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REPRODUCIBLE D/Pd RATIO >1 AND EXCESS HEAT CORRELATION BY 1-μs-PULSE, HIGH-CURRENT ELECTROLYSIS

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A high-current (up to 100 A), short-pulse (1-μs duration) electrolysis technique is presented that permits high loading (D/Pd up to 1.2) of deuterium in palladium cathodes. Several different cold-worked palladium plates were used as cathodes, and some underwent surface treatments (oxidation or addition of intermetallic compounds). The surface-treated plates showed atypical deuterium absorption dynamics, and the D/Pd loading ratio exceeded 1. Moreover, during initial loading, these cathodes showed anomalous excess heat (up to 80%) far greater than the absorption enthalpy. The pure palladium surface plates did not show this effect.

I. INTRODUCTION

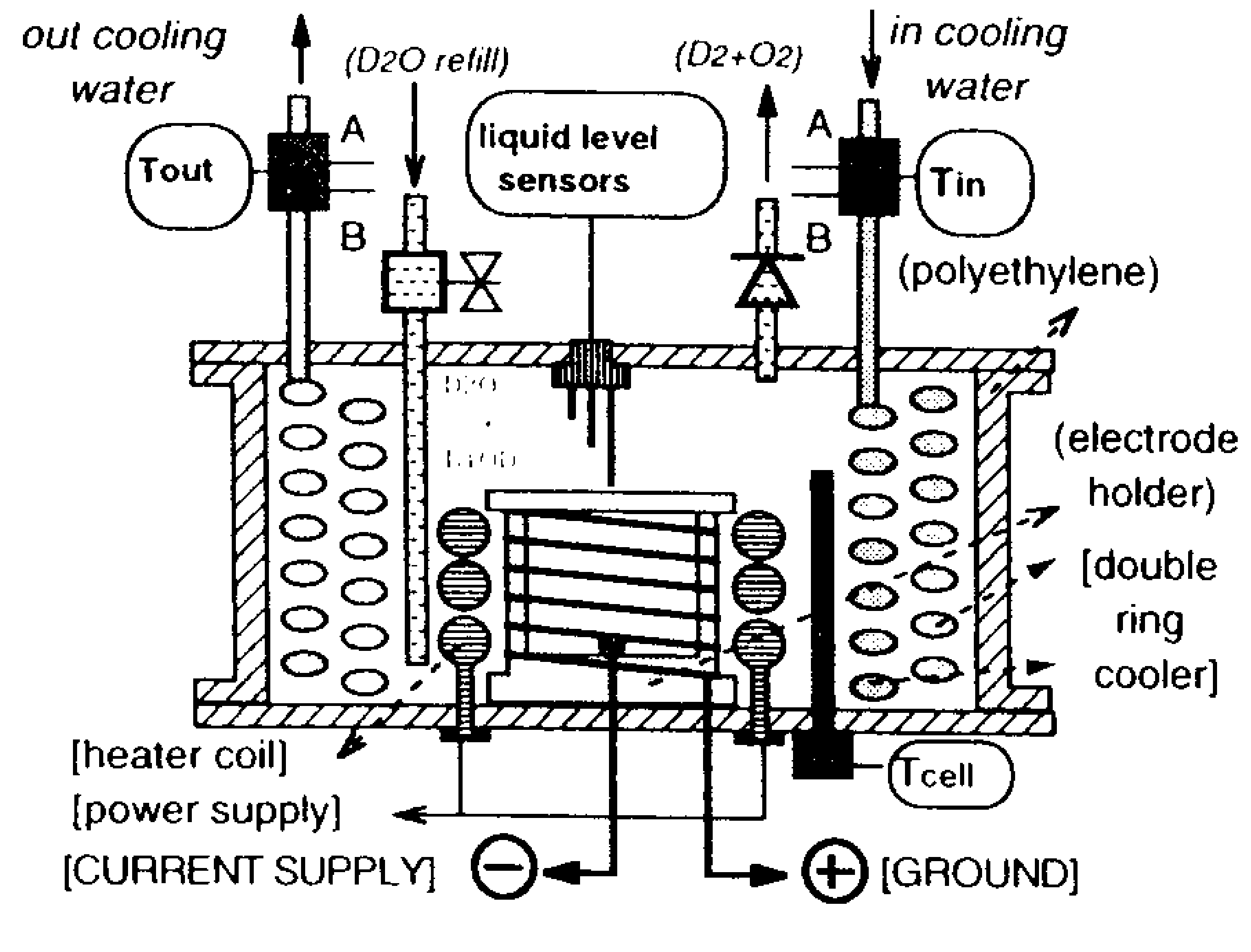
Electrolytic loading of deuterium in palladium has historically[1] been a standard technique for verifying cold fusion phenomena. Over the years, these techniques have been successively refined and improved. It is often cited that the success or failure of such experiments is critically dependent on the deuterium-loading ratio.[2,3] In this paper, we present a technique to achieve very high loading ratios in all the palladium specimens tested. We show that high loading by itself is no guarantee of excess heat. Surface preparation or doping the palladium with boron appear to be conducive to anomalous power production during electrolysis.

