Deuterium Overloading of Palladium Wires by Means of High Power μs Pulsed Electrolysis and Electromigration: Suggestions of a "Phase Transition" and a Related Excess Heat

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Abstract

We describe room-temperature hydrogen and deuterium loading of palladium wires by means of pulsed electrolysis and the electromigration effect. The D/Pd atomic ratio has been measured by means of the dependence of the resistivity upon the D/Pd ratio. Values of the D/Pd ratio up to 0.95 or even higher have been reached in short times. A correlation between an anomalous temperature rise and a resistivity "transition" of the overloaded palladium clearly appears.

1. Introduction

Hydrogen and deuterium palladium systems have been extensively studied within the field of metal–hydrogen systems and hydrogen storage applications [1]. Recently the interest in this field has increased in connection with the cold fusion hypothesis [2].

The deuterium (or hydrogen) palladium system shows a quite complex phase diagram and large variations of the structural and transport properties as functions of the molar fraction D/Pd [3] (H/Pd [4,

p. 73]). In particular, at constant temperature, the electrical resistivity of the system shows a marked maximum at a value of D(H)/Pd of about 0.75 (see Fig. 1 [5]). The relationship between D/Pd and electrical resistivity is currently used for the assessment of the D/Pd ratio through a simple measurement of the resistance, at least in gas loading systems.

Large D/Pd ratios can be achieved by means of very high pressure gas loadings. In fact D/Pd values around 1.0 have been reached at deuterium (hydrogen) pressures of about 22000 atm [6]. Such high pressure levels require obviously very specialized technology.
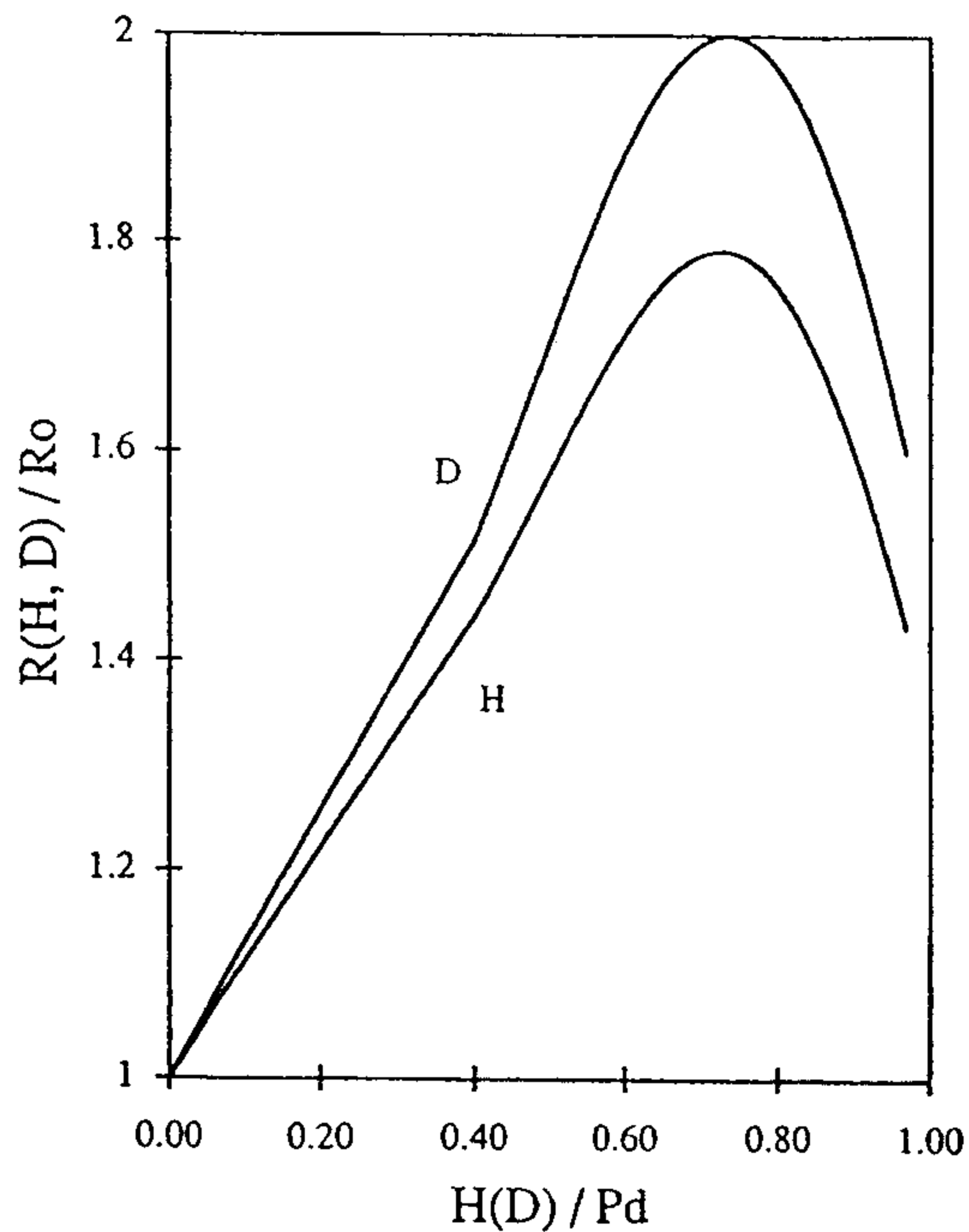
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Fig. 1. R/R_0 palladium resistance versus H(D)/Pd molar fraction.

On the contrary, deuterium loading by an electrochemical process, i.e. by means of dc electrolysis, appears to allow high D/Pd ratios [7–9], by operating with a quite simple experimental set-up. In fact the theoretical exponential dependence between the D_2 pressure over the Pd metal and the overvoltage (η) of the Pd cathode (with respect to the reference electrode) should allow one to reach high D/Pd ratios by means of relatively low cell overpotentials. These values should be easily reached since it is well known that η shows a linear increase with the logarithm of the normalized current density [10]. However, the overvoltage can be written as the sum of two components: $\eta = \eta_1 + \eta_2$. The term η_1 should be related to the Volmer process ($H^+ + e^- = H$) and only the second term should be exponentially related to the effective pressure [11]. As a consequence, the actual palladium overvoltage is generally too low to obtain D/Pd ratios consistently larger than 0.8. That means that the equivalent deuterium pressure generally achieved by dc electrolysis is not very high, i.e., in the range of 10–20 atm, as can be traced out from the D–Pd phase diagram. In order to exceed this limit, after the experiments of Fleischmann and Pons, some authors tried to increase the D/Pd ratio by increasing the cell potential.

