

# CODEPOSITION OF PALLADIUM AND DEUTERIUM

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*The quasi-one-dimensional model of isotope loading into a material relates the loading flux, the electric order/thermal disorder ratio, and other physical issues. The theoretical nonequilibrium deuterium/palladium ratio at the surface of a palladium electrode, previously shown to depend on the loading flux ratio, is corrected both for intrapalladium diffusion of the loaded deuterons and for secondary changes in electrode volume, possibly explaining the often considerable time elapsed until the onset of the desired reactions.*

## INTRODUCTION

Several hurdles remain in the successful utilization of the cold fusion phenomena.<sup>1</sup> Most important is the improved characterization and preparation of palladium of sufficient integrity into which to successfully load<sup>2</sup> and activate<sup>3</sup> the isotopic fuel—deuterium. Adequate loading ( $\lambda_{D,Pd}$ ) must occur despite major difficulties involving the loading flux ratio,<sup>2</sup> the electric order/thermal disorder ratio, and other physical issues.<sup>2,4,5</sup> Additional difficulties include the often considerable time elapsed until the onset of the desired reactions.<sup>1</sup>

## MODEL

The quasi-one-dimensional (Q1D) model of isotope loading<sup>2,4,5</sup> has enabled the cathode deposition of ions to be investigated using nonequilibrium calculations.<sup>6</sup> In the absence of significant convection, the flux of each species (here deuterium and palladium cations) results from diffusion down concentration gradients and electropho-

## NUCLEAR REACTIONS IN SOLIDS

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retic drift.<sup>5,7</sup> The coupled equations follow (see Nomenclature on p. 129):

$$J_D = -B_D * \frac{d[D(z,t)]}{dz} - \mu_D * [D(z,t)] * \frac{d\Phi}{dz} \quad (1)$$

and

$$J_{Pd} = -B_{Pd} * \frac{d[Pd(z,t)]}{dz} - \mu_{Pd} * [Pd(z,t)] * \frac{d\Phi}{dz} \quad (2)$$

The mathematical solution for the time rate of change of the deuterium in any given volume is determined by these fluxes and Gauss's theorem. Deuterium and palladium entry to the cathode is electron limited. Three components of the deuterium flux are considered at the cathode. The first flux component is the entry of deuterons into the bulk of palladium  $J_e$ . The second flux component is the volume loss of deuterons secondary to gas evolution  $J_g$ . The third flux component is caused by those deuterons lost to all putative fusion reactions  $J_{fus}$ . The palladium flux at the cathode is simpler because of the absence of palladium gas formation. The mathematical solutions are determined both by the boundary conditions and by conservation of mass for both species. There is assumed conservation of deuterons with the exception of a loss  $J_{fus}$  to all putative fusion reactions.<sup>4</sup> However,  $J_{fus}$  is extremely small compared with most loading rates or gas-evolving reactions.<sup>2</sup>

By assuming that the fluxes are first order on the local concentrations of available material, then the first-order reaction rates of deuterium loading, gas evolution and fusion  $\sum K_i$ , and palladium deposition  $K_{Pd}$  are definable, enabling a possible solution. In the steady state, the initial coefficient  $[A_{0,D}]$  of the final spatial distribution of deuterons at the pericathodic interface has been derived<sup>2,4,6</sup>:

$$A_{0,D} = \frac{[D_{init}] * \left\{ \left[ \left( \frac{qE}{2k_B T} \right) - \left( \frac{\sum K_i}{2 * B_D} \right) * L_c \right] \right\}}{\left( \exp \left\{ \left[ \left( \frac{qE}{2k_B T} \right) - \left( \frac{\sum K_i}{2 * B_D} \right) * L_c \right] \right\} + \left[ \left( \frac{qE}{2k_B T} \right) - \left( \frac{\sum K_i}{2 * B_D} \right) * L_c \right] - 1 \right)} \quad (3)$$

As discussed,<sup>2</sup> this finding was augmented by the initial coefficient  $[A_{0,Pd}]$  of the final spatial distribution for palladium that is electrodeposited on the cathode in codeposition:

$$A_{0,Pd} = \frac{[Pd_{init}] * \left\{ \left[ \left( \frac{qE}{2k_B T} \right) - \left( \frac{K_{Pd}}{2 * B_{Pd}} \right) * L_c \right] \right\}}{\left( \exp \left\{ \left[ \left( \frac{qE}{2k_B T} \right) - \left( \frac{K_{Pd}}{2 * B_{Pd}} \right) * L_c \right] \right\} + \left[ \left( \frac{qE}{2k_B T} \right) - \left( \frac{K_{Pd}}{2 * B_{Pd}} \right) * L_c \right] - 1 \right)} \quad (4)$$

