

ON THE RELEASE OF ^3H FROM CATHODICALLY POLARIZED PALLADIUM ELECTRODES

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Release paths for tritium produced during electrochemical compression of deuterium in a Pd lattice are examined. Arguments in support of the reversal of diffusion caused by gas evolution on the electrode surface are presented.

I. INTRODUCTION

Tritium production via electrochemically generated deuterium in the Pd lattice was observed by, among others, Chien et al.,¹ Storms and Talcott,² Will et al.,³ and Szpak et al.⁴ Except for the massive production reported by Chien et al., the observed rates were low ($\sim 10^4$ atoms/s averaged over a 24-h period⁴). In this paper, we examine transport of the absorbed hydrogen and its isotopes out of the cathodically polarized Pd electrode. The model presented here differs from that proposed by Storms⁵ and Storms and Talcott-Storms,⁶ who concluded that the mode of transport out of the electrode interior is through capillaries produced by stresses associated with volume expansion. Here, we discuss an alternate transport route, namely, that resulting from the surface inhomogeneities associated with gas evolution.

II. ELECTRODE/ELECTROLYTE INTERPHASE

As reported earlier,⁴ tritium produced during prolonged electrolysis was transported out of the electrode interior by two distinct paths: the first resulting in the enrichment of both the electrolyte and gas phases, the second producing enhancement only in the gas phase. It was noted that transport out of the electrode interior was retarded by the addition of, for example, Al^{3+} ions to the

electrolyte. These observations and the emanation of weak X rays⁷ suggest that the nuclear events leading to the tritium production are located in close proximity to the electrode surface.

Transport of hydrogen (or its isotopes) out of the electrode interior, when under cathodic polarization, is possible by (a) convective flow of the hydrogen gas via interconnected voids forming, in effect, open channels and (b) hydrogen flux reversal generated by nonuniform primary current density distribution associated with gas evolution. Random distribution of gas bubbles results in local changes in current density (and overpotential), which, in turn, produce changes within the interphase. The discussion that follows is based on the model of the interphase structure with the following features:

1. The electrode/electrolyte interphase is an assembly of nonautonomous layers with its structure determined by the operating processes,⁸ while the interface is the contact surface (surface of discontinuity).
2. The absorbed hydrogen causes lattice distortion accompanied by volume changes and has high mobility.
3. At the relevant current densities, bubbles of gaseous hydrogen are formed and rapidly removed from the electrode/electrolyte contact surface.
4. Reaction sites are located in close proximity to the contact surface.

This model does not include (see Sec. IV) the following:

1. transport assisted by a random distribution of interconnected voids⁹
2. presence of a random distribution of nuclear reaction sites¹⁰
3. ionization of absorbed deuterium at high D/Pd atomic ratios¹¹
4. the effect of local volume changes on transport.¹²

III. FLOW REVERSAL ASSOCIATED WITH GAS EVOLUTION

The time rate of change of the absorbed deuterium in the electrode interior is governed by particle flux through the contact surface and transport in the bulk. In our model, we specify the electrode interior as consisting of N layers ($N = 1, 2, \dots, 10$) and initially assume a uniformly distributed particle flux (uniform current density). However, such an assumption is not valid for electrodes charged in the presence of gas evolution. To a first approximation, the effect that evolved gas has on the redistribution of absorbed hydrogen and its isotopes can be observed by setting the cell current to zero and watching how the system relaxes at the surface and in close proximity to the surface.