In order to assure continuous feeding of deuterium atoms at the surface of the electrode, the electrolytic process is generally performed under constant current (galvanostatic) conditions. In this way the cell potential grows with the current. It has been soon found that significantly high D/Pd ratios can be achieved under extreme conditions of the cathodic current density and potential. Nevertheless, very high current density values cannot be reached owing to the large presence of H_2 (or D_2) bubbles which reduce the "conduction channels". Moreover, the phase diagram of both the H–Pd and D–Pd systems shows that the temperature rise, due to the Joule effect inside the cells, opposes the hydrogen or deuterium loading. Finally, the Joule effect can eventually obscure anomalous heat generation at a low level.

In order to overcome most of the above problems, arising from the extreme cathodic mean current densities, short unipolar periodic pulses of high current density, with a proper dead time, have been employed.

In the dead times, the deuterium density, absorbed in the cathodic surface during the pulses, can decrease through two processes:

(a) migration toward the electrode core;

(b) production of gaseous D2 ($D + D \rightarrow D_2$);

(c) desorption by an electrolytic retro-discharge: $D \rightarrow D^+ + e^-$.

In order to strongly reduce the third, unwanted process, a rectifying diode has been inserted between the cathode and the pulse generator, so that the cell is electrically insulated and the current backflow is prevented. In this way during the dead time the D deloading drops, and each pulse increases the D loading of the Pd cathode leading to a self-biased dc condition.

The employment of unipolar current pulses is a mandatory requirement since it is well known that under sinusoidal ac conditions the efficiency of the electrolytic processes decreases as the frequency increases, in such a way that it is negligible in the KHz frequency range.

Recently, we have proved the possibility of an easy loading of hydrogen in $Y_1Ba_2Cu_3O_7$ [12] and in Pd [9] by means of unipolar high power μs pulsed electrolysis in an aqueous Li solution. Under these conditions electrolysis does occur with yields of

95%, measured through comparison of gases evolved from the cell and the charge flown into the circuit. This experimental result is quite relevant although up to now a satisfactory theoretical description of the unipolar pulsed μs electrolysis is not available.

Anyway high power pulsed electrolysis (HPPE) should be accompanied by a further important advantage. Indeed, Debye and Falkenhagen predicted in 1927, and Sach found in 1928 [13], that for alternating electric fields, if the period is equal or less than the relaxation time, τ, given by

$$\tau = 10^{-10}/c \text{ s},$$

where c is the normality of the electrolyte, the equivalent conductivity approaches the maximum, i.e. the equivalent conductivity at infinite dilution. At $c = 0.001$ Normal, the relaxation time is 10^{-7} s, so that at frequencies $\nu > 1.6 \times 10^6$ Hz, the conductivity of the electrolyte significantly increases. The same effect can be expected with HPPE. As a matter of fact, working with HPPE, we have measured conductivities of the electrolyte up to 5 times higher than the dc values. In our particular case it leads to an increase of both the peak current density and the effective overvoltage. Moreover, harmful effects caused by the temperature rise were reduced, allowing us more accuracy in the measurement of eventual anomalous heat effects.

A further enhancement of the local D/Pd value could be generated by the Coehn effect, i.e. by the electromigration effect [14]. In the electrotransport effect, the concentration variations within the palladium can be very large: the deuterons are forced to move along the Pd cathode (deuteron current) because of the voltage drop $V(x)$ along the cathode. Indeed, in an equilibrium state, the deuterium concentration at a fixed point x is given by [4, p. 277]

$$c(x) = c(0) \exp[-eZ^* V(x)/k_B T], \qquad (1)$$

where e is the electron charge, k_B is the Boltzmann constant, and T the temperature (K). Z^* is the "effective charge number" of H (D) in Pd, which is equal to 1 at low concentrations (H/Pd < 0.6) [14], while it reduces to 0.1 at high concentrations (> 0.8) [15] and/or at high temperatures. In the absence of the surface H deloading, the stationary state will be reached when the incoming deuterons are exactly compensated by the outward diffusion of deuterons.

The actual local deuterium concentration in such an equilibrium state will result to be higher than in the absence of the Coehn effect.

Our experimental set-up, described in Section 2, has been designed in order to investigate the H (D) loading of a palladium wire both by pulsed electrolysis and by the Coehn effect. In Section 3 the experimental data are presented. Conclusions are drawn in Section 4.

2. Experimental set-up and calorimetric calibration

As remarked in the introduction, in order to obtain large values of the D/Pd molar fraction by the electrolytic process, it is necessary to obtain:

(A) large current densities, which implies large anode–cathode voltages;

(B) a low mean electrolytic current.

Moreover, for a further increase of D/Pd by the Coehn effect, large voltage drops between the ends of the cathode are necessary.

For these purposes, both the geometrical configuration and the features of the pulsed bias of the cell have been optimized.

As far as the geometrical configuration is concerned, since the D amount absorbed in the cathode is proportional to the cathodic surface and the D/Pd molar fraction involves the cathode volume, D/Pd increases with the ratio S/V between the effective surface S and the cathode volume V. This ratio is optimized by a wire shape as thin as possible. The use of a single wire coaxial to a cylindrical anode allows one to obtain higher values of the wire surface current density for a fixed value of the power dissipated by the Joule effect in the solution, because of the reduction of the current density in the solution.

Moreover, a reduction of the wire diameter increases the unit length resistance, leading to an increase of the voltage drop along the wire. This factor, positive for the Coehn effects, is furtherly strengthened by an increase of the total wire length.

However, we have the following problems:

(i) an intrinsic lower limit of the diameter of the wire, due to the embrittlement phenomena occurring in D or H loading;

(ii) the heat dissipation along the wire produced by the current. The consequent higher temperature causes two negative effects on the D concentration:

(a) following Eq. (1), the first regards the Coehn effect and it consists in the decreasing of Z^*;

(b) according to usual PTC curves, the second effect regards a D/Pd decrease more evident at higher D concentrations.

As regards the optimization of the cell bias, the unipolar pulsed electrolysis allows large overvoltages, avoiding problems arising from large mean current densities. Moreover, the use of current pulses with HF harmonics as large as possible has a positive effect on the above problems. As a matter of fact, the effective conductive section of the wire decreases because of the skin depth (δ), which decreases as the frequency increases ($\delta = (\rho/\pi\mu\nu)^{1/2}$, where ρ is the resistivity, μ is the magnetic permeability and ν is the frequency). It is then possible to use thicker wires, thus reducing the technological drawbacks of embrittlement, cracking and even breaking of palladium. Thus we have to optimize the rise time within the limits of pulse generators. We reach the compromise of a rise time of 100 ns at our typical operating current and voltage (peak current 20 A, peak voltage 200 V).

