

# STUDY OF DEUTERIUM CHARGING IN PALLADIUM BY ELECTROLYSIS OF HEAVY WATER

ELECTROLYTIC DEVICES

**KEYWORDS:** *electrochemical loading, deuterium diffusion, palladium*

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*Two different polarization regimes have mainly been used during electrolytic deuterium loading of palladium cathodes to produce an excess of heat in "cold fusion" experiments. Most of the experimentalists apply a constant current density, while some prefer to work with a square-wave current. The different effects of the two techniques on the deuterium dynamics through the cathode are not yet very clear. Thus, a transport model supported by a computer code is used to describe the evolution of the deuterium concentration profile inside a palladium membrane cathode for both operating conditions.*

## INTRODUCTION

It has been well established that deuterium (or hydrogen) can be loaded in the palladium lattice even above the loading ratio  $x = \text{deuterium/palladium (D/Pd)} \cong 0.8$  (atoms of deuterium per atom of palladium).

We now quote from the current literature some features of deuterium-palladium compounds, showing that deuterium atoms exceeding the  $x = 0.8$  D/Pd ratio have a distinctive kind of interaction with the lattice.

1. It has been observed for hydrogen in palladium<sup>1,2</sup> that between  $x = 0.6$  and  $x \sim 1$ , the diffusion coefficient of deuterium (and hydrogen) in palladium increases steeply by almost two orders of magnitude over to  $2 \times 10^{-6} \text{ cm}^2/\text{s}$  (Ref. 1). Such a value is fairly similar to the diffusion coefficient of many electrolytes in aqueous solution. This effect is very surprising but can be explained by assuming that the energy variation required for an atom to move from one lattice site to

another decreases as the concentration increases. Since the diffusion coefficient follows the Arrhenius law

$$D = D_0 \exp(-E/kT),$$

a steep increase must be expected if the energy barrier between two allowed positions has decreased.

2. It is known<sup>3,4</sup> that the volume change ( $\Delta V/V$ ) of the palladium lattice cell as a function of the loading ratio is a straight line, which shows a change in slope approximately at  $x = 0.8$ . This means that for higher concentrations, the interaction between the deuterium atoms and the palladium lattice changes.

3. The palladium electronic configuration is  $[\text{Kr}]4d^{10}$ . However, its metallic behavior permits hybridization with the broad band 5sp. The electrons fill the 4d band up to the Fermi energy, leaving 0.36 available states per palladium atom at the top of the band. In the palladium-deuterium compound, the deuterium electrons fill a group of low-lying states, with high symmetry well below the Fermi energy,<sup>5</sup> then fill the available states in the 4d and 5sp bands. This is a low-cost operation until free states are available; then, it is mandatory to increase the Fermi energy, which can be very expensive in terms of energy balance for the system.

4. Measurements of magnetic susceptibility and electronic specific heat<sup>5</sup> show that the density of states close to the Fermi energy decreases when the hydrogen content increases. However, Hall effect measurements<sup>6</sup> show a steeper decrease of the Hall constant for  $x = 0.83$  hydrogen/palladium atoms corresponding to an increase of the electrical conductivity for the same concentration. The two sets of measurements are consistent only if one assumes that for  $x \cong 0.8$ , a new kind of carrier must be considered.

These features prompt us to propose the following picture for the transport model. The deuterium atoms in the palladium lattice can be considered almost

bounded (slow diffusion) below a loading ratio  $x \sim 0.8$  (nevertheless, they perform  $>10^{10}$  change/s of lattice positions at room temperature). When the loading ratio increases around the threshold value of 0.8, the deuterium mobility increases more than two orders of magnitude, and the diffusing atoms can be considered as being in a high-mobility state, similar to an electrolyte moving through a solution under thermodynamic potential. This picture is very close to the dense plasma state proposed for such a system by Crowley.<sup>7</sup>

The proposed model is based on the following assumptions:

1. The deuteron sublattice is decoupled from the palladium lattice.
2. The deuteron/deuteron interaction is short-range with a typical length of the order of the electron screening length in metals.

