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Observations of Strong Resistivity Reduction in a Palladium Thin Long Wire Using Ultra–High Frequency Pulsed Electrolysis at D/Pd>1*

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Abstract

We performed a ultra–short width high voltage pulse electrolysis using a thin Pd wire cathode; a diluted electrolytic solution of D2O+LiOD was used in a peculiar wire–turned electrodes geometry.

The deuterated Pd loading was evaluated by the D/Pd normalised electric resistance curve (R/Ro). After a long time of electrolysis a very high D/Pd loading (1:1 or more) was reached.

Very low R/Ro (< 0.1) Pd wire was measured after switching off the electrolysis and this effect lasted for several minutes. The Deuterium deloading occurred in several typologies (fast and slow terms) showed as a resistance transition on the Pd wire.

This effect can be related to a peculiar surface structural condition.

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Apparatus Set–Up

In order to reach very high loading (D/Pd > 1) a new approch in respect to the typical loading techniques has been developed.

An electrodes cylindrical geometry has been adopted: a PTFE cylinder, as electrodes holder (5 cm diameter, 30 cm length), has been turned by 2 parallel wires (1 cm of distance). The Pd wire (100 mm diameter, 160 cm length) has been located as cathode and a Pt wire (1 mm diameter) as anode [Fig. 1]. This geometry has been adopted to enclose in a symmetrical electric field along the cathode and moreover to produce ìwellî correlated electric fields: wire transversal (electrolytic type) and wire longitudinal (Ohm conductive type).

The electrolytic solution adopted was very diluted (LiOD–D2O at 0.25 mN), having a high electric resistance (several KW) between the electrodes, in order to have a very low transverse current; in such a way is possible to apply a high voltage to the electrodes.

The Pd wire has been tested on 5 different points (4 sectors: ab, bc, cd, de, Fig. 1) in order to measure the resistance (of the order of 10 W at D/Pd= 0.75) of each segment by mean of an a.c. resistance bridge realised by a proper home–made circuitry. We applyed a sinusoidal electrical current I(t) = Io sin wt , with w = 628 103 rad/s, Io = 10 mA (the total voltage drop along the wire was not producing self–electrolysis), we measured the AC voltage in 5 pick–up points (a,b,c,d,e) in respect to ground. The AC leakage current in the electrolyte is quite small because the impedance ratio between electrolyte and Pd wire was grather than 102.

The power supply applied to the electrodes has been realised by an other home–made pulse generator circuit [ref.1]. The pulse consists in a high frequency trapezoidal–like shape (rise time < 4 ns, about 20 ns width, amplitude between –40 and –80 V) having a repetition rate of about 27 MHz. This circuit is connected at the top edges of the electrodes. At the bottom edges of the Pd electrode is connected an other circuit (based on some high–power Zener diodes) in order to limit at a constant value the minimum drop voltage between anode and cathode. The motivation of this other circuit consists on to increase the current (or better to say: the voltage) along the wire without increasing the current along the electrolytic solution: in such a way the deuteron electromigration into the Pd wire can be increased producing a higher loading at the more cathodic point of the Pd (at the top edge).

Motivation and Test Procedure

The main goal of the pulse electrolysis consists on the reaching of a very high D/Pd loading which needs, to be sustained, a strong electric field onto the cathode surface. It is not convenient to apply a direct high voltage because in this case a high electrolytic current should be generated having the only effect to produce a lot of bubbles (D2 electrolytic gas at the cathode); it is our opinion that very high current density at the cathode does not increase anymore the D/Pd value but moreover it is lowering of this value. Instead, the high voltage pulse generates the necessary strong electric field at the surface and because the short time being on, the mean current (and the relative gas production) is quite low. Obviously, the peak pulse must be repeated after a time much lower than the diffusion (deloading) time of the Deuterium coming out from the Pd surface (we estimate it of some ms) [ref. 2].