The ratio of Eqs. (3) and (4) did show that the use of codeposition of palladium from palladium salts in a deuterium-containing solution<sup>2,3,7</sup> can be used to attain a much more rapid onset of (at least local) full loading. Thus, the initial coefficient of the deuterium/palladium ratio at the surface of a palladium electrode with the full inclusion of palladium cation codeposition<sup>2,7</sup> has been discussed<sup>2</sup>:

$$A_{0,D/Pd} = \frac{\left( \exp \left\{ \left[ \left( \frac{qE}{2k_B T} \right) - \left( \frac{K_{Pd}}{2 * B_{Pd}} \right) * L_c \right] \right\} + \left[ \left( \frac{qE}{2k_B T} \right) - \left( \frac{K_{Pd}}{2 * B_{Pd}} \right) * L_c \right] - 1 \right) * [D_{init}] * \left\{ \left[ \left( \frac{qE}{2k_B T} \right) - \left( \frac{\sum K_i}{2 * B_D} \right) * L_c \right] \right\}}{\left( \exp \left\{ \left[ \left( \frac{qE}{2k_B T} \right) - \left( \frac{\sum K_i}{2 * B_D} \right) * L_c \right] \right\} + \left[ \left( \frac{qE}{2k_B T} \right) - \left( \frac{\sum K_i}{2 * B_D} \right) * L_c \right] - 1 \right) * [Pd_{init}] * \left\{ \left[ \left( \frac{qE}{2k_B T} \right) - \left( \frac{K_{Pd}}{2 * B_{Pd}} \right) * L_c \right] \right\}} \quad (5)$$

This loading ratio has indicated the possibility of sufficient loading very close to the electrode surface with a time constant related to the relaxation of palladium from the solution onto the cathode. If a minimal loading ratio is required for the desired cold fusion reactions, then the maneuver would be an important control point of these reactions. This is shown in Fig. 1, which presents the derived peak local loading ratio based on these assumptions, with and without codeposition. The loading ratio is shown for a range of electrical ordering energies.

However, except for the relaxation time interval, Eq. (5) indicates that this generation of loading sufficiently would be nearly instantaneous, which is simply not observed. Therefore, we have now corrected Eq. (5) (and the volumes to which it refers) both for observed intrapalladium diffusion of the loaded deuterons and for the secondary changes in electrode volume.

The first-order diffusion rate was included for its impact on the local surface concentration, thereby calculating the local depletion secondary to internal redistribution in the bulk metal. Within the metal, the deuterium diffusion has been considered by several models. Anharmonic effects,<sup>8</sup> optical and acoustic phonon spectra, material defects, grain boundary dislocations, and fissures<sup>9</sup> all influence the deeper loading of the metal. These mechanisms may lead to a relative decrease in the surface concentrations of deuterons and thus the local surface loading ratio. The local loading ratios were derived using the simple redistribution mechanisms, with the understanding that the actual three-dimensional mechanisms are what actually accounts for the phenomena. The diffusivities are such (Table I) that only the term for the hydrogen isotope appears to be important to first order. The volume change, albeit small, was also included in the final calculation.

TABLE I  
Diffusivities of Materials in Palladium

Substance	Deuterium (cm <sup>2</sup> /s)	$E_a$ (kJ/mol)	References
Hydrogen	0.0029 to 0.0053	22.2 to 22.8	See Oriani, <sup>10</sup> Chemical Rubber Company Handbook, <sup>11</sup> and Swartz <sup>12</sup>
Deuterium	0.0027	19.8 to 20.5	
Tritium	0.0048	39.4	
Palladium (self-diffusion)	≪0.00001	266	

