/Ro=1 at room temperature): this process is completed roughly in a week.

3.1 – Electromigration tests

To check the effectively of the electromigration effect (EM) we performed some tests applying a direct current generator to the bottom edges of the electrodes and connecting the top edges with a 10 Ohm resistor (initial Pd wire and Pt wire are both about 20 Ohm). In such a way, most of the input current is flowing through the electrodes, producing a consistent voltage drop along the wires, while the current flowing between the electrodes (electrolytic current) is a small part of it. We operated in these conditions:

– electromigration current of 250 mA;
– electrolytic current of 20 mA;
– input voltage of about 12 V (voltage drop along the wires roughly about 5 V);
– cooling flow of 6.5 ml/s (cell temperature quite similar to the room temperature).

In this test the cathode absorbed D up to D/Pd=0.75 in a few hours but this value had not overcome even after some days (fig. 3–A,B). The initial absorption speed of the MC sector (Pd_bottom–down) is quite higher than the less cathodic sector (LC: Pd_down–up), but both sectors reach the same maximum concentration (D/Pd=0.8) showing similar shapes. Looking at the fig. 3, the peak value of R/Ro=2.05 seems to be higher than that one expected (R/Ro=2), because at this current the wire temperature is increased roughly of a tenth of centigrade degrees.

During this electrolysis the input current was increases up to 1 A but, after operating temperature correction (temperature increases because joule effect), the absorption value seemed to be not changed.

We repeated this test several times (starting each time with the same fully deloaded Pd wire) reproducing the same values.

3.2 – High voltage tests

In this case, the electrodes at the top edges, are electrically disconnected and a voltage generator is applied to the bottom edges points (ordinary electrolysis).

We operated in these conditions:

– input voltage of 50 V (voltage drop along the wires roughly about 2 V);
– electrolytic current of about 100 mA;
– cooling flow of 6.5 ml/s (cell temperature quite similar to the room temperature).

In a few hours the loading peak is reached by both MC and LC (Less Cathodic) sectors and after long time (many hours) the loading process, even if not in a stable way, produces high loading (up to D/Pd> 0.95). In fig. 4.A, it is possible to see the loading trend as the normalised Pd wire resistance in the time: during the loading the wire (MC and LC sectors have very similar behaviours) can load up to D/Pd>0.9 and deload down to D/Pd=0.75 in an autonomy way.

4 – LOADING ANOMALOUS RESULTS

If we study in more detail the plot of fig. 4.A, during one of some over–loading (fig. 4.B), we can see a fast deloading effect occurring when the D/Pd concentration roughly achieves the value of 0.95 (returning, in short time, about less than a few seconds, to 0.85 value and slowly loading, tenth of minutes, again to 0.95 value). This effect (named "ramp effect") seems to occur several times in a cyclic way before disappearing after a strong deloading.

If we observe D/Pd loading along several days, we can record this effect several times. In fig. 5.A (as well as better in fig. 5.B where the time scale is enlarged), it is possible to observe again this effect occurring in a very similar way.

During the same test the input voltage was increased from 50 V to 100 V and this effect was again observed after several hours (fig. 6).

An interpretation of this effect can be related to an anomalous new phase transition occurring to the Pd–D lattice when the wire is over–saturated by absorbed Deuterium (we can call this "gamma" phase to distinguish it by the known alpha and beta phase of Pd–H system). In example, Deuterons are cumulated into the Pd (increasing potential energy as well as an elastic mechanical strain) until the gamma phase is achieved and then suddenly over–saturated Deuterons are released.

An other explanation of this effect can be possible if we congetture that an anomalous heat (because nuclear reactions) occurs into the wire when the value D/Pd= 0.95 is achieved, in such a way to highly increased the wire temperature bringing to a wire deloading (D/Pd= 0.85). This effect seems to be in agreement with the considerations reported by Dr McKubre after studying the heat in excess correlated to resistance–concentration curve by several experiments [ref. 6 and fig. 7]. Because this effect occurs in very short time, we have no way to record a relevant (average) heat in excess.

In order to check this interpretation, similar tests with Hydrogen are in progress.

This effect is reproducible even if the reproducibility is still quite low because it is not easy to load the wire up to D/Pd> 0.9 (it seems to occur after long time of loading and almost in a spontaneous way).

Finally, this effect has been already observed and reported by the Group [7)] using a different experimental set–up and during a different motivated experiment.

5 – CONCLUSIONS

These measurements give a strong indications about the procedure to achieve high D/Pd loading in Pd wire.