The procedure adopted to perform the measurement was the following:

a) first loading at low frequency (0.5 ms width, 200 V amplitude, 5 Khz pulse rate [ref. 1])
b) the sample underwent to ultra–high frequency pulse electrolysis for many hours
c) suddenly the electrolysis was switch off
d) the resistance of the 4 Pd–wire sectors were recorded
e) the measurement lasted until the resistance peak was reached and then decreasing
f) repetition of these statements (b–>e) several times.

Results

A direct measurement of D/Pd was not possible to perform with this apparatus set–up (the total Pd wire mass was just 160 mg). As a loading reference, we adopted the well known curve of R/Ro vs D/Pd [Fig. 2] as reported in literature [ref. 3]. Because the peak value of the curve corresponding at R/Ro=2 is relative at D/Pd=0.75, to state if the D/Pd value is higher, it is necessary to record the resistance value occurring during the deloading: if this resistance increases during the deloading it means we are on the right side of the curve (otherwise we have the opposite condition). We adopted this criterion to realise if we had overcome the peak value after a long time electrolysis.

Several loading/deloading cycles have been performed using the same Pd wire running at the same nominal pulse supply conditions.

A very low resistance effect occurred several times (only at the a–b wire sector, as in Fig. 1, while the other sectors appeared to be over–charged up to R/Ro down to 1.2) and this effect performed different typologies.

In one experiment [Fig. 3] a low constant resistance value (roughly about zero) lasted for about 6 minutes and the transition time (R/Ro from 0 to 2, where D/Pd is equal at 0.75) was very short (less than 5 s, the minimum quantum computer acquisition time). The loading time, necessary to get this effect, was of about 2 hours.

In an other experiment (after about 15 hours of loading time) the R/Ro behaviour looks similar [Fig. 4]; for about 16 minutes the wire resistance was very low and the transition lasted about 30 s. As reported above, the resistance stands very low and steady for several minutes and later it appears unstable for few minutes (but still at low values) before the ìtransitionî. We can suppose that this instability is related to the wire deloading: it occurs an interaction between the wire (still heavily loaded but not so high like the previous steady status) and the a.c. resistance bridge circuitry. Perhaps this unstable status, occurring at this over–loaded Pd wire (sector a–b), can be related to the wire surface degrading. In short, it looks as a reactive response of the impedance of the wire to whom it is applied a sinusoidal current of the a.c. bridge.

In a case [Fig. 5 a,b,c] three sequential loading/deloading cycles (respectively of 10, 20, 30 minutes of loading time) have been performed. The low resistance standing time seems related to the loading time and the transition time is quite long (several minutes).