A diffusing gas of screened deuterons is the resulting structure for the model.

## THE MODEL

Some experiments indicate that anomalous heat may be produced during electrolytic charging of deu-

terium into palladium if the loading ratio is  $>0.8$  (Kunimatzu et al.<sup>8</sup> and McKubre et al.<sup>9</sup>). A typical feature of the first experiments was the need for a long precharging procedure, as long as weeks or even months, for the anomalous effect to appear. More recently, a pulsed technique has been used,<sup>10,11</sup> consisting of applying either a sawtooth current (just at the beginning of the run) or alternating low currents/high currents with long periods ("lo-hi" technique), resulting in a much more efficient charging mechanism. This behavior inspired us to study theoretically the loading and transport dynamics of deuterium in palladium in the framework of lo-hi electrolysis.

The model considers the palladium cathode as a membrane (with a very high surface-to-thickness ratio) separating two regions. Two different instances have been considered:

1. The cathode is totally immersed in an electrolytic cell.
2. Only one side of the cathode participates in electrolysis, while the other is exposed to an environment containing  $D_2$  gas (see Fig. 1).

In accordance with the picture of the deuteron screened gas into the palladium lattice, we can write an

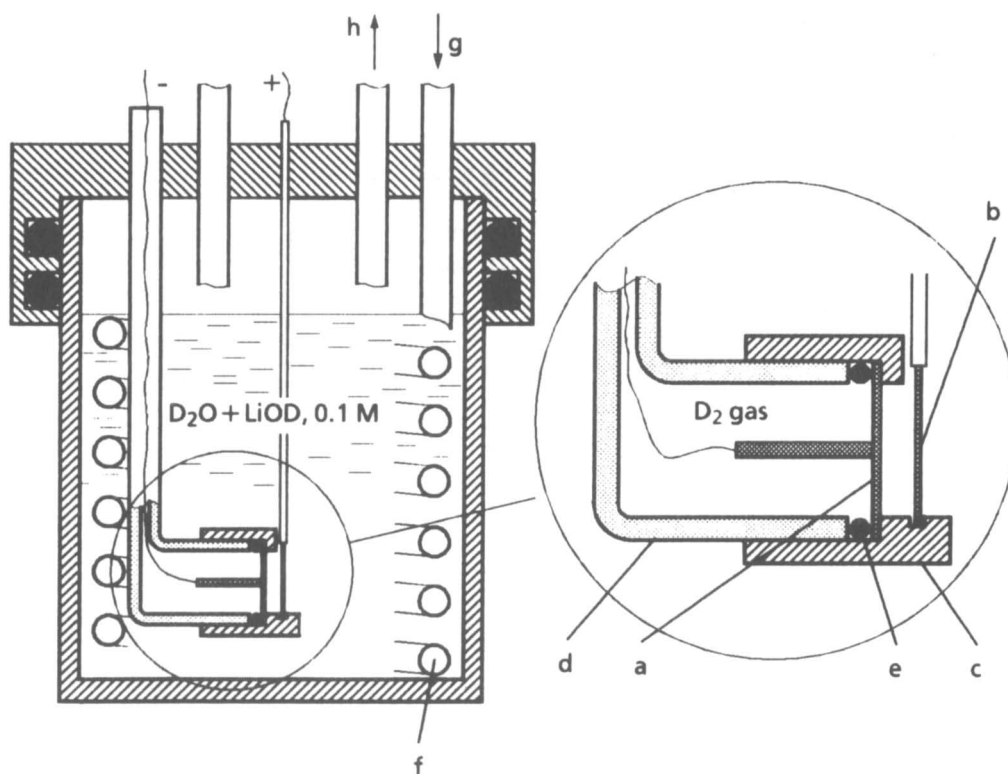


Fig. 1. Schematic drawing of the apparatus where a is the cathode, b is the anode, c is the Teflon support, d is the glass pipe, e is the o-ring, f is the glass coil, g is the cooling water inlet, and h is the water outlet.