In order to reduce the Joule effect we reduce the pulse duration (t_w) and the repetition rate (f_r). As a consequence, the mean value of the current density is quite low.

As far as the pulse duration t_w is concerned, under our experimental conditions we have observed the existence of a minimum to obtain electrolysis. With $t_w = 300$ ns the Faradaic electrolytic efficiency is about 5%; nevertheless, the self-polarization of the cell due to a ultra fast power diode (Fig. 2a, UFPD) used as a decoupler, between the power pulser and the cathode, raises the efficiency to a value as large as 95% [16].

Although the duty cycle of the pulse must be low, it must nevertheless be high enough in order to avoid the deloading between pulses. This effect is reduced by the electrolytic surface coating of the cathode by impurities (mainly nickel from the anode and lithium). In any case the reduction of the spontaneous desorption is larger than the reduction of the forced absorption.

The following operating conditions have been typically used:

(i) the electrolyte concentration has been varied between 0.01 and 0.3 N LiOD;

(ii) the diameter of the Pd wires studied were 100, 250, 300, 500 μm;

(iii) the total wire lengths were 20, 50, 100, 200 cm.

The typical operating conditions of the input pulse are:

(a) rise time t_r of the pulse in the range 100–250 ns; the rise time increases with the peak current, however, with currents up to 25 A we still have 100 ns of rise time;

(b) fall time between 100 and 1500 ns (longer at lower electrolyte concentration) with an effective pulse duration between 750 and 1500 ns;
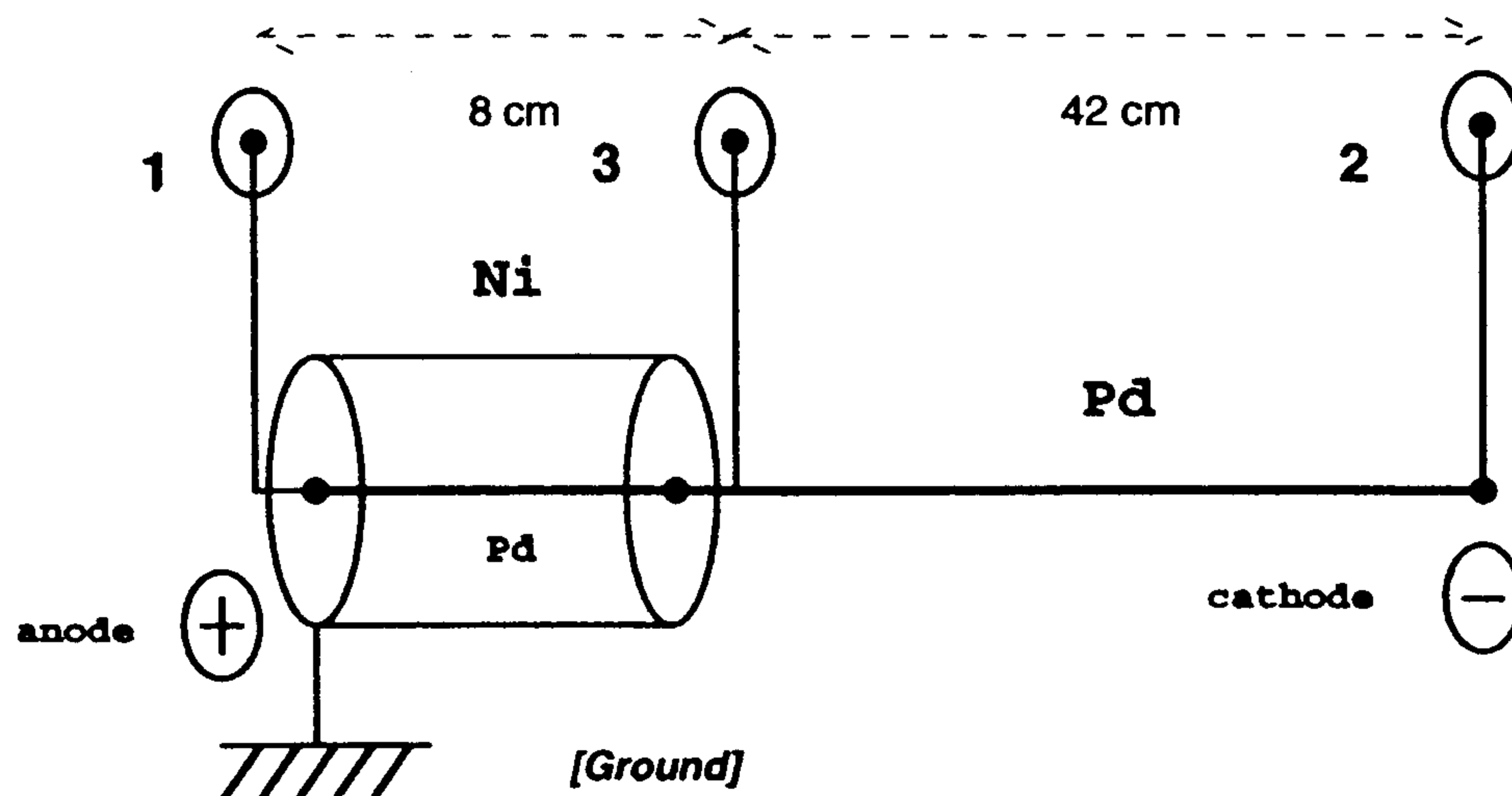

Fig. 2. Electrodes principle scheme.

(c) duration of the flat region 500 ns;

(d) repetition rate is between 5000 and 20000 Hz;

(e) peak voltage $(V_2 - V_{GND})$ between -80 and -200 V;

(f) peak current density along the wire [2]: 50000–300000 A/cm^2;

(g) cathodic peak current density: 10000–100000 mA/cm^2; for comparison, the typical values of the mean current density in cold fusion experiments ranges between 64 and 1000 mA/cm^2.

With the above geometrical configuration and pulsed bias conditions, the experimental apparatus has been designed in order to measure:

(i) the time dependence of the D/Pd ratio;

(ii) the contribution of the electromigration effect on the D concentration;

(iii) the eventual presence of excess heat.

The electrolytic cell vessel is made of commercial glass, and contains a LiOD–D$_2$O solution.