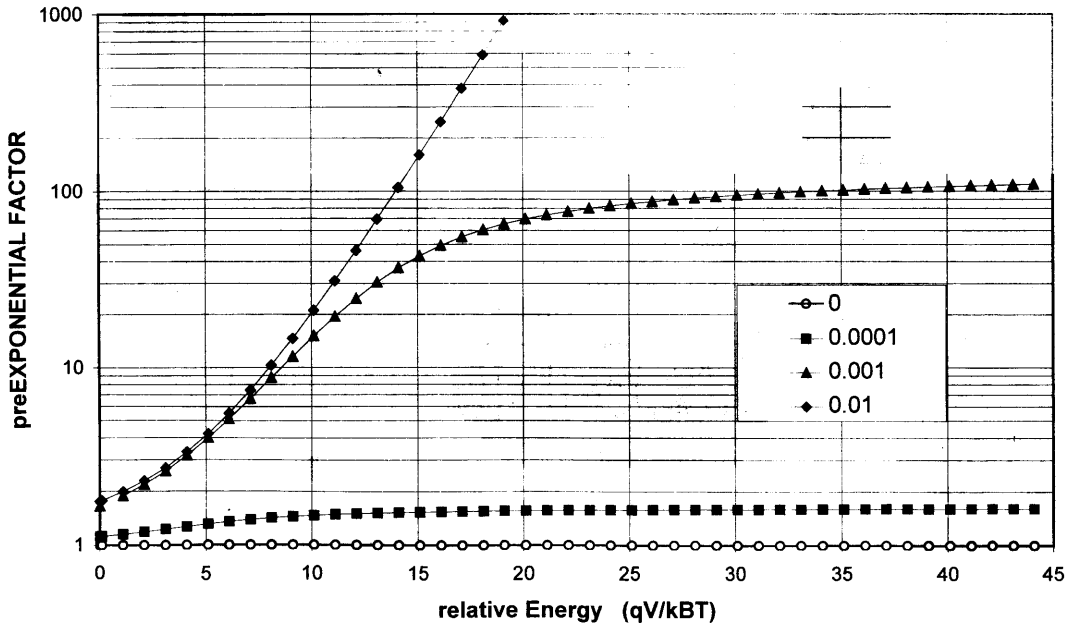


Fig. 1. Preexponential peak local loading ratio: These four curves are the derived preexponential factor for the peak local loading ratios both with (solid circles, triangles, squares) and without (open circles) codeposition. The preexponential factor is shown for a range of electrical ordering energies in units of electrical energy compared with kinetic energy  $k_B T$ . The three codeposition curves are for 0.1, 1, and 10 mA. The diffusivity of the palladium ions in solution is estimated as 10% that of the deuterium ion itself.