expression for flux, which depends locally on both concentration and electric field,

$$J = -D \left( \nabla C - \frac{Fz^*E}{RT} C \right), \quad (1)$$

where

$D$  = diffusion coefficient

$F$  = Faraday's constant

$E$  = local electric field

$C$  = concentration of the deuterons

$R$  = gas constant

$T$  = temperature

$z^*$  = effective deuteron charge (electrotransport).<sup>12</sup>

Fick's diffusion coefficient for the hydrogen isotopes in palladium changes with their concentration<sup>13</sup> according to

$$D(C) = D^* f(C),$$

where

$$D^* = D_0 \exp(-\Delta E/kT)$$

and  $D(C)$  is connected with the mobility or Einstein diffusion coefficient  $D^*$  by means of the thermodynamic factor  $f(C)$ . For the sake of simplicity, the authors assumed a constant value for  $D$  ( $1 \times 10^{-6} \text{ cm}^2/\text{s}$ ) because the study is performed for a deuterium concentration above  $x = 0.75$  (see the initial condition). In the investigated concentration field ( $0.75 < x < 0.95$ ), the hydrogen diffusion coefficient values reported in literature<sup>1</sup> fluctuate within a factor of 10, which corresponds to the experimental uncertainty.<sup>1</sup> Data for deuterium in palladium for  $x \geq 0.8$  are still not published, so we were forced to use the corresponding hydrogen data.<sup>1</sup>

In the considered system, there is no electric field directly applied across the membrane electrode; thus, without upsetting the screened deuteron picture, we will neglect the electrotransport term of Eq. (1) for the flux evaluation.

The mass transfer equation in transient conditions can be written as

$$\frac{\partial C}{\partial t} = \nabla J. \quad (2)$$

The initial condition is

$$C(x,0) = C_0, \quad (3)$$

where  $C_0$  is the initial deuterium concentration (corresponding to  $x = 0.75$ ). The boundary conditions are

$$C(x_0, t) = \begin{cases} C_1 & t_0 < t < (2n + 1)t_s \\ C_2 & (2n + 1)t_s < t < 2(n + 1)t_s \\ & (n = 0, 1, 2, \dots) \end{cases}, \quad (4a)$$

where  $2t_s$  is the period of the pulsed electrolysis;

$$x = L \quad \frac{dC_s}{dt} = [K_{ads}P(1 - \theta_g^2) - K_{des}C_s^2] + J_d, \quad (4b)$$

where

$\theta_g$  = fraction of saturated adsorption sites on the gas-side surface {when  $\theta_g$  is close to 1, the saturation is achieved, and the adsorption contribution to the mass balance [Eq. (4b)] vanishes}

$P$  = evolving deuterium pressure in the gas side [see Eq. (5)]

$J_d$  = diffusive flux passing through the membrane electrode for  $x = L$

$$J_d = -D \left. \frac{\partial C}{\partial x} \right|_{x=L}$$

$K_{des}$  ( $\text{cm}^{-2} \cdot \text{s}^{-1}$ ),  $K_{ads}$  ( $\text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{atm}^{-1}$ )

= desorption and adsorption constants respectively. The values of the kinetic constants have been extrapolated from the literature.<sup>14</sup>

$C_s$  = deuterium concentration on the gas side of the cathode.

Also,

$$x = \frac{L}{2}; \quad \frac{\partial C}{\partial x} = 0. \quad (4c)$$

Condition (4a) describes the electrolysis side of the electrode; condition (4b) is obtained from a mass balance on the surfaces, which describes the gas side of the electrode by taking into account the deuterium flux from the bulk, the desorption from the cathode gas side surface, and the adsorption from the gas; condition (4c) refers to symmetric electrolysis (the membrane cathode is between two equal anodic plates).