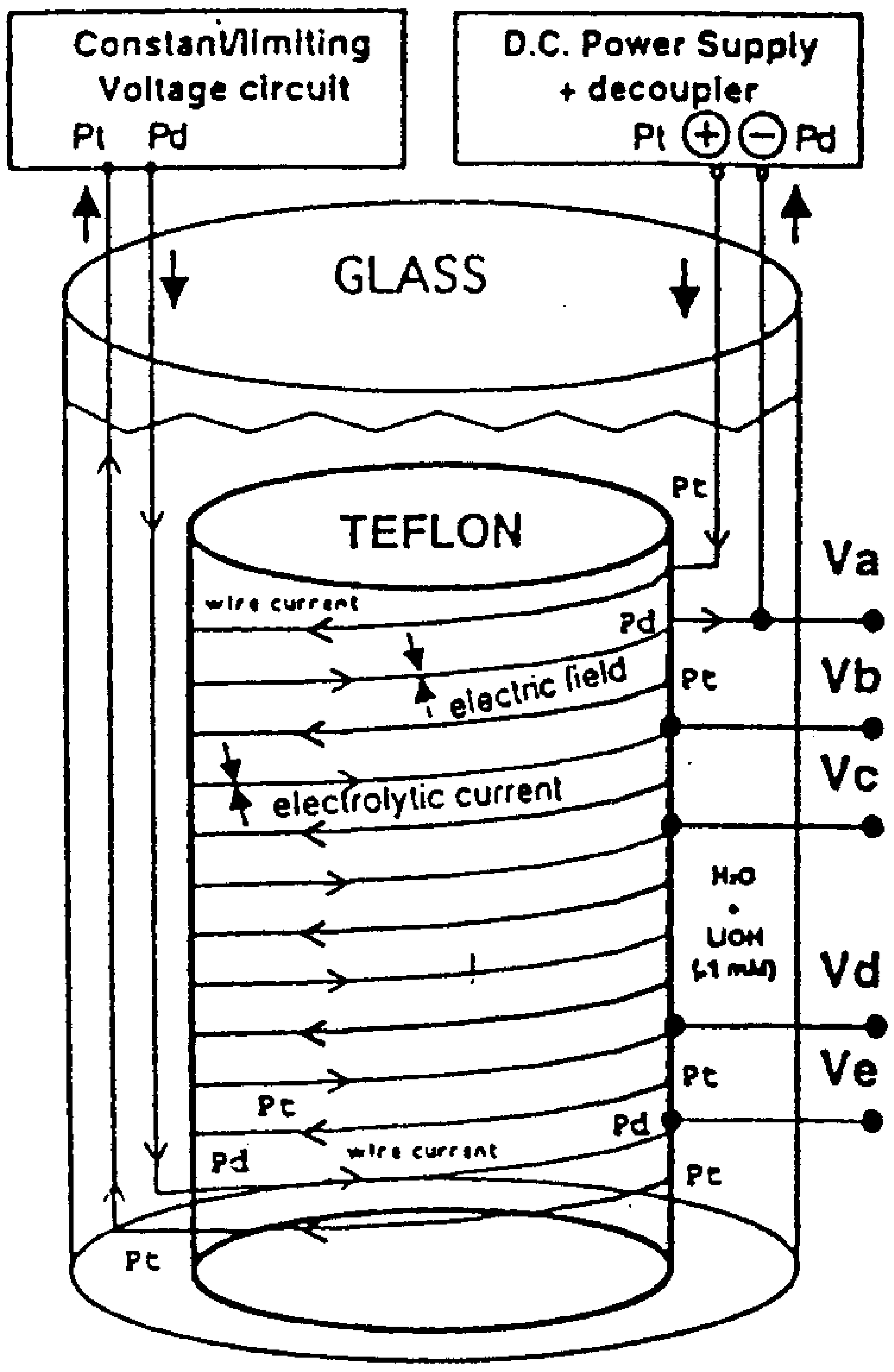

FIG. 1 – Electrolytic Device: Pd cathode and Pt anode wires are twisted around a PTFE cylinder. The electrolytic solution is very diluted. Along the Pd wire, some electric sensors are pointed