A palladium wire is immersed in the electrolytic solution. As shown in Fig. 2, two portions of the whole wire can be separately considered. The electrolysis mainly occurs between a first part (side 1–3 in Fig. 2) of the wire (effective length about 6 cm) and a coaxial nickel cylinder (internal diameter 12 mm) used as anode. The two ends of the cylinder are closed by two PTFE discs which support the coaxial wire. The external surface of the cylinder is insulated from the solution by means of a PTFE tape. The time dependence of the deuterium electrolytic loading is evaluated by on line measurements of the wire resistance. This side of the wire is also a source of deuterium (or hydrogen) for the other long portion (side 3–2 in Fig. 2) of the wire (the sink). This side, used to detect the electromigration effect is rounded on a cylindrical plastic support containing the calibration heater. The sink was located inside the solution mainly for a full calorimetric control.

In the following we call the end of the wire

coaxial with the anode "active". The other end is labelled "Coehn".

Negative voltage μs pulses are applied to end 2 of the palladium wire, which is indeed the most negative point of the system.

Some details of the experimental apparatus are described in Fig. 3a.

The $V_2 - V_3$ voltage drop allows us to measure the resistance of the Coehn end, giving information about the electromigration effect and the presence of self-electrolysis, which can occur between the two opposite turns of the coil for a voltage drop larger than 2 V (nominally the voltage necessary to dissociate heavy water is 1.54 V).

In self-electrolysis, one half of the wire behaves as an anode and the other as a cathode: this means that in principle, in the steady state, in the whole wire there would be regions in which deuterium is loaded and others in which deuterium is deloaded.

Moreover, the voltage difference between the 2–3 end and the anode (grounded), can determine the electrolysis, which can occur in this side of the wire only through percolative paths toward the anode. However, at the moment, the evaluation of these very small effects is quite difficult.

The significant electrochemical potentials should be measured with respect to the reference electrode, however, since the potential of the reference with respect to the anode is practically constant at constant temperature, for enough low mean currents (< 100 mA/cm^2), the potential $V_{1,2,3}$ can be considered.

The voltage peak values V_1, V_2, V_3 (see Fig. 3a) are acquired through ultra-fast passive peak detectors (Fig. 2b).

The actual overpotential should be measured by the out-of-phase cathode–anode voltage (V_{oph}), that is the cell voltage a few μs just after the fall edge of the input pulses [17]. In our case a rough estimate of the overvoltage is performed through a fast and simple circuit (Fig. 3c), which cuts the powerful input negative pulse and gives an output signal equal to a mean cell voltage between pulses. Different output voltages can be compared only at fixed operating conditions.

The voltage pulse at V_2 generates a peak current read by means of a fast rise time (20 ns), high peak current capability (5000 A) current monitor (Pearson

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[2] Some tests were performed with a current density as large as 500000 A/cm^2. These values of the current density are not too far from typical regions of the pinch effect in hot fusion studies, so we can expect even the emission of soft X-rays. We are planning to build an experimental set-up to clarify this point.

411, 100 mV/A) and transformed to a dc level through a fast, low-drop, low-leakage, Shottky diode (HP2800) and ceramic capacitor (Fig. 3d).

We estimated the D/Pd ratio from measurements

of the wire resistance in each of the two ends of the wire (the active and the Coehn sides). The resistance measurements were performed in two ways: in situ (by the volt-amperometric method) and, for compari-
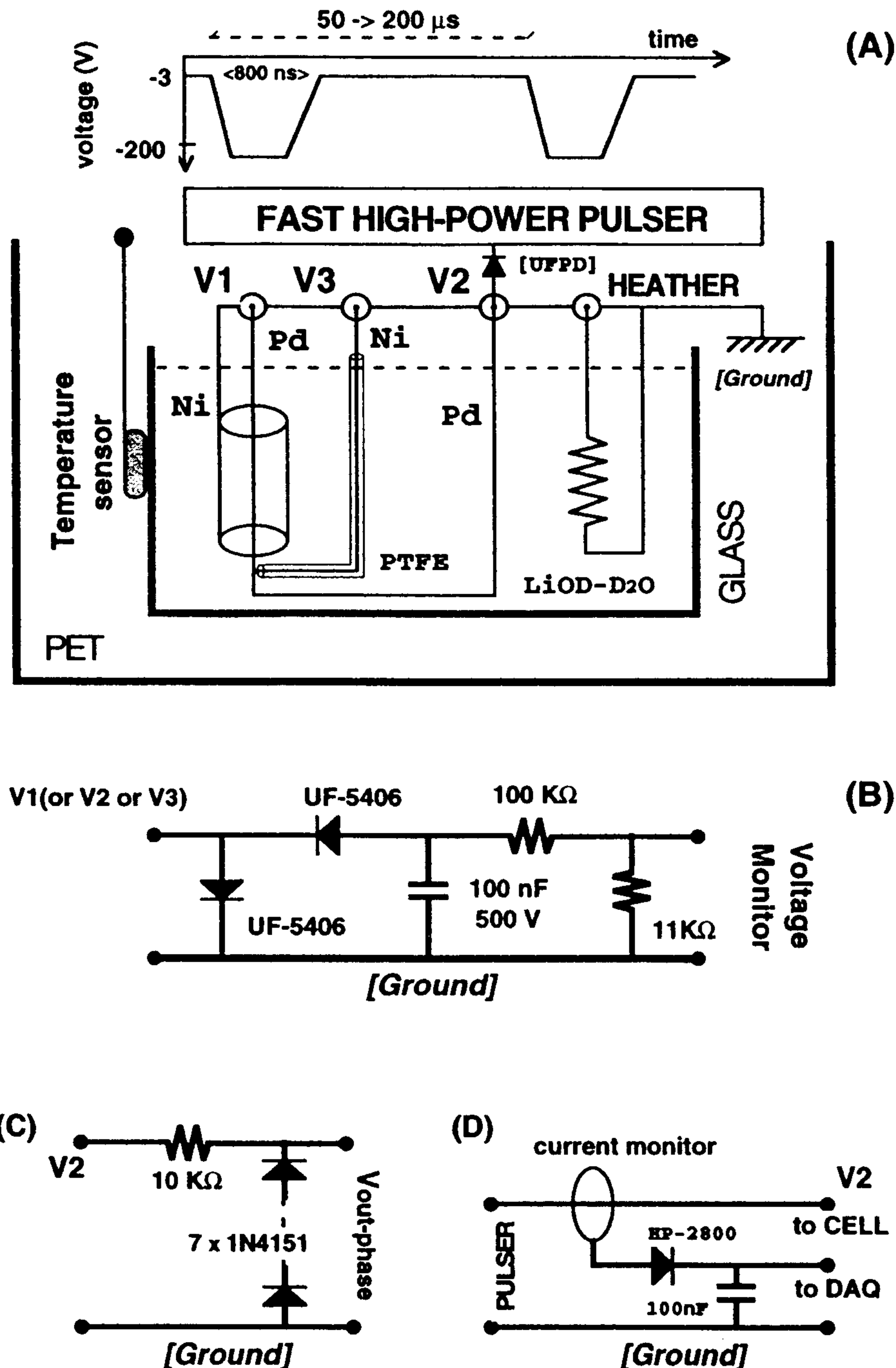

Fig. 3. (a) Apparatus set-up. (b) Peak detector circuit. (c) V_{oph} circuit. (d) Current circuit.

son, by ac bridge measurements (HP 4262 LCR METER operating at 120 Hz, 1 kHz, 10 kHz) just after switching off the pulse generator, disconnecting the pulser and all the pulse detectors.