The progress in electrode loading, as well as other pertinent information, is obtained by numerically solving the following set of equations¹³:

$$\frac{d\eta}{dt} = \frac{1}{C_{dl}} (I - j_1 - j_2) , \quad (1)$$

$$\frac{d\theta}{dt} = \frac{1}{\Gamma_m F} (-j_1 + j_2 + j_3 + j_4) , \quad (2)$$

$$\frac{d\zeta_1}{dt} = -\frac{1}{\delta} \left[\frac{j_4}{Z_m F} + k_d Z_m (\zeta_1 - \zeta_2) \right] , \quad (3)$$

and

$$\frac{d\zeta_i}{dt} = \frac{k_d Z_m}{\delta} (\zeta_{i-1} - 2\zeta_i + \zeta_{i+1}) , \quad (4)$$

where

j_1 = charge transfer current for Volmer path

j_2 = charge transfer current for Heyrovsky-Horiuti path

j_3 = equivalent current for Tafel path

j_4 = equivalent current for the absorption step

Γ_m = maximum number of sites per unit area

Z_m = maximum number of sites per volume

θ, ζ = fractional occupation sites

δ = layer thickness

C_{dl} = capacitance of the double layer

F = Faraday constant.

Equations (1), (2), and (3) state that deuterium is deposited onto the electrode surface by the Volmer path and removed by the Heyrovsky-Horiuti path, the Tafel path, and absorption.

Changes in the surface concentration $\Gamma_m \theta(t)$, overpotential $\eta(t)$, and absorbed deuterium within the layers $Z_m \zeta(t)$ during the electrode loading (at $I = 40 \text{ mA/cm}^2$,

$t = 100 \text{ s}$) followed by complete unloading are shown in Figs. 1a and 1b for two diffusion coefficients $D = 10^{-10}$ and $D = 10^{-8} \text{ cm}^2/\text{s}$ (rate constants: $k_d = 2.0 \times 10^{-4}$ and $k_d = 2.0 \times 10^{-2}$). It is seen that on loading, the time-dependent surface coverage and electrode overpotential are identical, but the distribution of the absorbed hydrogen differs. For the selected set of rate constants, the transport is diffusion controlled in Fig. 1a, while Fig. 1b illustrates the surface control. The situation is quite different immediately after cell current termination; i.e., the direction of deuterium transport is reversed. In particular, during the first 900 s, the surface coverage is transport controlled [note: as indicated, $\theta(t)$ is less for $D = 10^{-10}$ than for $D = 10^{-8} \text{ cm}^2/\text{s}$]. After this time period, a complete overlap of $\theta(t)$ curves indicates surface-controlled events.

The formation, growth, and detachment of electro-generated hydrogen gas bubbles have a profound effect on the overall process(es) in both the solution and metal side of the interphase. The effect of gas bubbles on the outflow of absorbed hydrogen by the exchange between the absorbed and adsorbed atoms is simulated by tracing its distribution in close proximity to the contact surface, here limited to the first three layers (Figs. 2a and 2b). In modeling tritium outflow, two factors are important: the residence time and the change in chemical potential of adsorbed hydrogen at the bubble formation site. Here, we arbitrarily assumed the nuclear reaction sites to be in the second layer (i.e., in close proximity to the contact surface) and calculated the change in the distribution of absorbed hydrogen as a function of time resulting from setting the cell current to zero. The rate at which this change occurs is governed by bulk transport. This difference is illustrated in Figs. 2a and 2b for $D = 10^{-8}$ and $D = 10^{-10} \text{ cm}^2/\text{s}$. In highly concentrated systems,¹¹ where the diffusion coefficient may be as high as $10^{-5} \text{ cm}^2/\text{s}$, rapid exchange between the absorbed and adsorbed species favors tritium release as suggested in Ref. 4 rather than by the convective flow in channels.

IV. DISCUSSION

The evolution of gas bubbles on the electrode surface precludes uniform distribution of the current density and, therefore, overpotential. This, in turn, results in the removal of an external force acting on interphase of the hydrogen-loaded electrode and ensures local formation of gradients. How deep into the electrode interior these gradients extend depends on the residence time of the gas bubbles and the relaxation time of the process(es) under consideration. In addition to the electric potential gradients operating within the interphase, gradients arising from the volume changes and their effect on the transport should be considered. Moreover, if a nuclear event takes place, its net energy must be added. The