It seems that a high electric field must be applied between electrodes (at least 50 V of potential must be applied) and the electrolytic current must be as low as possible (tenth of mA, at least after having achieved the resistance–loading peak).

Electromigration effect, by alone, does not help to overcome the resistance–loading peak; may be it is useful to be applied after getting a high loading (a proper study is in progress).

When the loading overcomes D/Pd=0.9 a "ramp effect" occurs preventing to increase furtherly the loading. Perhaps, this "phase transition" is due to a local highly warming of the Pd wire that can be in agreement with a sudden and short production of heat of the wire (the origin of this heat could be nuclear instead of lattice mechanical forces and so Hydrogen comparing tests are required).

In conclusion, if we do not discover a proper procedure to mantain steady the high D/Pd value and for long time the "eventual" heat produced, it will be very difficult to measure and make useful this heat.

REFERENCES

(1) M. Fleishmann and S. Pons. J.Electroan.Chem. 261 (1989) 301.

(2) B. Baranowski et al. Journal Less Common Metal 158 (1990) 347.

(3) M. McKubre et al. In proc. Symp. on Hydrogen storage materials, batteries and electrochemistry. Eds. D.A. Corrigan and S.Srinivasan, Electrochem Soc. Inc. (1992) p. 269.

(4) A. Coehn. Elektrochem. 35 (1929) 676.

(5) G. Preparata. In proc.of 2nd Workshop on The loading of hydrogen/deuterium in metals, characterisation of materials and related phenomena. October 1995, Asti, Italy.

(6) M. McKubre et al. "Loading, Calorimetric, and Nuclear Investigation of the D/Pd System." In proceedings: Fourth International Conference on Cold Fusion, December 6–9, 1993, Lahaina, Maui, Hawaii. EPRI TR–104188–V1, Proceedings July 1994– 3412 Hillview Avenue, Palo Alto, 94304 California (USA)

(7) F.Celani, A.Spallone, P.Tripodi et al. "Deuterium overloading of palladium wires by means of high power ms pulsed electrolysis and electromigration: suggestions of a "phase transition" and related excess heat." Physics Letters A, 214 (1996) 1–13.