As regards the calorimetry, the heat analysis is complex, since the energy balance among many terms must be taken into account. In order to avoid these problems, our system operates as a quasi-iso-peribolic calorimeter according to the DOE report [18]. A calibration heater is cyclically (every 6 hours) powered in order to determine the ratio between the power given to the cell and the corresponding temperature difference rise. In this way we calculate the so-called "cell exchange constant" K_{exc} (°C/W) at various temperatures and overall experimental conditions (aging of solution due to glass dissolution by LiOD, different bubbling due to different electrolytic currents and so on). The temperature is presumed to be spatially isothermal due to bubbling arising from electrolysis and to the low height of the cell (10 cm).

The thermometer is an integrated silicon circuit (AD590), with a metallic case connected to ground in order to minimize pick-up noise. The thermometer operates at a quite large sensitivity (ratio output voltage/input temperature 10 mV/°C), in order to reduce systematic errors that may arise from unpredicted variations of the "reference ground" at the input of the multiplexed-multimeters (HP3457A). The thermometer is located on the external wall of the cell (Fig. 3a), in front of the region between the palladium wire and the heater used for calibration.

The temperature difference between the cell and an external source at a fixed temperature (the environment kept at constant temperature of 20 ± 2°C) is continuously monitored and acquired.

A first test of the "cell exchange constant" K_{exc} is performed before the start-up of the loading for heater dissipated power values (W_d) up to 10 W: as expected a decrease of K_{exc} with the increase of the input power has been found. This reduction can be roughly approximated by a linear dependence: $K_{exc} = K_0(1 - W_d/W_0)$, with $K_0 = 4.6$°C/W and $W_0 = 45$ W. In an analogous way we have determined the differential "cell exchange constant" K'_{exc} (°C/W) as the increase of ΔT corresponding to 1 W increase of the input power. K'_{exc} is a function of ΔT_0 which is the starting value of ΔT before the additional power is applied. For ΔT_0 lower than 30°C, a roughly

linear lowering is determined: $K'_{exc} = K_0(1 - \Delta T_0/T_0)$, with $T_0 = 73$°C. Obviously such measurements require stationary conditions, so that for each operation condition, times longer than the time constant of the full apparatus (about 40′) are necessary.

In order to determine the power dissipated by the electrolytic process (W_{el}), or rather the electrical power supplied by the external word (W_{ex}), two different procedures have been used:

(1) by the use of a storage digital oscilloscope, the time dependent input current and input voltage (V_2) are acquired, so that the input mean power can be computed;

(2) since a dc power is supplied to the pulser used for the electrolysis, W_{ex} can be determined by the difference in the powers supplied to the pulser with the electrolytic cell connected and without it.

The two evaluations have been performed for different values of W_{ex} between 2.5 and 7 W; the values obtained with the two different methods are equal within ca. 5%. A further calorimetric calibration test of the full apparatus has been performed without the heater by an evaluation of K_{exc} at the beginning of an electrolytic process, for small input electrolytic power, starting with the cell temperature equal to room temperature. Within ca. 10% the ratio between the temperature rise and the electrolytic power evaluated with the two previously described methods is in agreement with the measurement of K_{exc} by means of the heater.

Finally the electrical power exchanges given by measurement instruments are properly taken in account, by measuring W_{ex} both in the presence and in the absence of voltage and current monitors.

It is not easy to estimate the portion of the input power actually dissipated in the electrolytic cell and the power loss by the Joule effect along the electrodes. For instance for a total $W_{ex} = 5.6$ W, by the first method a rough estimate of the power dissipated in the Coehn end of the wire is 3.5 W. Nevertheless, for our purpose, only the overall "cell exchange constant" is necessary, so that the above distinction can be neglected.

Moreover, given the very small mass of the wire (50 mg), heat exchanges between the cell and the wire due to both endothermic and esothermic loadings or deloadings are negligible in stationary conditions.

The operating conditions and measurements of the whole apparatus are computer controlled and acquired.

3. Main results

With the above experimental set-up about 20 loading processes have been performed. In each loading experiment we measured the time dependence of the D/Pd ratio from measurements of the wire resistance in each of the two ends (active and Coehn) of the wire. At the same time we evaluated the excess heat production by measurements of the cell temperature and by the calibration method described in the previous section. Each value of the relevant physical quantities is acquired every 2.5 s.