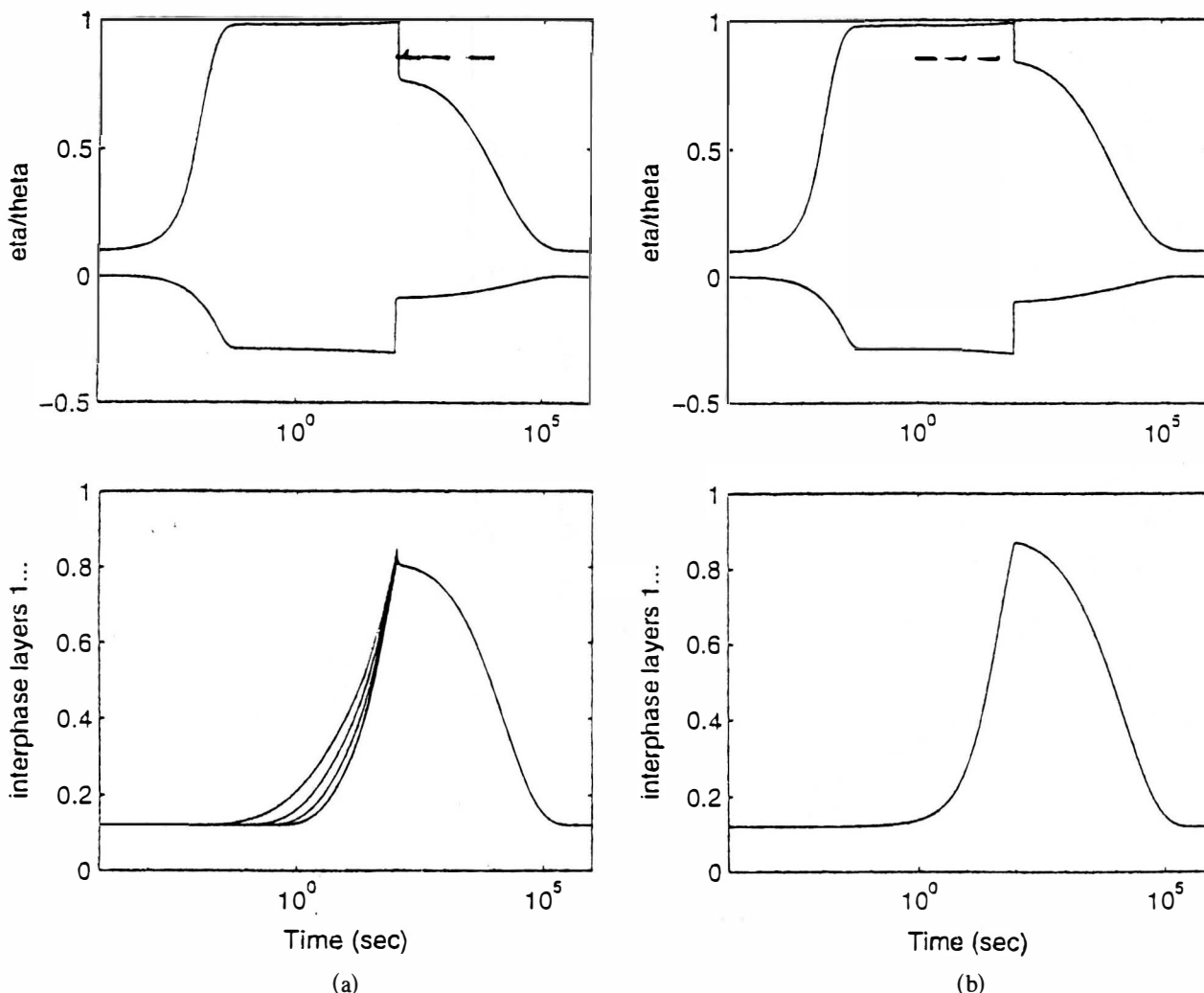


Fig. 1. Time-dependent characteristics of absorption and desorption. Modeling parameters: $N = 10$, $\theta_0 = 0.1$, $\zeta_0 = 0.12$; $\Gamma_m = 10^{-11}$ mol/cm²; $Z_m = 10^{-1}$ mol/cm³; $\delta = 10^{-5}$ cm; rate constants: $k_1 = 10^5$ cm³/mol·s; $k_2 = 10^2$ cm³/mol·s; $k_3 = 10$ cm²/mol·s; $I = 40$ mA/cm², loading time $t = 100$ s. Upper: deuterium distribution as a function of time: (a)—for $D = 10^{-10}$ cm²/s and (b)—for $D = 10^{-8}$ cm²/s. Lower: surface coverage and overpotential as a function of time: (a)—for $D = 10^{-10}$ cm²/s and (b)—for $D = 10^{-8}$ cm²/s.

resultant question is, Do these events affect transport properties, and, if so, could they promote flow reversal without first creating capillaries? In particular, we address the question of whether or not the formation of capillaries is the only condition that promotes the removal of tritium produced during cathodic polarization out of the electrode interior.

We note that the transport of absorbed hydrogen through a Pd lattice, and particularly within the interphase at high D/Pd ratios, is described by the flux density of the Einstein-Smoluchowski equation

$$j = \beta c f(x) - D \frac{\partial c}{\partial x} - c \frac{\partial D}{\partial x}, \quad (5)$$

where function $f(x)$ arises from the interaction of Tritium atoms with external strain¹⁴ and electric¹⁵ fields and where

β is the mobility (defined here as the ratio of average velocity to applied force). Since concentration and temperature gradients are expected at the nuclear reaction sites and, at high D/Pd ratios, the diffusion coefficient is a function of concentration,¹¹ Eq. (5) is preferred for the examination of transport in close proximity to the contact surface. Depending on conditions, some of the terms in Eq. (5) can be omitted; thus,

1. For dilute solutions, where D is a constant, only the $D\partial c/\partial x$ term is retained.¹⁶

2. In the presence of voids, two cases can be differentiated: (a) discrete voids exhibiting distribution in size and position and (b) interconnected voids with channels extending to the contact surface. If the former applies, D is a function of position, and term $\partial D/\partial x$ is retained. If