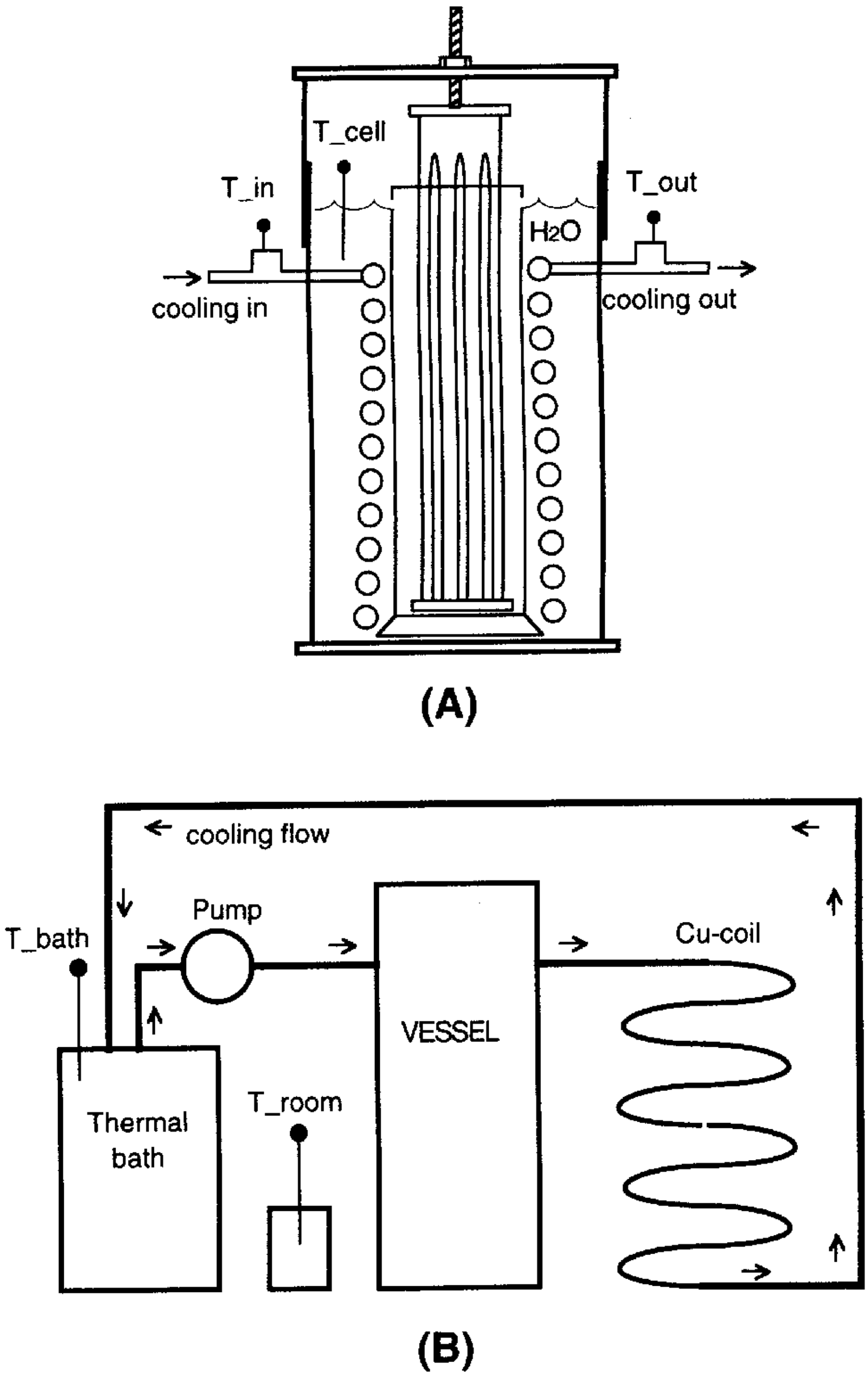


FIG. 1 – Apparatus set–up:
A) Inner vessel; the electrolytic cell is immersed in a cooling bath.
B) Cooling system outside the vessel: the thermal bath is at room temperature.

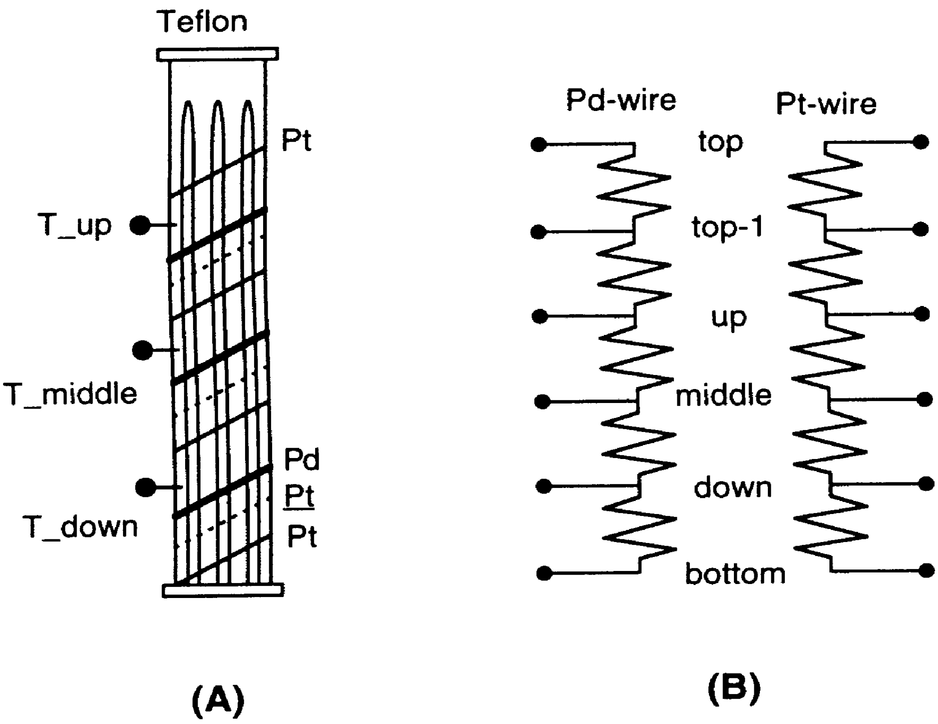


FIG. 2 – Electrodes set–up (Pd cathode, Pt anode and Pt reference):
A) Electrode wires are turned around a teflon cylinder.
B) Cathode–anode electric scheme with voltage picks up.