II. THE EXPERIMENTAL SETUP

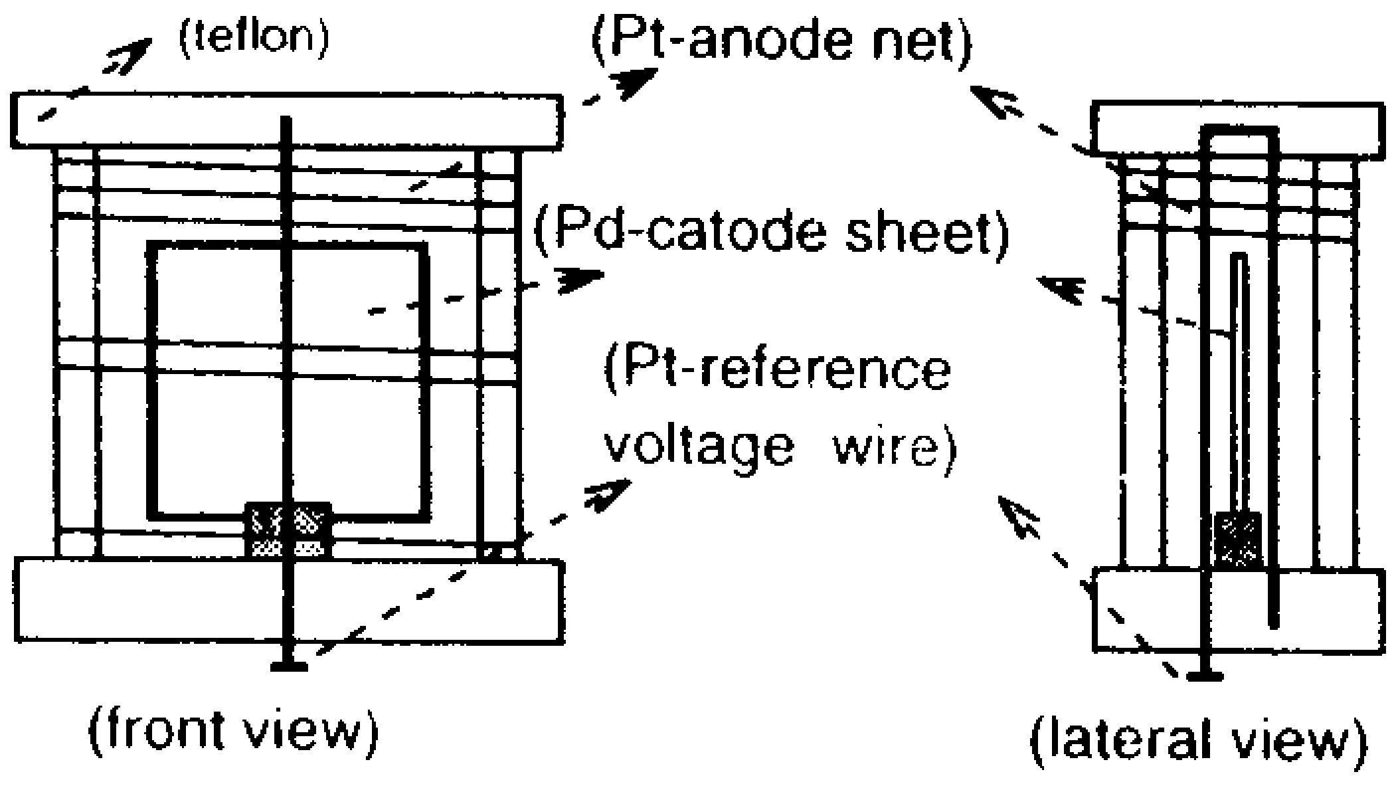
Our electrolytic system was presented at the Fourth International Conference on Cold Fusion,[4] where the calorimetry was described in some detail. We used a flow calorimeter composed of a cylindrical polyethylene vessel containing a double copper coil (Fig. 1). The copper coil was protected from the electrolyte by a thermally conductive plastic layer (polyacrylic isocyanate). Ordinary water, passing through the coil, cooled the solution. Seven temperature sensors were located appropriately to measure the heat production and to cross-check the calorimeter operation. The anode was a platinum wire net coiled around a Teflon sample holder in a proper geometrical shape to smooth a nonuniform electric field at the edges of the plate. In this way, we reduced the effect of the deuterium discharge at the edges of the plate due to the strong electric field gradients. The platinum net was substantially shorted to avoid adding indeterminate inductance or magnetic fields to the system.

A platinum wire reference electrode was located 3 mm in front of the two sides of the palladium plate. The platinum anode (1-mm-diam) net was 1 cm from the cathode; the electrolytic solution used was 0.3 M/ℓ LiOD D_2O. An electrovalve was inserted along the outgoing gas pipe just to define a close volume ($\sim 150\ \mathrm{cm}^3$) to store the gas coming from the electrolysis (Fig. 2).

A circuit (Fig. 3a) was devised to generate high-peak-current pulses (rise time <300 ns at 100-A peak). The pulse was generated by a capacitive unipolar discharge triggered by a pulse generator. The circuit



a) Inner cell



b) electrode holder

Fig. 1. Inner cell design and electrode holder. (a) Inner cell: the input and output of the cooling water is kept under control by two double independent temperature sensors. (b) Electrode holder: the platinum anode wire net was turned in an opportune way to produce higher electric field density on the edge of the cathode plate.

(Fig. 3b) worked in two stages. First, the capacitors charged slowly from the voltage supply (τ of $\sim 10\ \mu s$). Second, the fast electronic switch (gated by the trigger pulse) connected the charged capacitors to the cell electrodes, which produced a very high current in a short time (typically 1 μs). When the active switch connected node C to A, the capacitor was charged through the D1 diode. A 10 kΩ in parallel with diode D1 reduced the voltage drop during capacitor charging and suppressed oscillations during discharge. When node C was connected to B, the capacitor was grounded through the cell while the gate was on (the discharging pulse time was a few microseconds, and the D2 diode was direct polarized). The electrodes in the electrolyte, under a fast current pulse, could be considered to be a reactive dipole circuit; we put the D2 diode before the connection with the cell to avoid charging the intrinsic capacitance of the cell between pulses.

We calibrated the circuit using an equivalent resistor instead of the cell. We performed additional tests using a gold plate cathode to estimate the electrolytic