The terms  $C_1$  and  $C_2$  are the surface concentrations on the electrolysis side in low and high current, respectively. These concentration values have been calculated by applying the Enyo theory for hydrogen adsorption on cathodes during electrolysis.<sup>15-17</sup> The theory states a relationship between the surface concentration, the overpotential, and the current density:

$$\bar{C} \frac{d\eta}{dt} = J - J_0 \{ \gamma \uparrow \exp(\beta f \eta) - \gamma \downarrow \exp[-(1 - \beta) f \eta] \},$$

$$\gamma \uparrow = \frac{\theta}{\theta_0} \exp[\delta u(\theta - \theta_0)],$$

and

$$\gamma \downarrow = \frac{1 - \theta}{1 - \theta_0} \exp[-(1 - \delta)u(\theta - \theta_0)],$$

where

$\bar{C}$  = double-layer capacitance

$\eta$  = cathodic overpotential

$J_0$  = exchange current density<sup>15-17</sup>

$J$  = current density

$\theta$  = surface coverage

$\theta_0$  = equilibrium surface coverage

$\beta$  = symmetry factor<sup>18</sup>

$f = F/RT$

$\delta$  = constant ( $0 < \delta < 1$ ) (Refs. 15, 16, and 17)

$u = U/RT$  [ $U$  is the interaction parameter in the adsorption isotherm 15 kJ/mol hydrogen (Ref. 18)].

The Enyo equation has been applied considering that the adsorption transient on the cathode surface is very fast ( $10^1$  to  $10^2$  s) compared with the lo-hi current period of the pulsed electrolysis ( $10^3$  to  $10^4$  s), and solved with respect to  $\theta$  at the steady state. Differences in the surface concentration of the order of 5% have been calculated between lo-hi current states (i.e., from 30 up to 300 mA/cm<sup>2</sup> and  $-0.35 < \eta < -0.5$  V): At low current, the surface coverage is 0.94, while at high current, the  $\theta$  value is  $\sim 1$ . Such behavior of the cathodic hydrogen adsorption on palladium has been observed experimentally.<sup>8</sup>

The gas flux from/toward the cathode produces a variation of the number of deuterium molecules in the gas phase and thus a pressure variation through the state equation:

$$\frac{\partial P}{\partial t} = \frac{RT}{V'} \frac{\partial N_{GAS}}{\partial t}, \quad (5)$$

where  $V'$  is the gas volume and the derivative on the right side, describing the evolution of the deuterium in the gas phase, is evaluated by the desorption-adsorption flux.

The numerical solution of the differential equations (2), (4b), and (5), describing the mass transfer process, has been solved numerically by using a simulation language (CSMP). The intrinsic capability of the simulation language allows us to integrate on a variable (i.e., the time) through a language statement. To solve the distributed parameter model describing the transient diffusion [Eq. (2)], we subdivided the spatial domain into 20 intervals (corresponding to 0.025 mm each) and then solved the diffusion equation as a system of difference equations:

$$\frac{dC_i}{dt} = \frac{C_{i+1} - 2C_i + C_{i-1}}{\Delta x},$$

where the subscript  $i$  ( $i = 1$  to 20) indicates the interval and  $\Delta x$  is the spatial integration step. The routine

evaluates, through Eqs. (4b) and (5), the gas-side surface concentration and the gas pressure, integrating internally on the time variable. The computer routine allows one to solve the transport equation with the interface boundary condition (4b).