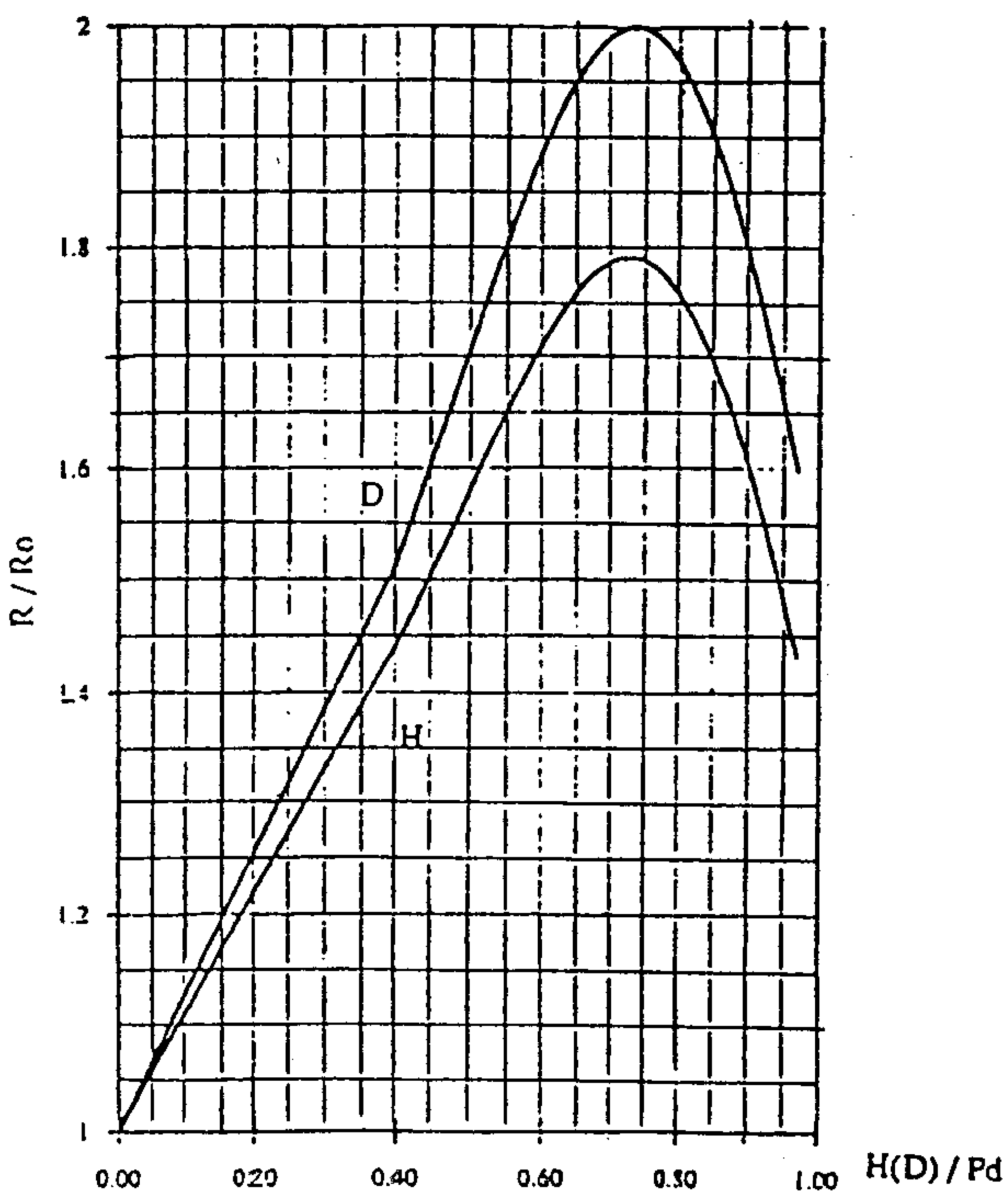

FIG. 2 – D/Pd Resistance curve: in this curve the resistance almost linearly increases with the loading. At the D/Pd=0.75 the normalized resistance has the peak value of 2 (1.8 for H/Pd). The curve is known up to the point D/Pd=0.95 and R/Ro=1.6.