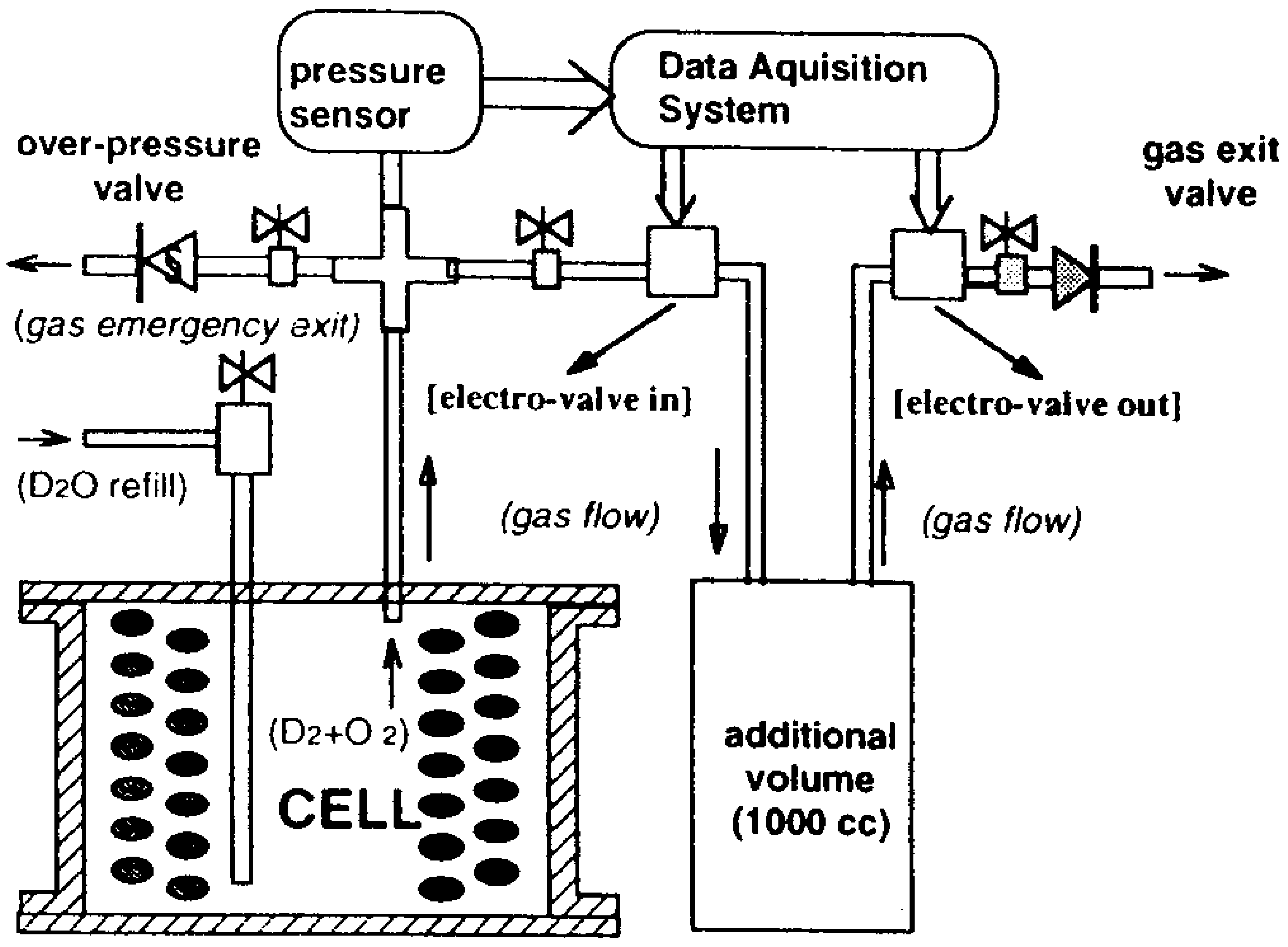
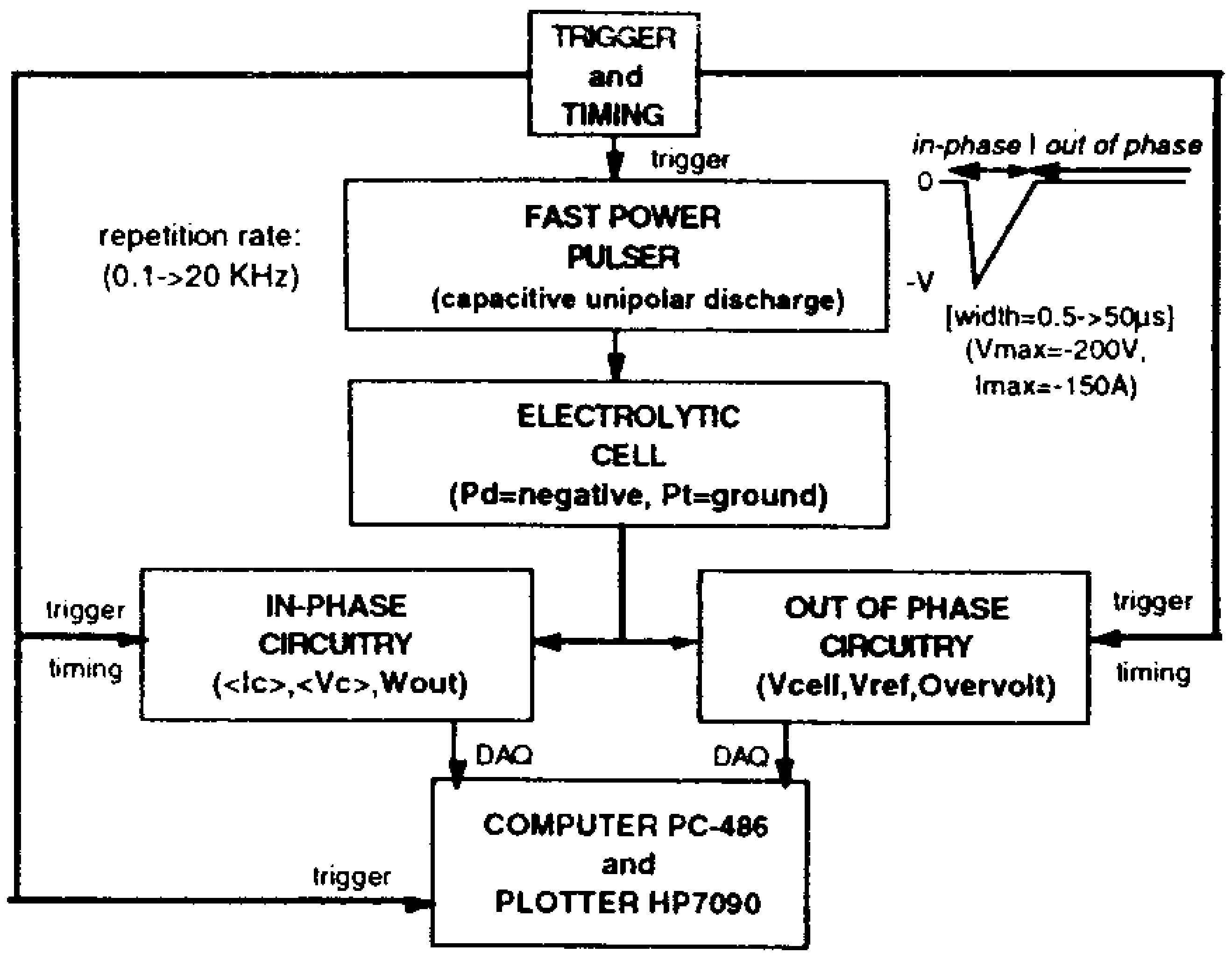
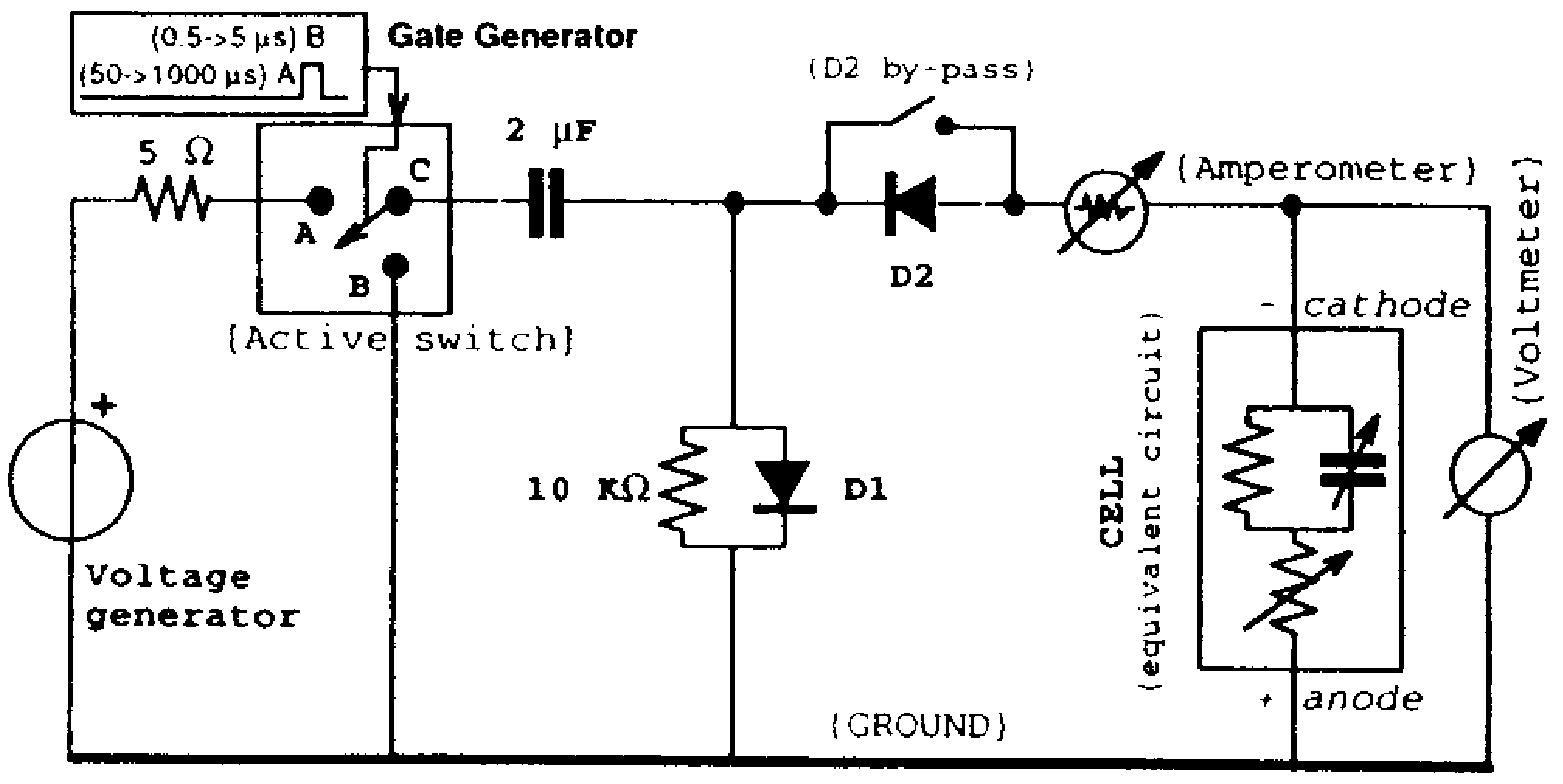