## RESULTS

The main feature of pulsed electrolysis is that the system is continuously forced away from its equilibrium, and strong concentration gradients arise in the bulk at a high loading ratio. Figure 2a shows the concentration profiles for two contiguous slabs beneath the surface in a palladium cathode dipped in pulsed electrolysis (the period is  $\sim 3000$  s) with a symmetrical electric field. Figure 2b shows the same for continuous electrolysis. The crossing of two concentration profiles in Fig. 2a for a certain time means that density waves

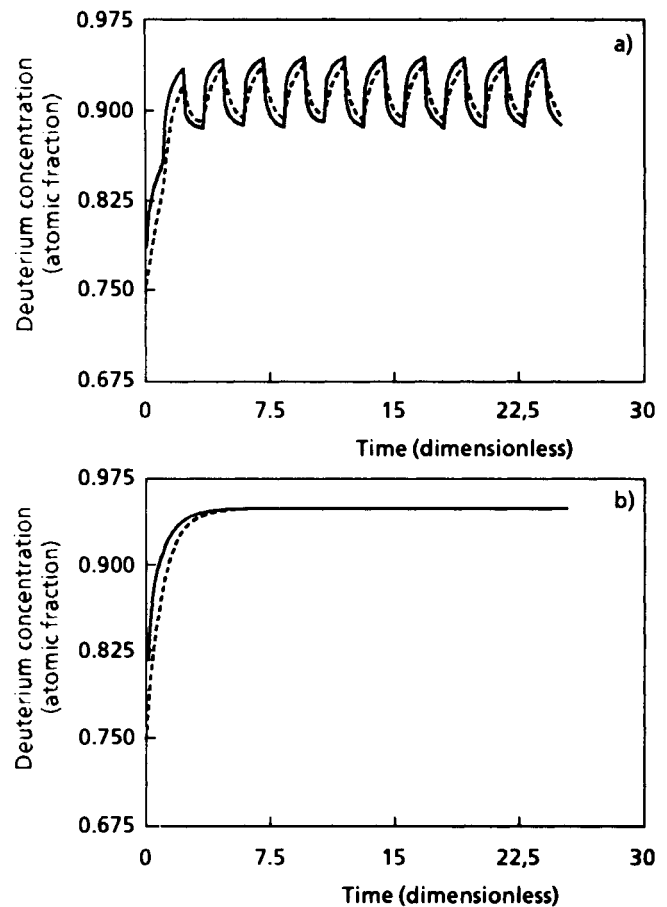


Fig. 2. Concentration profiles of two contiguous slabs compared with dimensionless time; y axis represents the real loading ratio D/Pd, for (a) symmetric pulsed electrolysis and (b) symmetric continuous electrolysis, upper curve describes the concentration evolution in a slab just beneath the surface.

move into a palladium membrane during pulsed electrolysis. The dimensionless time used for the plots was calculated by means of the diffusion time, which is  $\sim 2500$  s, since the membrane cathode is 0.5 mm thick and the considered diffusion coefficient is  $1 \times 10^{-6}$  cm<sup>2</sup>/s. Therefore, each dimensionless time unit should be multiplied by 2500 to get the duration of the experiment (in seconds).

Figure 3a shows the pulsed electrolysis case (the period is  $\sim 3000$  s) with asymmetrical boundary conditions. Figures 3a and 3b refer to different current periods. If the lo-hi current period is too long, the system tends to its steady state, and the effect of the crossing of two concentration profiles is reduced.

One of the most interesting features of asymmetrical electrolysis is the behavior of the flux of deuterium atoms through the separation surface between the palladium cathode and the deuterium gas.