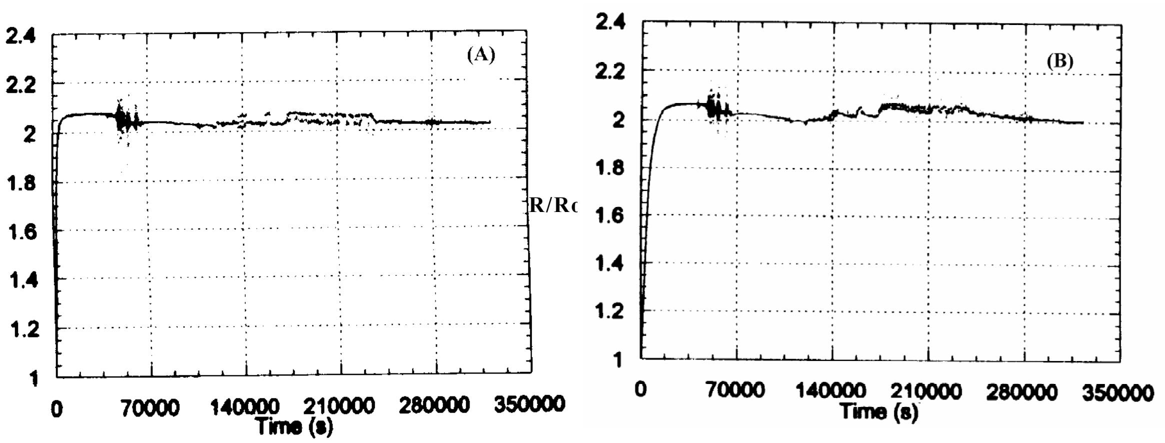


FIG. 3 – Electromigration tests:
A) Most cathodic sector (Pd bottom–down);
B) Less cathodic sector (Pd down–up).