Fig. 2. Outgoing cell gas system: Two synchronized electrovalves were used to control the electrolyte gas pressure inside the cell volume.



a) circuitry: block scheme



b) electronic circuit: principle scheme

Fig. 3. High-power pulse circuitry. (a) Block scheme of the triggered fast-pulse generator and additional circuitry modules to acquire the electric parameters. (b) Electronic scheme of the fast-power pulse: A gate generator (active switch) controls the discharge and restoring time of the capacitor.

efficiency of the system. For cross-checking purposes of electrolysis and Faraday Law applicability under short-pulse conditions, we simply used a direct current source to measure the electric charge flow and the volume of electrolytic gases produced. Substituting the direct current with a pulsed current having the same mean value (i.e., the same amount of charge flowed in the same period of time), we measured the gases developed, and we called the ratio of these gas masses (by the pulsed and direct currents) the electrolytic efficiency of the system. The efficiency was >95%. If we performed the same test closing the D2 diode bypass, the efficiency dropped to 5%: This means that the D2 diode is relevant to the pulsed system functionality.

A circuit measured the electric charge involved in each pulse (i.e., this charge was ~12.8 μC corresponding to 200 μJ/pulse in the experimental procedure described in Sec. III). The electric power involved in each pulse was measured by a fast analogue multiplier by using the current that passed through the electrodes and the voltage between them.

The pulse generator selected the start and stop time of the measurement. Another circuit (out-of-phase) measured both the voltage of the cathode and the voltage of the platinum wire floating electrode (RHE), which was put in the solution 3 mm from the cathode. These voltages were used to determine the overvoltage parameter.[5] The out-of-phase voltage measurements were performed after a delay (30 μs) from the end of the power pulse, when the palladium/platinum system was electrically decoupled from all circuitry by two high-power fast recovery diodes (40HFL80S05) connected in series.

III. EXPERIMENTAL PROCEDURE

The common initial loading procedure for all plates is described as follows.