The authors observed experimentally<sup>10</sup> that the pal-

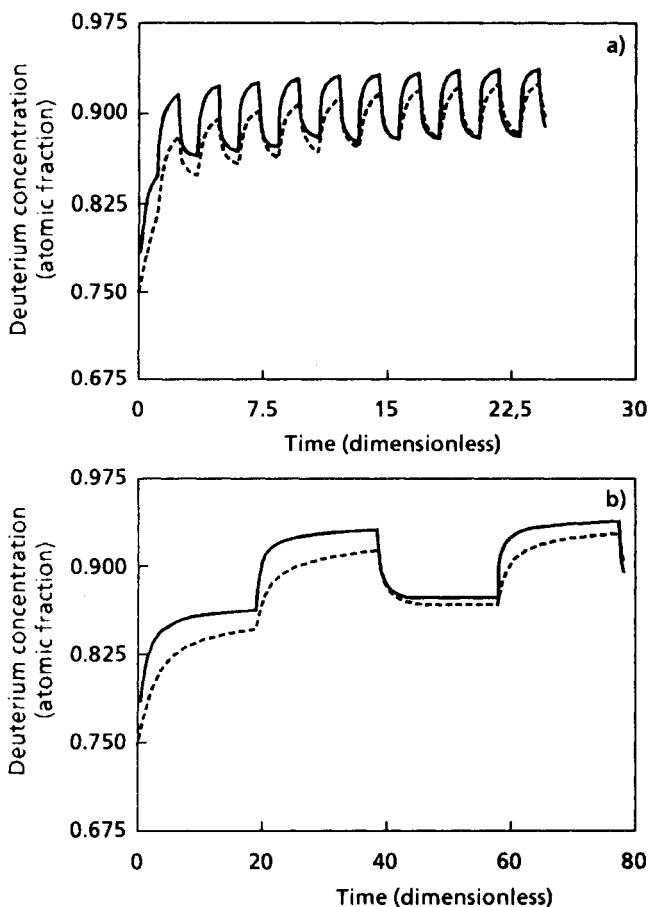


Fig. 3. Asymmetric pulsed electrolysis, concentration profiles compared with dimensionless time; y axis represents the real loading ratio D/Pd, obtained with (a) a short lo-hi period and (b) a long lo-hi period (four times longer than Fig. 3a).

ladium cathode acts as a deuterium permeable membrane, as is well known. The throughput flux is a function of both the gas pressure and the surface concentration at a fixed temperature, according to the phase diagram.

The flux is higher when the gas pressure is lower than the equilibrium pressure allowed for a certain surface concentration  $C_s$ . However, since  $C_s$  depends on the lo-hi current period, the permeating flux oscillates according to it (Figs. 4a and 4b). This behavior cannot be simply explained by the cathode temperature variation during pulsed electrolysis; however, by using the kinetic condition (4b) to describe the gas-side surface, the model reproduces the observed behavior quite well (see Fig. 4).

## CONCLUSIONS

It was observed experimentally<sup>10</sup> that there is a strong correspondence, well reproduced by the model, between the applied current value and the deuterium flux through the palladium membrane cathode in an asymmetrical configuration. The deuterium flow rate through the membrane increases by increasing the current density. This effect is equivalent to an increase of deuterium surface concentration on the palladium cathode: When the current increases, the total coverage of the adsorption sites is achieved; this is in accordance with other experimental results.<sup>8</sup> In other words, in a mass transfer process, controlled by the concentration gradients, a flux increase corresponds to higher gradients. Therefore, the enhancement of the current is related to the increase of deuterium concentration on the electrolysis side.

The model is not concerned with heat production; however, many experiments indicated a correlation between excess heat production and deuterium concentration in the cathode.<sup>8,9</sup> Then, it must be very useful to know exactly the concentration profile inside the electrode.

The highest deuterium concentration values are achieved with the continuous symmetric electrolysis, but the period of lo-hi current affects the charging efficiency and creates concentration dynamics that might be closely connected to the appearance of heat excess.<sup>11</sup> The experiments show that there is a correlation between the lo-hi current frequency, the deuterium dynamics, and the heat production.<sup>10</sup>

One of the most interesting features of the system under study, evidenced by the calculations, is the actual presence of density waves moving in the bulk of the electrode. These low-frequency concentration waves could induce a local gradient profile reversed with respect to the mean concentration gradient. Such behavior is a straightforward consequence of the proposed picture of deuterons as diffusing gas.