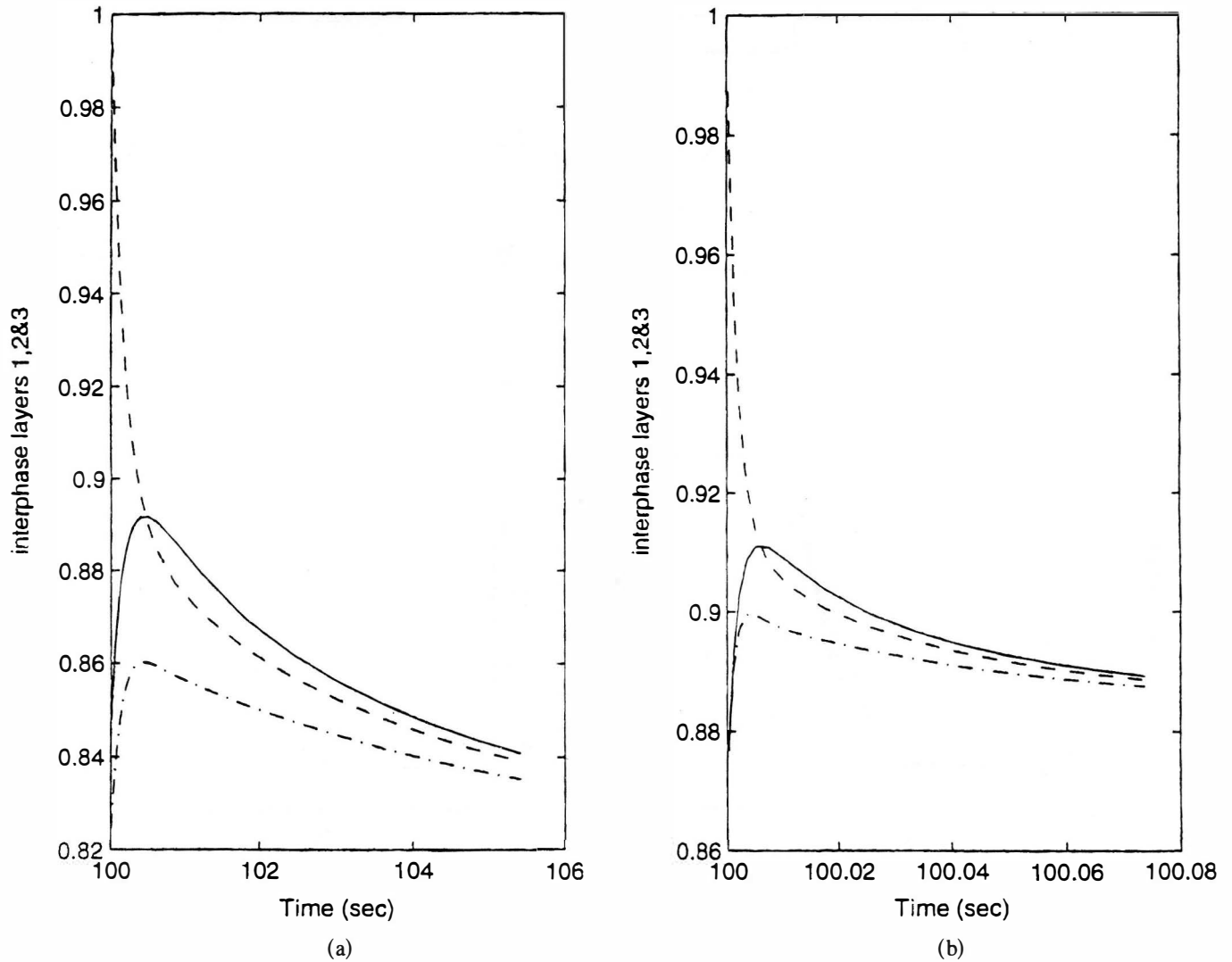


Fig. 2. The T distribution in the first three layers with $\zeta_2 = 1$. Modeling parameters as in Fig. 1. Solid line, first layer; dashed line, second layer; dashed-dotted line, third layer. (a)—for $D = 10^{-10} \text{ cm}^2/\text{s}$ and (b)—for $D = 10^{-8} \text{ cm}^2/\text{s}$. Note difference in timescale.

the latter applies, $\partial D/\partial x$ is dropped and $f(x)$ represents the pressure gradient, i.e., we have a case of diffusion assisted by a convective component.

3. If a nuclear reaction (e.g., production of tritium) occurs, not only are all terms retained but a source term must be added, resulting in the temperature gradient $\partial T/\partial x$.

As the hydrogen concentration increases, voids containing molecular hydrogen are formed. When their internal pressure exceeds the strength of the electrode material, channels extending in all directions are created, as illustrated in Fig. 3. Some of them reach the contact surface and allow a rapid outflow of hydrogen, thus preventing the initiation of nuclear events such as tri-

tium production, alternatively, their termination. Consequently, it is important to determine conditions that promote channeling. This has been discussed by Bockris and Subramanyan¹⁷ and Flitt and Bockris.¹⁸ Briefly, conditions that promote channeling are related to the mechanism of the hydrogen evolution reaction¹⁷ (HER) and the energetics of adsorbed hydrogen atoms.¹⁸ In particular, fast j_1 slow j_3 favors channeling, while slow j_1 fast j_3 and slow j_1 fast j_2 do not. In other cases, such as fast j_1 slow j_2 , coupled j_1 slow j_3 and coupled fast j_1 slow j_2 may promote channeling, depending on rate constants of the participating paths.