1. The pulse generator was rated at 5 kHz, the main voltage supply energized the power capacitors at 50 V, and the pulse width discharge was set at 0.5 μs, which produced a peak pulse current of ~16 A. These conditions were equivalent to an electrolytic mean current of ~64 mA. The peak input voltage at the palladium cathode was ~32 V from a 50-V power supply. The difference was due to losses in the MOSFET power switches, cable, connectors, diodes, and series shunt resistance (0.1 Ω) to measuring the current. The plate dimensions were 25 × 25 × 1 mm. If one takes into account a nickel sample holder surface of ~1 cm^2, the effective area of the plate exposed to the electrolyte was 11.5 cm^2. The mean current density was 5.56 mA/cm^2. The peak current density was ~1390 mA/cm^2.

2. The electrolytic gases that developed at the electrodes were collected in a fixed volume (~150 ml) at (measured) room temperature, and the pressure was continuously calibrated. When the pressure reached 60 mbar, the electrovalves were opened for a short time (1 s) so gases could escape: We defined this as a pressure cycle.

3. The cooling water flow rate was measured together with the input and output temperatures to calculate the heat produced.

4. To calculate the deuterium-loading factor, we assumed Faraday's law and the gas laws and so calculated the quantity of gases expected from a pressure cycle; we assumed that all of the shortfall was due to absorption of deuterium in the palladium cathode (but see the following exception).

5. To check this, we made two independent tests. In some cases, we weighed the charged palladium electrode after electrolysis, we heated the plate to 250°C for 24 h to expel the deuterium, and then we reweighed. The difference confirmed our assumptions. In other cases, we substituted the palladium plate by a similar gold plate, and there was shortfall of only 1% in the volume of gases produced (i.e., a false loading factor of 0.01). This was due to D_2 absorbed by cell materials (solution, polyethylene, heater, Teflon, etc.). This D_2 absorption occurred only during initial loading and slowly decreased with time (it disappeared in our case after ~600 C of electrolytic charge), and the deuterium/gold reached a maximum value of 0.01. In the calculations, we took into account this small effect and made appropriate corrections to the data.

IV. ABSORPTION BEHAVIOR OF PALLADIUM PLATES

We tested six cold-worked palladium sheets (25 × 25 × 1 mm) designated: T05 (Tanaka K.K.) and I63, I65, I85, I120, and I340 (IMRA MATERIAL). The Tanaka plate (T05) (with a very high hardness value of 300 Hv) was prepared with specific impurities (2780 parts per million) enclosed during the melting preparation: The high hardness is related to the doping. The IMRA plates were pure cold-worked palladium (with hardness values < 200 Hv). The I120 was a Pd-Ag alloy (10% silver).

Figures 4a, 4b, and 4c show the absorption rates (in moles per second per square centimetre) and the D/Pd loading as a function of time (and the total electric charge passed between the electrodes) for the I65, I85, and I120 pure surface palladium plates; the absorption rate provides information about the quantity of deuterium flowing through the palladium surface per time unit and surface unit. Clearly, the deuterium absorption was very high initially and decreased smoothly to zero as the loading increased to a plateau value. Of course, the absorption rate is a function of surface area, while the final loading factor is a bulk parameter. The absorption curves have a similar shape, and the process is quite reproducible.

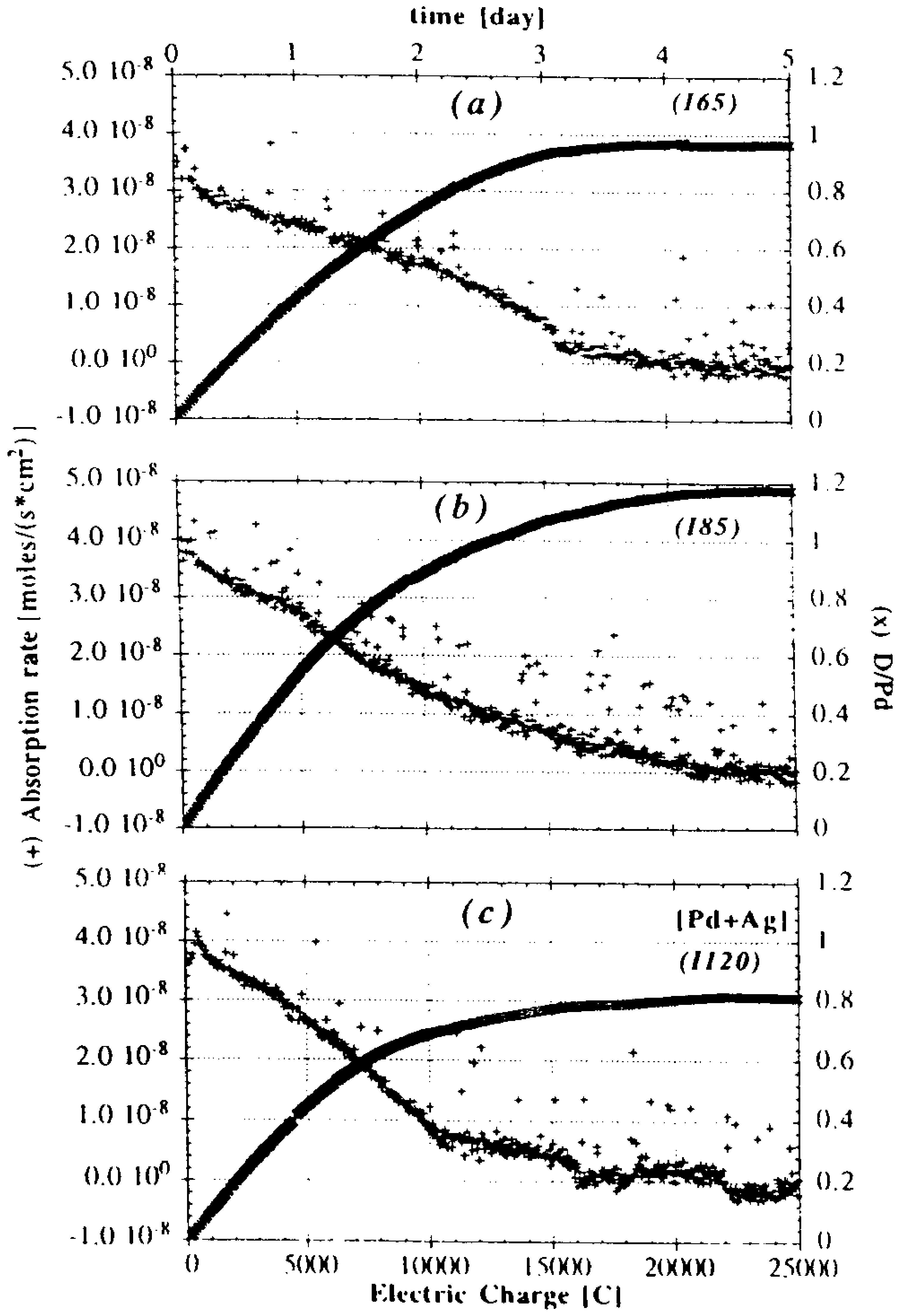


Fig. 4. Paladium plates: absorption rate and D/Pd ratio compared with time and electric charge. (a) I65 plate, (b) I85 plate, and (c) I120 (Pd 90%, Ag 10% alloy): the D/Pd ratio means D/(Pd|Ag).