The accordance between the model results and the experimental data concerning the pressure evaluation

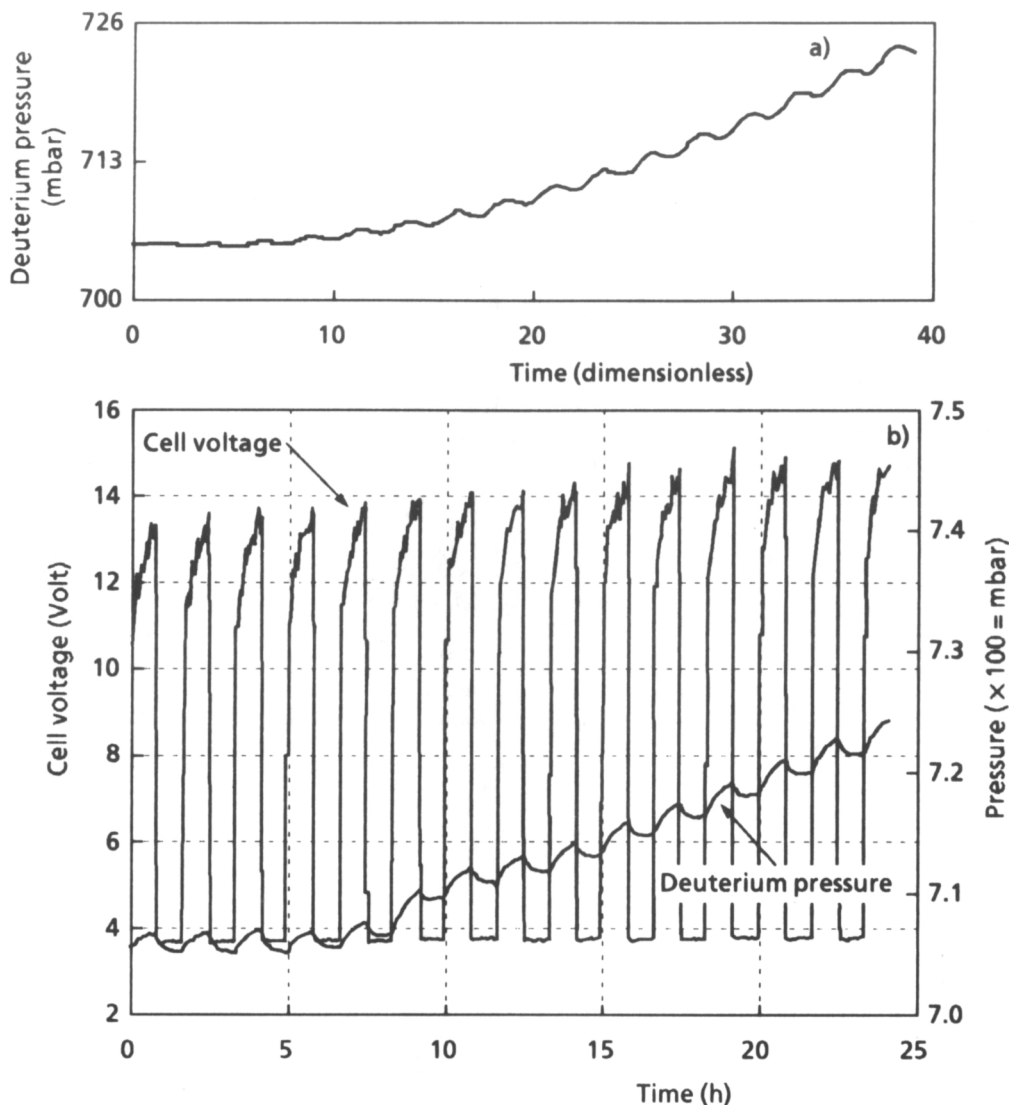


Fig. 4. (a) Theoretical pressure evolution compared with dimensionless time (20 to 200 mA, 3000-s period). (b) Experimental pressure evolution in the gas side compared with experimental time. The deuterium flux through the palladium cathode increases and decreases according to the lo-hi states (20 to 200 mA, 3000-s period).

in the gas side is a confirmation, in terms of mass transfer, of the Enyo theory of the hydrogen adsorption on palladium during electrolysis.

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