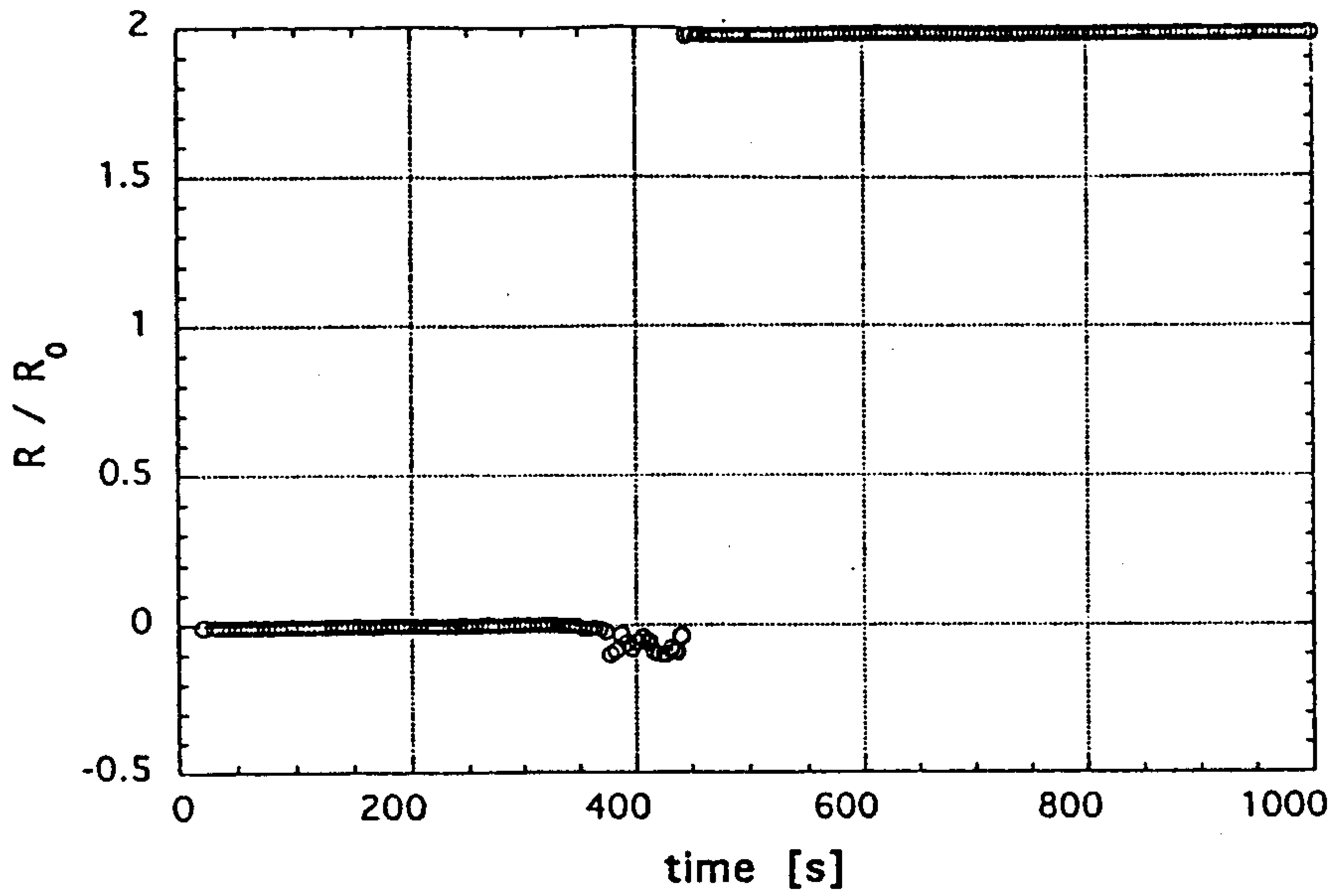

FIG. 3 – Resistance vs time: After switching off the electrolysis the Pd wire resistance is very low for about 7 minutes and the transition time is less than 5 s. The value R/Ro=2 is relative to the ratio D/Pd=0.75. Loading time was about 2 hours.