In this section we show the results of a loading process performed under the following conditions:
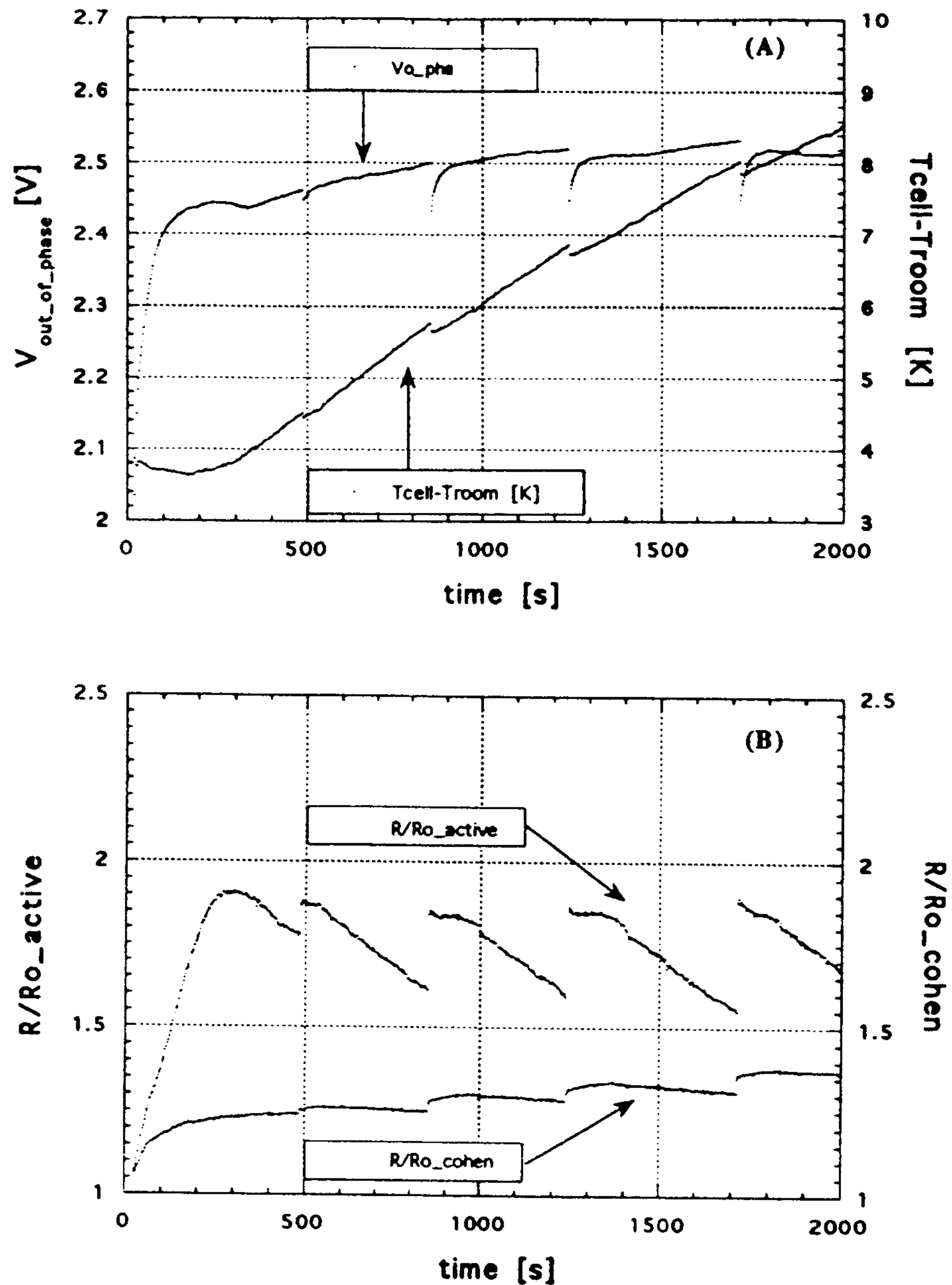
(i) initial electrolyte concentration 0.03 LiOD

Fig. 4. (a) Trend of V_{oph} and trend of the difference between cell and room temperature during the first 2000 s. (b) Resistance ratio of the active and the Coehn side of the wire during the first 2000 s.

(with a final value of about 0.02 LiOD), corresponding to a dc resistance equal to about 30 Ω in our geometrical configuration;

(ii) Pd wire diameter: 100 μm;

(iii) total wire lengths 6 + 44 cm, corresponding to an initial resistence equal to about 7 Ω.

The operating conditions of the input pulse are:

(a) rise time 100 ns;

(b) initial fall time about 300 ns (increases to typically 600 ns at the end of the loading);

(c) duration of the flat region 500 ns;

(d) repetition rate 10000 Hz.

(e) peak voltage $(V_2 - V_{GND})$ 200 V;

(f) peak current: 5 A initial (steady state 3 A);

(g) mean electrolytical power: initial about 6 W, steady state 3.9 ± 0.2 W;
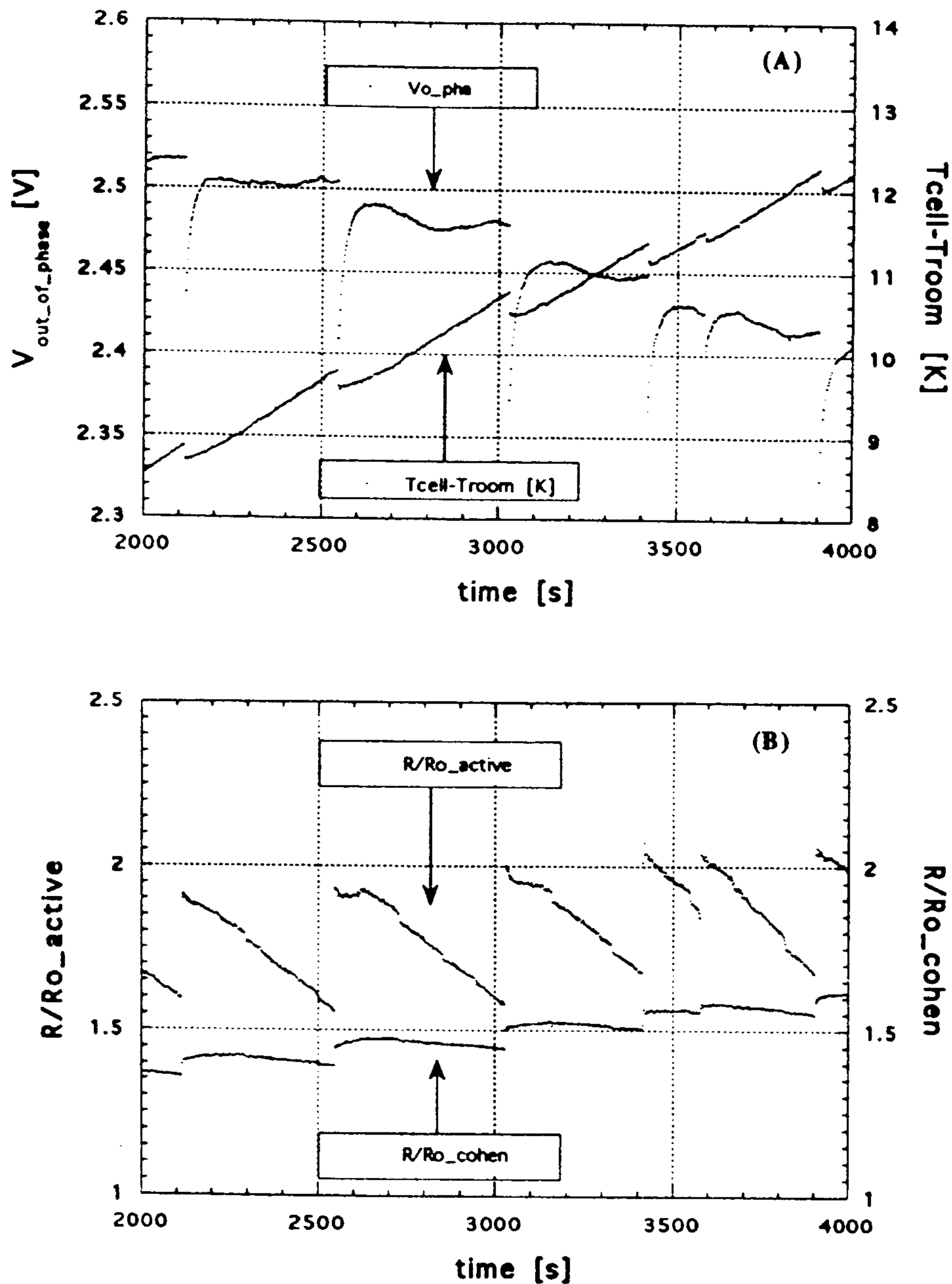
Fig. 5. (a) Trend of V_{oph} and trend of the difference between cell and room temperature between 2000 and 4000 s. (b) Resistance ratio of the active and the Coehn sides of the wire between 2000 and 4000 s.