The I63 and I340 plates were specially treated by our procedure, subsequently verified independently.[6] We heated the plates to ~700°C using an oxidizing flame for a processing time of some minutes.

After this treatment, the plates showed a thin surface oxide layer (blue color) and a high resistance to the concentrated nitric acid attack. In contrast, the T05 plate was doped with a boron compound during melting and later cold worked: The boron impurities were present up to a few percent in the plate. This plate presented a very high hardness (~300 Hv).

Figures 5a, 5b, and 5c show the absorption rates on the T05, I65, and I340 loading plates. The absorption curves are different compared with the previous plates: For ~1 day, these curves are flat and later fall faster. This suggests that the surface barrier permits absorption to stay about constant, so that the total amount of absorbed deuterium is higher in a shorter period of time.

We can exclude any significant heat production due to electrolytic reduction of PdO. We can estimate the amount of surface PdO by weighing the plate. It is ~0.5 μm thick (0.07 mmol corresponding to 1 part per thousand of palladium). About 5 C of current would be required to reduce this compared with at least 6700 C to achieve a D/Pd loading ratio of 1.

The I63 and I340 plates, which had the same PdO surface treatment, have a similarly shaped absorption curve, so they exhibit the same barrier absorption dynamics. The phenomenon is easily reproducible. In addition, the boron-doped T05 plate absorption curve shows a similar shape to the previous two plates: a flat region (lasting ~1.5 days). It may be that during cold working, boron diffuses to and concentrates at the surface, and a similar barrier effect occurs.

Figures 4 and 5 show that high loading ratios (exceeding 1.1) were reached in all the plates tested. The

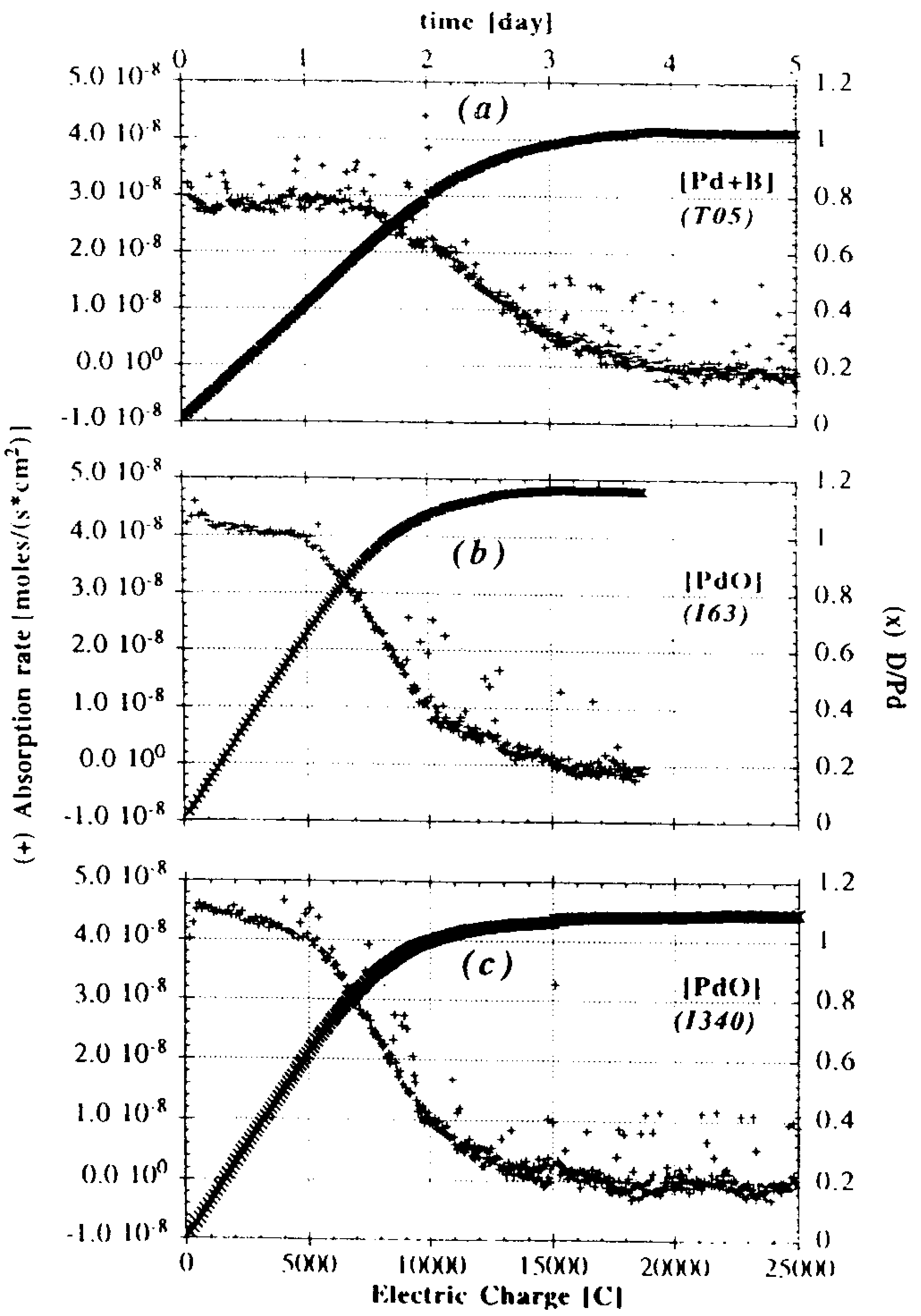


Fig. 5. Palladium-modified surface plates: absorption rate and D/Pd ratio compared with time and electric charge. (a) T05 plate: boron impurities (a few percent) addition, (b) I63 plate: surface treated with PdO, and (c) I340 plate: surface treated with PdO.

only exception was the I120 plate, which is a Pd-Ag alloy and which has a palladium concentration of 90% (in this case, the D/Pd value was calculated as D/(Pd + Ag). Moreover, the I63 and I340 plates (with PdO surface treatment) seem systematically to exceed the value 1.1. The loading parameter is not well correlated with the absorption rate because it is a bulk rather than a surface parameter. The most indicative parameter from a surface point of view must be the absorption rate.