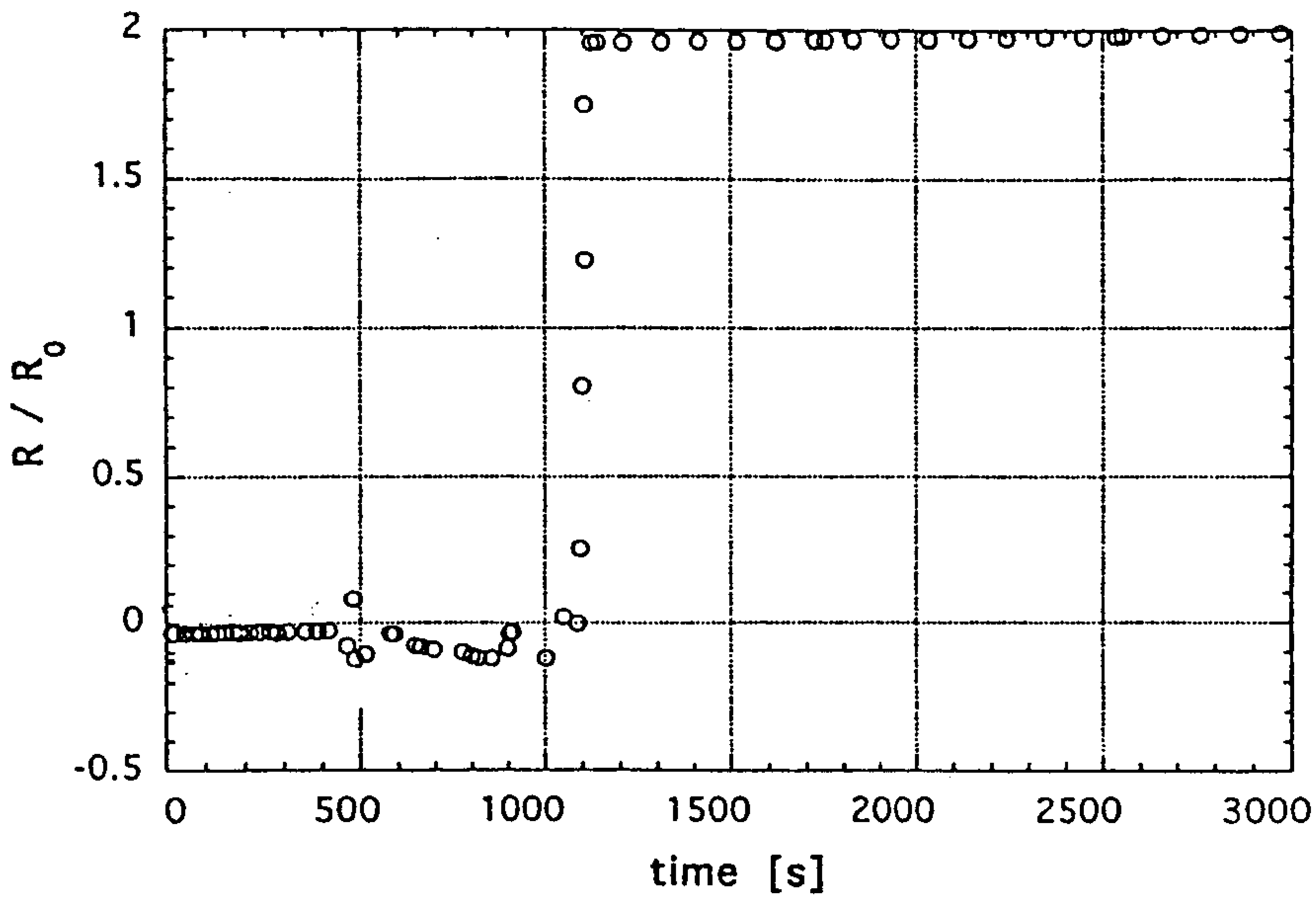

FIG. 4 – Resistance vs time: after switching off the electrolysis the Pd wire resistance is very low for about 15 minutes and the transition time is about 30 s. It is not shown, but after some hours the R/Ro value decreases much lower than 2. Loading time was about 15 hours.