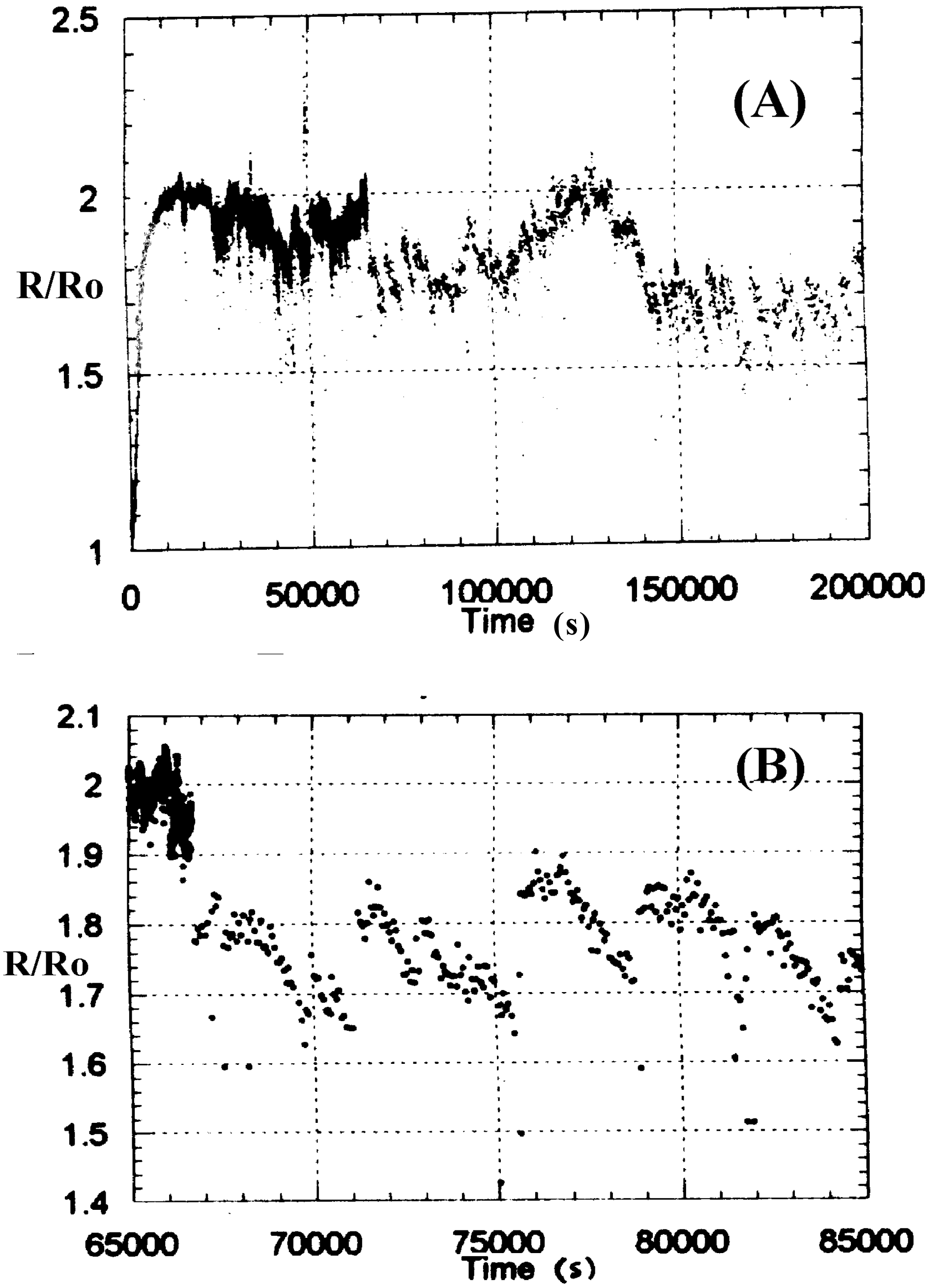
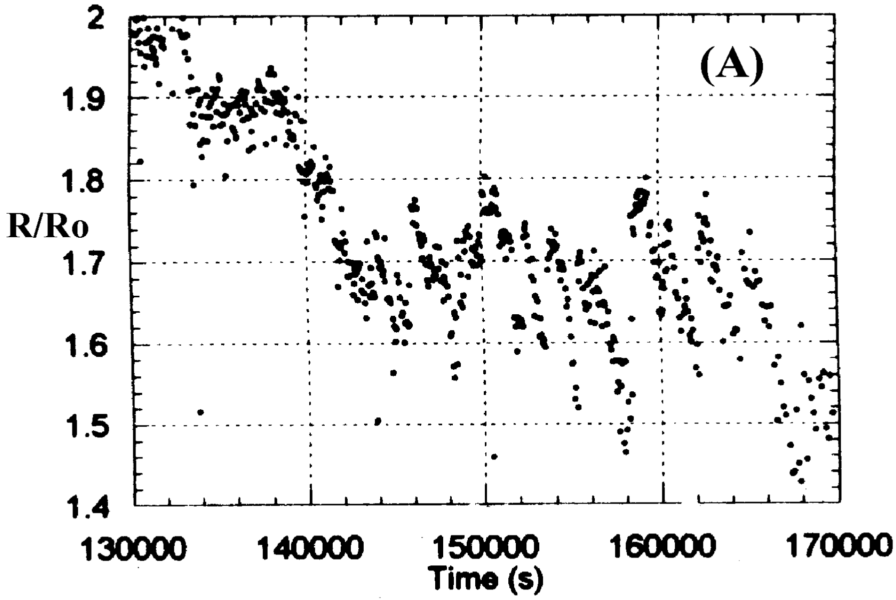


FIG. 4 – Electrodes high voltage test (50 V):

A) Most cathodic normalised resistance shows high loading;

B) A region time enlarged of previous plot shows details of high loading values achieved (D/Pd > 0.9).