(h) steady state peak current density along the wire: 40000 A/cm^2;

(i) mean cathodic peak current density: 20 A/cm^2;

The time dependences of the out-of-phase voltage and of the difference between the cell temperature and room temperature are reported in Figs. 4a, 5a, 6a, in the temporal ranges $0 < t < 2000$ s, $2000 < t < 4000$ s, $78000 < t < 80000$ s respectively.

In the same temporal ranges in Figs. 4b, 5b, 6b

the time dependence of the resistance in the active and Coehn portions of the wire are reported.

The resistance ratio reaches its maximum value in the active end 250 s after the beginning of the electrolysis. In the subsequent 240 s the R/R_0 ratio decreases.

In our graphics the maximum for R/R_0 is about 1.9, while in Fig. 1 this value is about 2.0. This difference could be due to the fact that the first
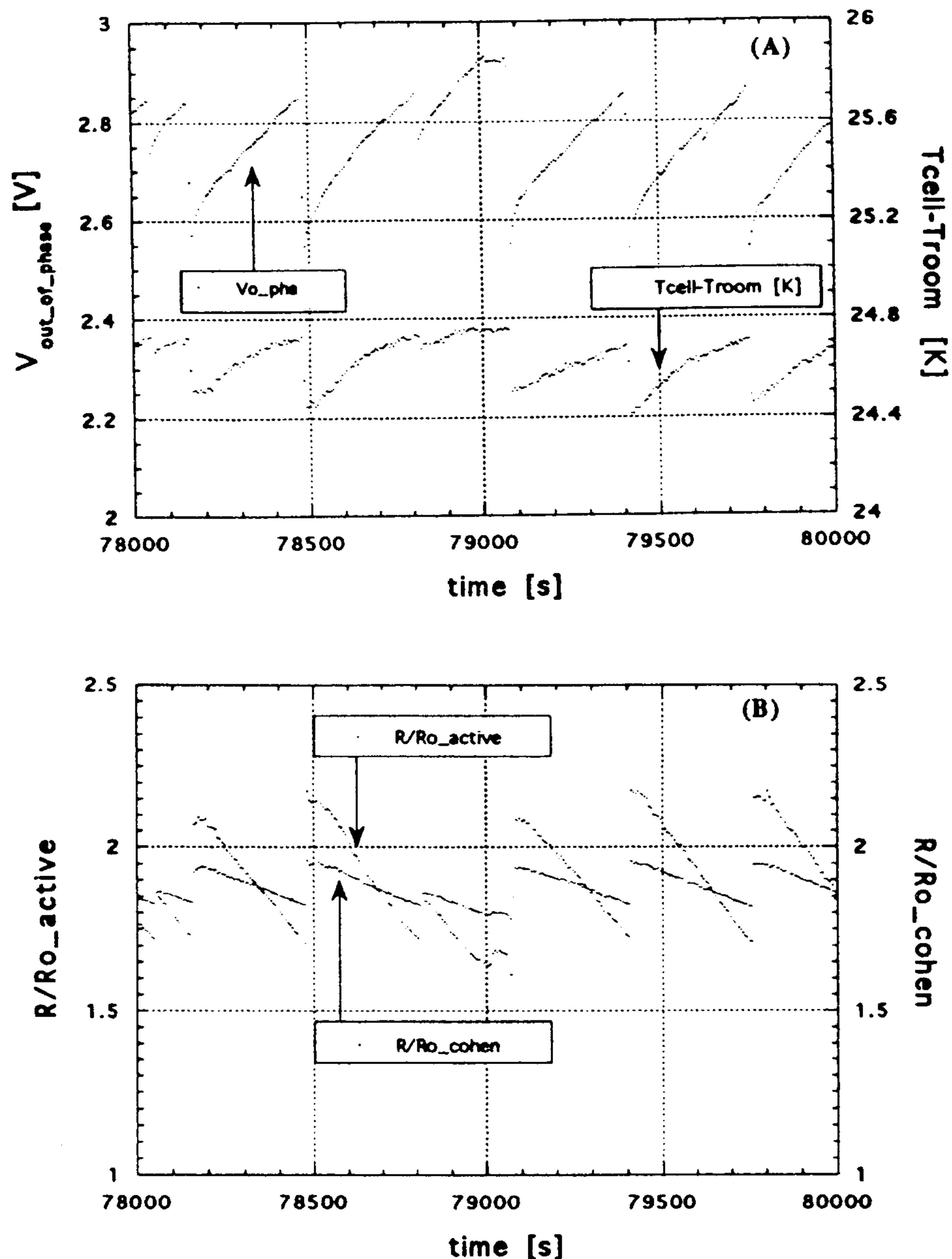

Fig. 6. (a) Trend of V_{oph} and trend of the difference between cell and room temperature between 78000 and 80000 s. (b) Resistance ratio of the active and the Coehn side of the wire between 78000 and 80000 s.

measurement of the resistence (R_0) is overestimated because the acquisition rate does not so fast acquire the real first resistance value.

The initial growth of the resistance is obviously generated by the deuterium loading. Since the Pd resistance as a function of the D concentration shows a maximum at D/Pd about 0.75, the subsequent reduction could be generated both by a further loading or by a deloading. In order to discriminate between the two possibilities, after 450 s from the beginning, the electrolytic process has been, in some cases, interrupted and at constant room temperature, the resistance of the wire has been measured outside the cell by the ac bridge during the spontaneous deloading of the wire. Since these measurements show that the resistance of the wire first increases and subsequently decreases, we are completely sure that the decrease of the resistance between 250 and 490 s is due to the further loading of the wire.

In this way we can conclude that in only 490 s the average D/Pd ratio reaches a value of about 0.85.