Because the chemical potential gradient $\nabla\mu$ is the generalized force for the flow of matter, it is instructive to transform Eq. (5) into

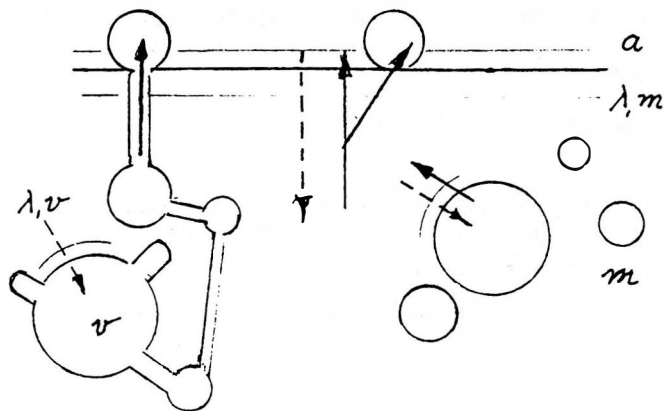


Fig. 3. Schematic representation of interconnected (left) and discrete (right) voids. Arrows indicate flux direction: dashed line, during loading; solid line, during unloading. Values λ , a , v , and m are defined in text.

$$v = -\frac{D}{RT} \frac{\partial \mu}{\partial x} + \left[\beta f(x) - \frac{\partial D}{\partial x} \right], \quad (6)$$

where $v = j/c$ is the average particle flux velocity, and to use this equation to discuss the transport of tritium from the reaction site to the bulk of contacting phases.

Consider a fully charged Pd electrode containing discrete and interconnected voids of varying size distributed throughout the electrode interior, shown in Fig. 3. In the absence of mass flow, the polarized electrode represents a closed system subject to the action of an external force η . Under these conditions, equality of chemical potential can be assumed, i.e., $\mu^{(a)} = \mu^{(\lambda, m)} = \mu^{(m)} = \mu^{(\lambda, v)} = \mu^{(v)}$, where superscripts denote the respective locations:

λ, m = subsurface layer

m = bulk metal

λ, v = subsurface/void gas layer

v = gas in the void.

Qualitatively, the effect of formation and growth of the gas bubble reduces and, for a brief period of time, eliminates the external force acting at the point of contact. Since $\mu^{(a)} = f(\theta, \eta)$ (Ref. 17), it follows that upon the reduction of η , a condition $\mu^{(v)} > \mu^{(\lambda, v)} > \mu^{(m)} > \mu^{(\lambda, m)} > \mu^{(a)}$ exists, resulting in production of localized gradients, $\nabla \mu$, and exit of deuterium, and, respectively, tritium from the electrode interior into either the electrolyte or the gas bubble [paths A and B (see Ref. 4)]. Quantitative assessment would involve the relaxation times of the individual steps. There is some experimental evidence suggesting the importance of the $(\lambda, m) \rightarrow (a)$ step in the course of unloading.¹⁹

V. CONCLUDING REMARKS

In summary, we note the following:

1. Tritium production requires high D/Pd atomic ratios. This requirement is met if there are no channels reaching the contact surface. The electrogenerated tritium is distributed among voids and bulk material. Should new conditions arise that create channels, e.g., a change in the HER mechanism, a short time release of tritium would take place. In our experimental work,⁴ there is no clear evidence for this to occur.

2. Conditions believed to affect the initiation of the Fleischmann-Pons effect is the existence of gradients and other "hidden variables."¹² Such conditions do exist in the vicinity of the contact surface and are, in part, due to evolving gas bubbles. The thickness of the active region depends on the residence time of gas bubbles and the dominant transport step. The estimated thickness for diffusion control is in the micron range.

3. Gas evolution promotes a continuous exchange between the Tritium atoms residing in the subsurface layer with those in the adsorbed state. Atoms in the adsorbed state exchange with the molecules of the contacting electrolyte phase or gaseous phase, leading to two distinct transfer paths.

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