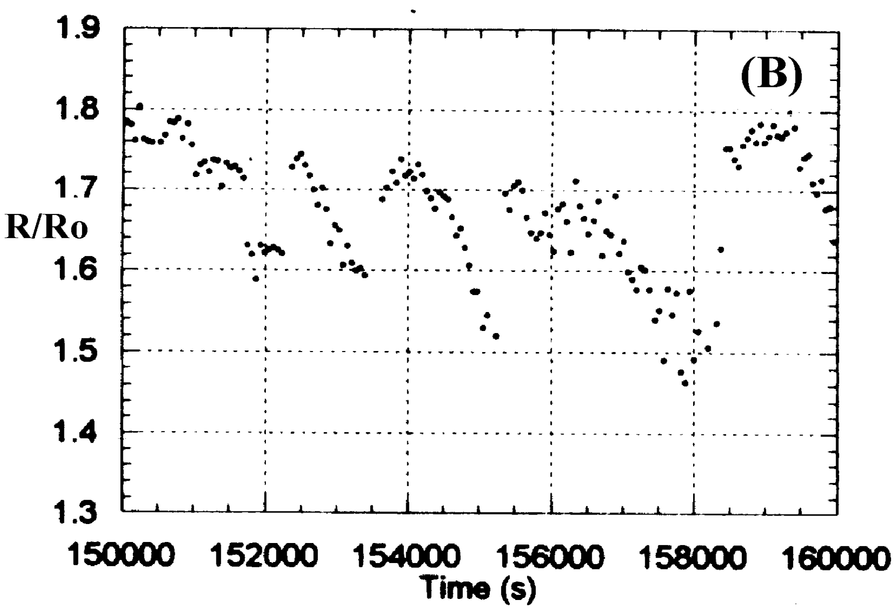


FIG. 5 – Ramp effect occurs several times during the run:
A) Most cathodic sector shows the effect during a high loading;
B) Enlarged time region of previous plot: ramps for R/Ro between 1.6–>1.8.

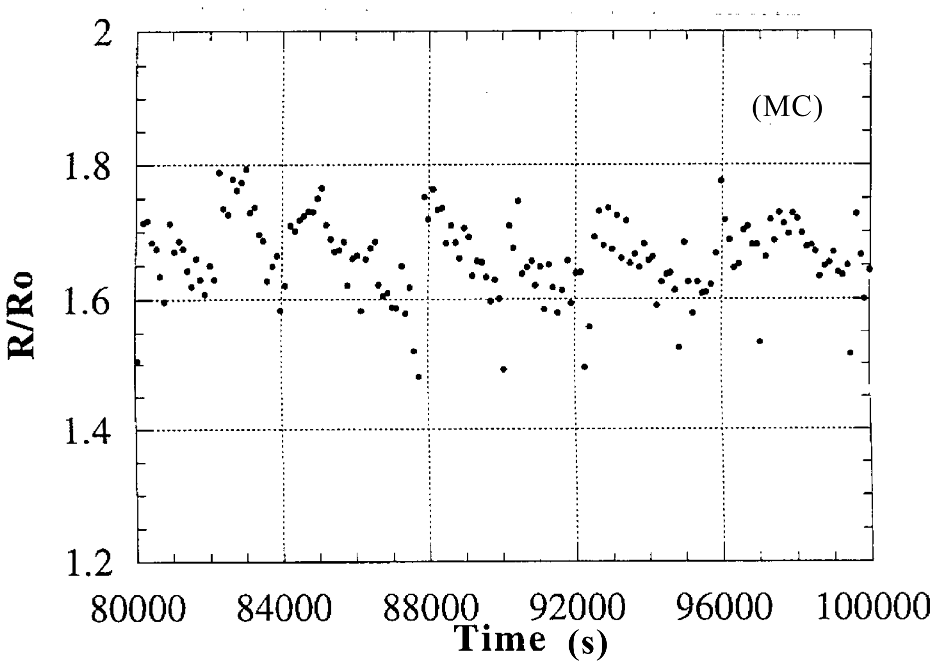


FIG. 6 – Ramp effect occurring about one day later after increasing electrolysis voltage from 50 to 100 V. The effect is similar to the previous ones and it is ranging from 0.85 to 0.95 D/Pd value.

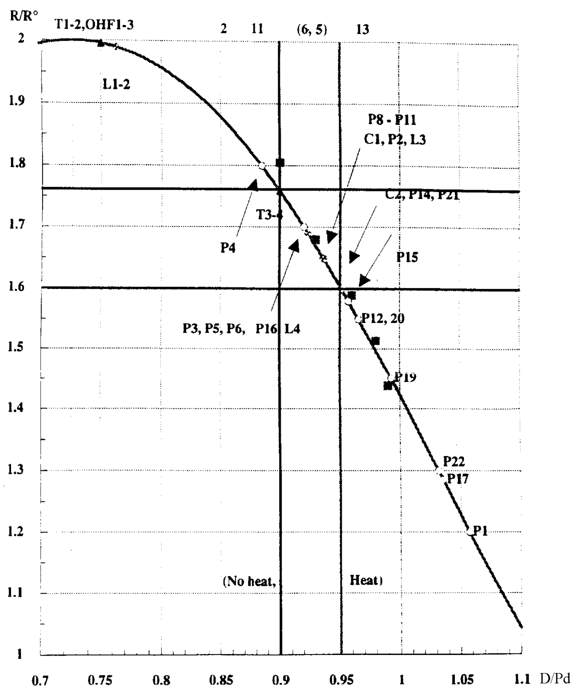


FIG. 7 – Experimental data of Pd–D normalised resistivity vs D/Pd at high loading (D/Pd> 0.75) related to the heat in excess occurrence [as reported in ref. 5].