V. EXCESS HEAT RESULTS

The usual controls that use the gold plate instead of the palladium cathode were performed. These tests were used as a reference to calculate the input/output energy involved in the pulsed electrolysis process, as well as the absorption rate and the overvoltage parameters. The initial loading conditions for all the tested plates were the same. After that (~1 week later), several operating parameters were changed: peak amplitude, repetition rate, and pulse width.

Let us now consider some measurements of the excess heat occurring during initial loading for the I65, I63, and I340 plates (Figs. 6a, 6b, and 6c). To calculate excess heat variation, we subtracted from the output heat produced by the cell, the effective input electric energy corrected for the energy to produce the electrolytic gases. The data were referenced to some gold plate blank tests occurring before and after the palladium plate tests.

The I65 plate (with a pure palladium surface) did not show any excess heat (at the beginning, the cell was colder than the operating temperature produced by the input power of ~1 W). In contrast, the I63 and I340 plates (with a PdO surface) showed relevant excess heat peaks during the same absorption rate flat region time (lasting ~1 day). The I63 plate electrolysis was performed with the cell temperature colder than the operating temperature produced by the input power. During the test of the I340 plate, we took care to operate with the cell temperature at the same value of the temperature at the expected stationary regime. After this anomalous energy peak, these plates seemed to remain at an approximately +50% flat excess heat permanent regime.

From these observations, we make the following conclusions regarding excess heat production:

1. The phenomenon, in our case, seems to be related to surface effects.

2. Even high D/Pd-loading ratios (>1) do not guarantee production of excess heat.

3. The absorption rate seems to be an indicative parameter and characterizes barrier effects. Significant excess heat seems to be related to anomalous high absorption rates.

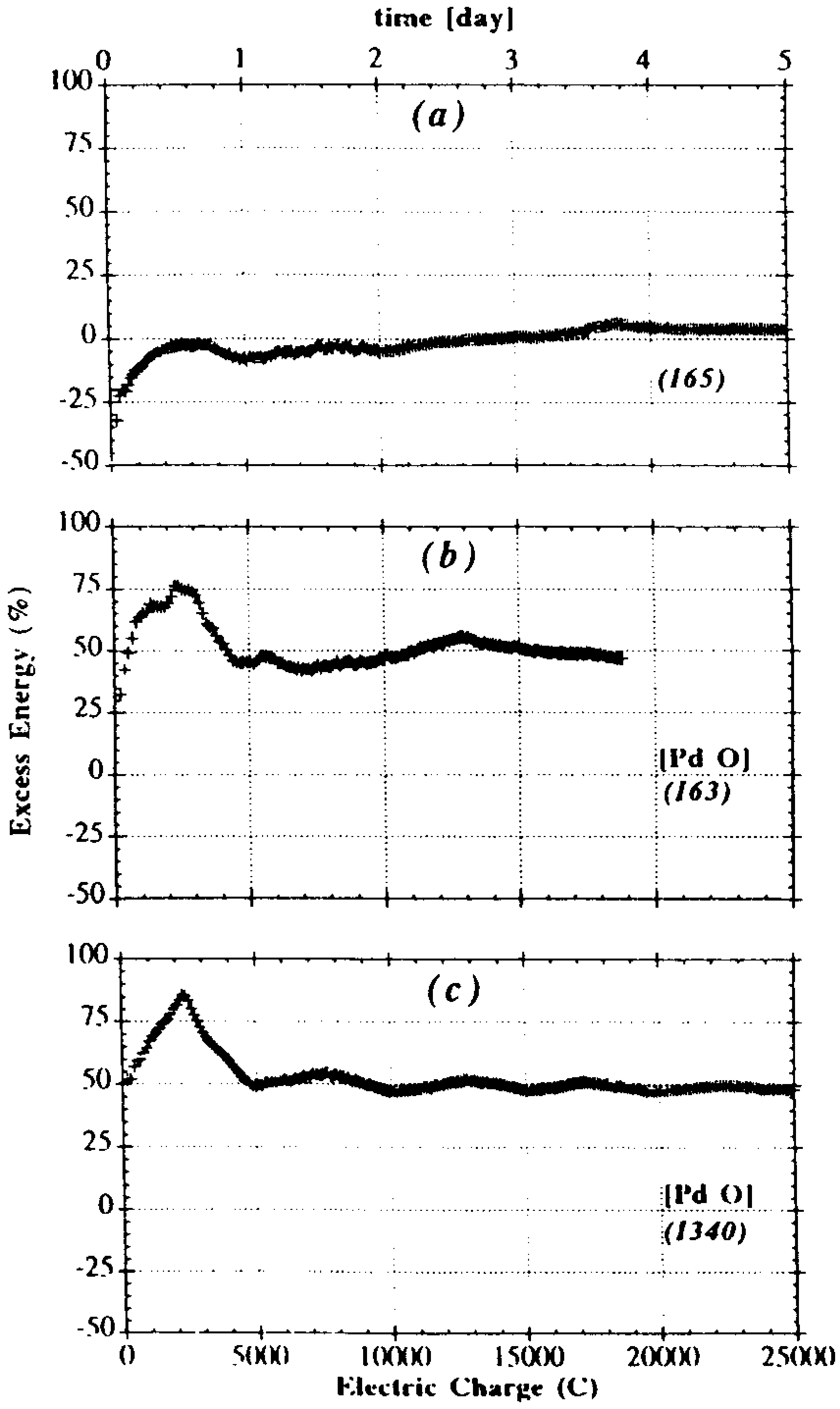


Fig. 6. Palladium plates: excess energy variation (%) compared with time and electric charge. All data are referenced to the gold blank tests. (a) I65 plate: pure palladium plate, clean surface, (b) I63 plate: surface treated with PdO, and (c) I340 plate: surface treated with PdO.