In the same time interval the resistance of the Coehn wire increases too. This means that also in this portion of the wire some, probably inhomogeneous, loading occours.

In the active wire, after 450 s, the resistances ratio "jumps" abruptly and comes back to a value corresponding to a D/Pd ratio of about 0.80. It can be supposed that the back transition, corresponding to a very fast deuterium desorption, occours only if a critical D/Pd value is reached. This jump is observed only when the height of the applied voltage pulse is higher than a threshold value (about 130 V with our configuration).

Corresponding to the jumps of the resistance in the active portion of the wire, a less pronounced jump of the resistance appears in the Coehn end. It seems reasonable that this portion of the wire is inhomogeneously loaded both by the electrolytic and by the electromigration process. In this way, if only a limited portion of the Coehn end is involved in the transition, a lower jump of the resistance is measured.

For $t > 500$ s the loading and the back "phase" transition have an almost periodic behavior. Sometime, like at 3600 or at 78800 s, anomalous transitions are observed both in the active and in the Coehn region. In the active end, after the second

resistance jump (at about 900 s), the amplitude of the jumps is approximately constant, while a continuous drift toward higher resistance values appears; anyway, as shown in Fig. 6, for long times a saturation condition is reached. These effects could be caused by the combined effects of the temperature rise shown in Figs. 4a, 5a, 6a and the monotonically increasing temperature dependence of the resistance. Remembering that $(\mathrm{d}R/R)/\mathrm{d}T = 0.2\%/°C$ for the Pd with D/Pd > 0.6, the final temperature of the cathode is 50°C larger than the environment.

We notice that the increasing of the wire resistance and the increasing of the dilution of the solution, due to the electrolysis, contribute to reducing the current and the input power. For this reason we measured an output power decreasing with time. Nevertheless, sometimes we observed that the energy gain increased spontaneously from about 50% to 150%.

In the Coehn end the amplitude of the jumps increases and saturates only after a rather long time (of the order of 80000 s), as shown in Fig. 6b. At the same time the drift toward higher resistance values is more proununced. Both these features can be explained by a slower loading of this portion of the wire, so that in most of the length the resistance rises and back transitions occur in a restricted portion of the wire, which increases with time.

As far as the time dependence of the out-of-phase voltage is concerned, as shown in Figs. 4a, 5a, 6a, a strict correlation with the resistance occurs: the overvoltage increases with the loading and any back transition of the resistence corresponds to a fast decrease of the overvoltage. As shown in Fig. 5a, between 2000 and 4000 s the V_0-phase decreases. This effect is determined by the well known decrease of the overvoltage as the temperature goes up. Indeed a decrease equal to 0.002 V/°C is consistent with the experimental data, taking into account that the local temperature of the wire surface is higher than the external thermometer temperature.

The time dependence of the temperature difference ΔT between the cell temperature (T_{cell}) and the room temperature (T_{room}) is shown in Figs. 4a, 5a, 6a.

As shown in Fig. 4a, the loading start with a bath temperature about 2.08°C higher than room temperature. In the first 200 s, in spite of the power dissi-

pated by the electrolytic process and the power emitted by the esothermic loading (for D/Pd lower than 0.8), a small temperature decrease (0.02) appears, corresponding to a negative total energy balance: the heat given to the external environment is higher than the dissipated power. It seems impossible that the presence of endothermic centers, suggested by some authors [19], can account for such temperature lowering.

For $t > 200$ s the temperature increases and asymptotically reaches the mean value of 24.6°C.

Corresponding to the resistance jumps, fast drops of temperature are measured. Such a behavior appears incomprehensible, unless the presence of electrical noise is supposed. Nevertheless, this hypothesis too is questionable, since the jumps determine a long time temperature decrease and the amplitude of the measured temperature jumps is not simply correlated to the amplitude of the other jumps observed.

The key point of anomalous heat measurements is the evaluation of the "cell exchange constant" evaluated after a very long time has elapsed, so that stationary conditions are assured.

From the ΔT value shown in Fig. 6a and by the measurements of the electrolytic power with the two described methods, we get an apparent K_{exc} above 6°C/W, while under the same conditions $K_{exc} = 3.7°C/W$ is expected. As a further check, in the presence of the electrolytic process the differential thermal K'_{exc} has been measured: $K'_{exc} = 3°C/W$ has been found in agreement with the calibration test previously performed.

At the moment the above experimental results can be explained only with the presence of excess heat. This excess heat seems to start (at low intensity) only 250 s after the beginning of the electrolysis and increases during the time following the behavior of bulk loading.

The excess energy obtained in the previously described experiment was about 50% (with a 5% accuracy) of the input power, i.e. typically about 5 W of excess heat. However, in other experimental conditions we have obtained a heat excess of up to 150%, under some unstable conditions.

A further test of the full apparatus has been performed by loading the wire with hydrogen, operating under the same experimental conditions. In this case we did not succeed in overcoming the maxi-

mum value of R/R_0. On the contrary, we registered a deloading after having reached the H/Pd value of 0.75. We had to change the experimental conditions and to increase the dilution of the solution to observe the same resistence jumps. We did not observe the same amount of energy: neverthless, a 15% excess heat has been found when we succeeded in reaching a very high hydrogen loading (of the order of 1 : 1).

4. Conclusion

We have proved that with the pulsed unipolar self-biased electrolysis it is possible to reach values of the D/Pd ratio above 0.8 almost in any kind of palladium wire, with a very short "waiting" time. Under some conditions we have shown that this value is obtained in only 200 s and a final value of D/Pd about 1 can be reached.

Moreover, under these conditions, in the framework of the calibration procedure of the isoperibolic calorimetry, an excess heat is clearly observed.

The total experimental results suggest us that the increase of the observed excess heat is probably related to:

(1) the decrease of the wire diameter;

(2) the decrease of the pulser rise time;

(3) the decrease of the LiOD concentration with reproducible results between 0.01 and 0.1 N (at lower concentrations an unstable behavior is observed);

(4) the increase of the repetition rate of pulses;

(5) the probable presence of some proper impurities (Ni, Pb, borosilicate), which cover the surface of Pd;

(6) the increase of the mechanical stresses of the wire (cold working), mainly because it increases the resistivity.

Almost all the previous experimental conditions show that the "overvoltage" value, together with the voltage drop along the wire could be the most important or even *key parameter* (as recently suggested also in Ref. [15]).

We also remark that in some experiments we measured a R/R_0 value less than 1. This behavior may suggest the possible formation of a superconducting state due to the extremely large density of the deuterium inside the palladium lattice, as proposed by some authors [20].

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