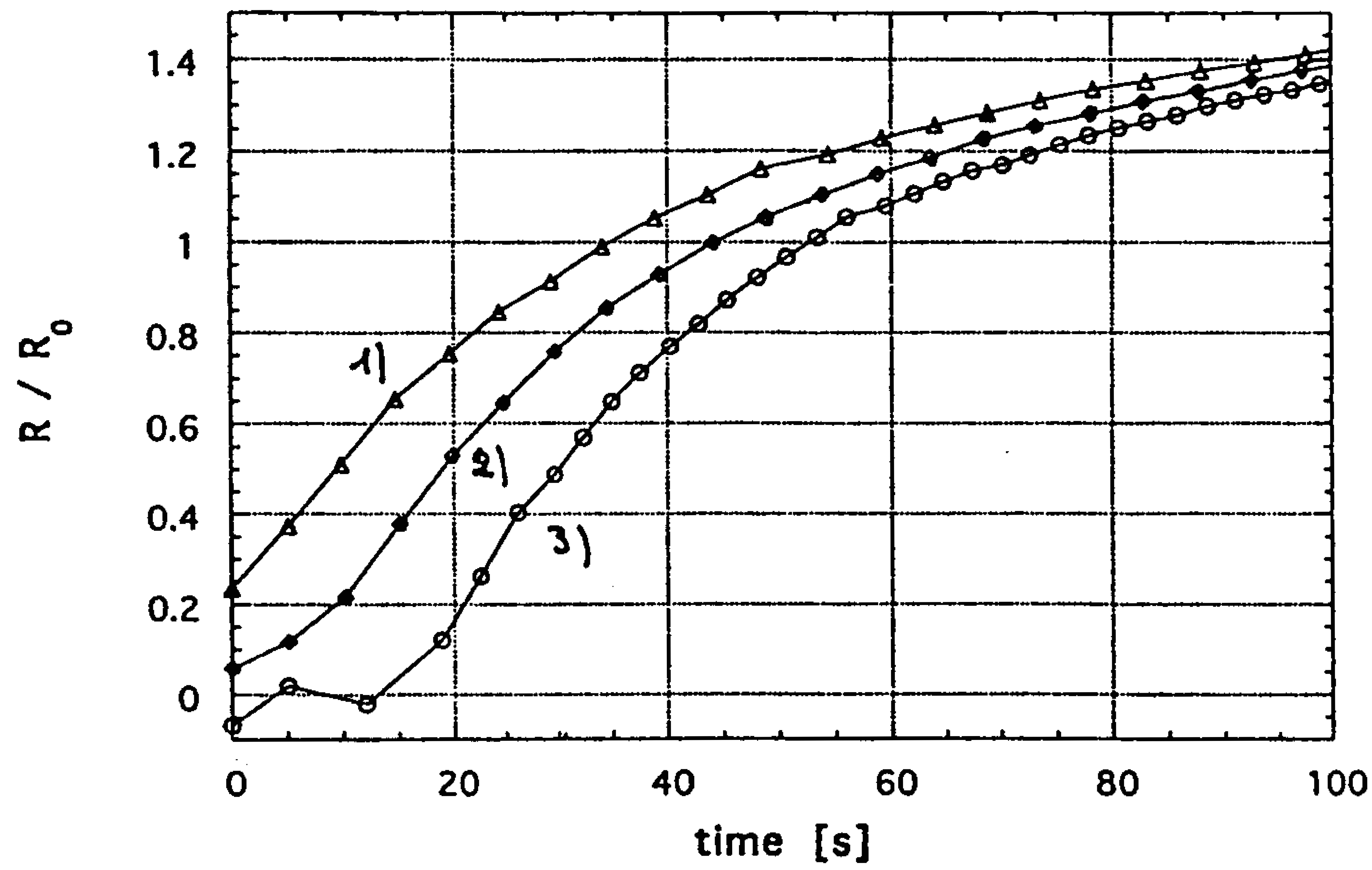

FIG. 5 – Resistance vs time: the Pd wire has operated for 3 load/deload progressive cycles: the resistance starts from very low values and needs many minutes to reach the value R/Ro=2 (not shown in the plot). The Pd surface structure probably plays an important role in this phenomenon. Loading times were respectively: 10, 20, 30 minutes.

Conclusions

In conclusion we can stress these points coming out from the observations of the phenomenon:

– High conductivity occurs in D–Pd overloaded system;

– Pulse shape seems to be related to this effect;

– Calorimetric measurements were not performed in this set–up (because the cooling flow was set at high level in order to work at constant temperature of about 26 ∞C) but anyway no high level of heat generation was recorded;

– Reproducibility is not still defined (all data are correspondent just to 1 wire);

– Investigation is not yet available with H–Pd system (only D–Pd system);

Finally we can suggest that something of structure modification occurs onto the over–loaded Pd wire surface; it is not still clear if the Li plays an important role for this sort of modified surface layer.

It is only defined at this time that the high frequency and high voltage pulse and moreover a quite long time loading are necessary to obtain this effect.

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