VI. METALLURGICAL AND SURFACE ASPECTS

We think that the ionic ^{3}Li present in the solution can play an important role depending on the metallurgical properties of the surfaces.[7] The overvoltage and plate surface resistance parameters could give indications about surface modifications during loading. To investigate these effects, we substituted gold plates for the palladium cathodes. We observed an increase of the overvoltage (up to 0.15 V) on the gold plate during the initial days of electrolysis. This seems to support the hypothesis of a very thin deposition (or absorption) of the lithium on the cathode surface.

In the past, we observed that mechanically hard plates (>170 Hv) permitted high D/Pd ratios, presumably because these hard plates reduced the possibility of cracks on the electrode surface. Palladium hardness no longer seems so important in reaching high deuterium loading as the high-pulse technique described seems to work independently of the metallurgical treatment of the palladium cathode. However, hardness and surface treatments still play an important role in creating conditions for excess heat.

VII. OVERVOLTAGE

The overvoltage on the palladium cathode exceeded gold (by up to 0.25 to 0.35 V after the Tafel contribution[7-10] subtraction) because of the deuterium absorption process and surface modifications (Figs. 7a, 7b, and 7c) (Ref. 2). It may be relevant to note that the overvoltage seemed to reach a value higher than 0.30 V in the case of the modified palladium surfaces (T05 and I63) compared with the pure palladium surfaces (I65), but overvoltage effects in general are not always reproducible (the I340 plate overvoltage curve is very different with respect to the similar I63 plate). Overvoltage is a function of solution temperature, surface micro cracks, and lithium and plate deformation; further study is required.

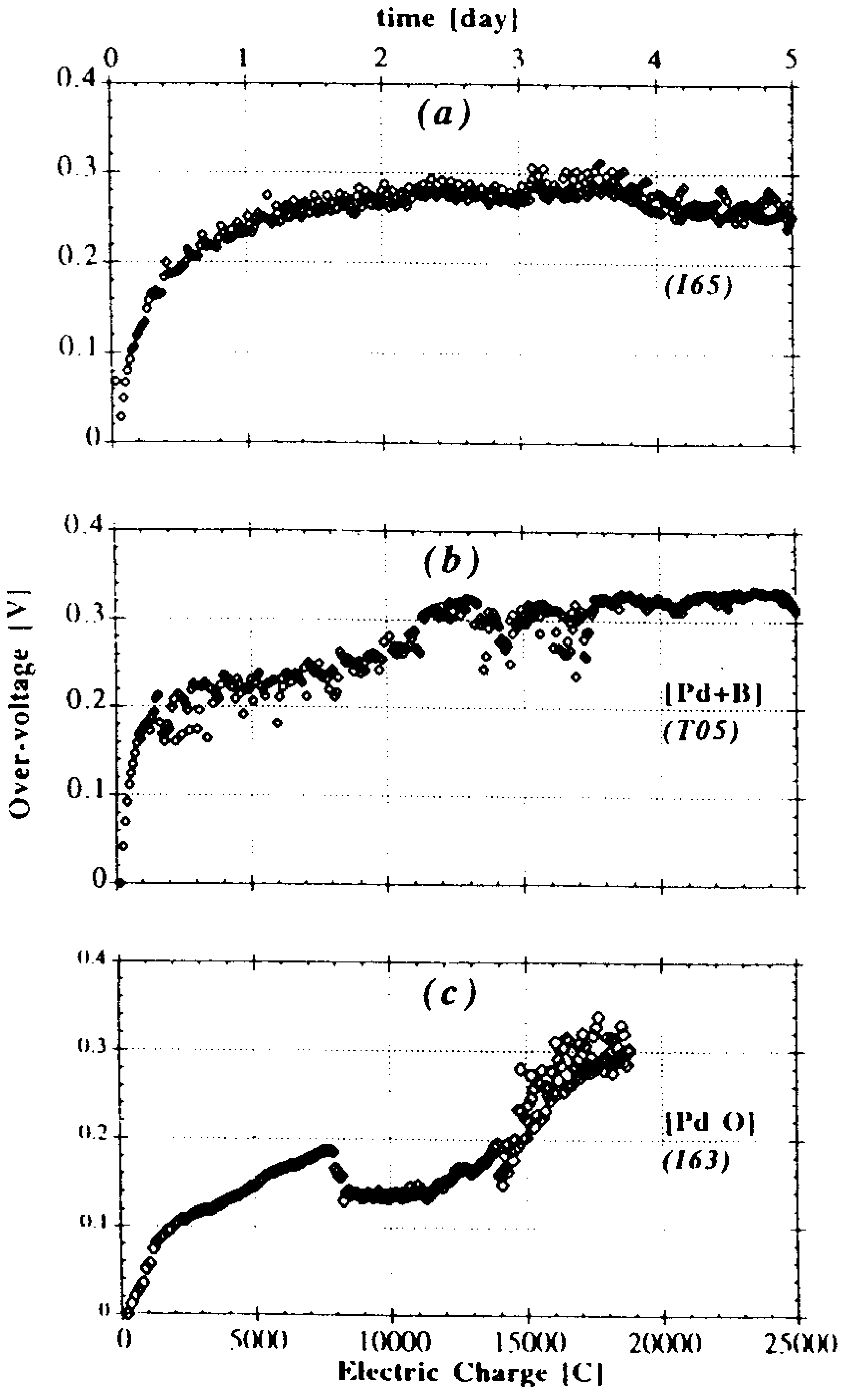


Fig. 7. Palladium plates: overvoltage compared with time and electric charge. The Tafel voltage contribute is subtracted. (a) I65 plate: pure palladium plate, clean surface, (b) T05 plate: boron impurities on the surface, and (c) I63 plate: surface treated with PdO.

VIII. CONCLUSIONS

Independent of the metallurgy of the palladium cathodes, we have developed a high-pulse technique to load high concentrations of deuterium in palladium (D/Pd > 1.1). However, surface treatment of the plates affects the absorption rate shape parameter (thin PdO films or palladium-boron compounds). Various palladium plates were tested, and these processes occurred in similar (reproducible) ways.

The absorption kinetics are particularly interesting. In our opinion, the absorption rate is a more reliable parameter than the D/Pd value for predicting the production of excess heat. Our techniques seem to give reproducible methods for loading palladium with deuterium.

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