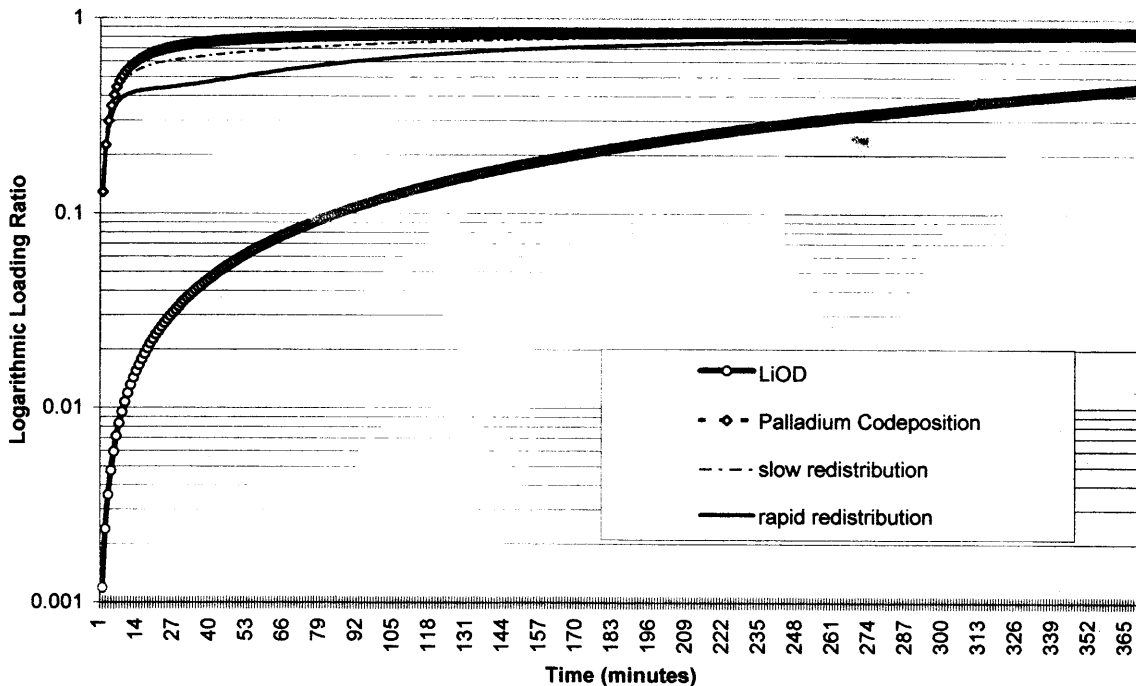


Fig. 2. Theoretical peak local deuteron loading and the impact of codeposition: These curves show the theoretical peak local and average deuteron/palladium loading ratios for four types of experimental arrangements. Four curves are shown. The lowest curve is for ordinary cold fusion electrolysis with LiOD as the solution. The upper three curves are for systems where palladium cations are also codeposited with the deuterons onto the palladium. The theoretical peak loading ratios are shown as a function of time. The top curve is pure codeposition and does not include redistribution within the palladium cathode. The two curves below it represent slow and faster internal redistribution. The model assumes solution and cathode volumes of 100 and 0.5 cm<sup>3</sup>, an electric current of 200 mA, and faradic efficiencies of 0.35 and 0.61 for palladium and deuterium, respectively.

## INTERPRETATION

The result of the calculations is shown in Fig. 2. Four curves are shown. The lowest curve is for ordinary cold fusion with LiOD. The upper three curves are for palladium cations codeposited with the deuterons onto the palladium. The theoretical peak loading ratio is shown as a function of time. Assuming that the reaction occurs when the loading factor approaches one, the values in Fig. 1 have been compared with independent tests of Pd,D codeposition on the cold fusion phenomena,<sup>1</sup> which confirm that the decrease of the time of onset of successful cold fusion reactions may be <1 h (Ref. 13). The impact of the internal diffusion in the electrode is to bring the calculations in fair approximation with what is observed. From a materials point of view, the observed turn-on time constant for the desired reactions with codeposition in such reactions<sup>2,7,13</sup> appears to be consistent with the rapid internal diffusion rate for deuterons within the palladium, probably related to the anharmonic<sup>8</sup> and other<sup>9</sup> unique characteristics of the loaded material.

## SUMMARY

In summary, the theoretical nonequilibrium deuteron/palladium ratio at the surface of a palladium electrode, previously shown to depend on the loading flux ratio, is now corrected both for intrapalladial diffusion of the loaded deuterons and for the secondary changes in electrode volume. Comparison with experimental data suggests yet another application and further confirmation<sup>14</sup> of the Q1D model of isotopic fuel loading into a material.

## NOMENCLATURE\*

$A$	= area ( $\text{cm}^2$ )
$A_{0,D}$	= initial coefficient of spatial distribution, deuterium ion ( $\text{mol}/\text{cm}^3$ )

\*In this paper, deuterium D represents atomic heavy hydrogen and is to be distinguished from both diatomic heavy hydrogen  $D_2$  and the deuteron  $d$ . At the electrode, intermolecular deuteron transfer occurs from the aqueous phase to the metallic electrode. This may occur in combination with an asymmetric infrared vibration. In this paper, for simplicity, the deuterons contained in the aqueous phase are represented by the symbol D. This is consistent both with what is done conventionally with protons (i.e., pH), because deuterium is contained as paired deuterons covalently bound to oxygen as heavy water, and at the electrodes, where after a two-phase process (involving adsorption of deuterons), diatomic deuterium gas  $D_2$  forms.

Also for these approximations, tritium and mixed species<sup>12</sup> are ignored at the cathode. As a final simplicity, in the equations, symbols for vectorial components and electric charge are not explicitly shown, although these are used to derive both the equations and their mathematical solutions. Hence, the deuterium ion should have a superscript + to formally distinguish it from monatomic un-ionized deuterium.

$A_{0,Pd}$	= initial coefficient of spatial distribution, palladium ( $\text{mol}/\text{cm}^3$ )
$B_D$	= diffusivity of deuterium ions ( $\text{cm}^2/\text{s}$ )
$B_{Pd}$	= diffusivity of palladium ( $\text{cm}^2/\text{s}$ )
$[D]_{init}$	= initial deuteron ion concentration ( $\text{mol}/\text{cm}^3$ )
$[D(z,t)]$	= deuteron ion concentration ( $\text{mol}/\text{cm}^3$ )
$E$	= electric field intensity (V)
$E_a$	= activation energy (J)
$F$	= faraday (96484.56 C/mol)
$I$	= electrical current (A)
$J_e$	= deuteron flux entering cathode ( $\text{mol}/\text{cm}^2 \cdot \text{s}$ )
$J_f$	= deuteron flux entering cathode to fusion reactions ( $\text{mol}/\text{cm}^2 \cdot \text{s}$ )
$J_g$	= deuteron flux evolving to gas ( $\text{mol}/\text{cm}^2 \cdot \text{s}$ )
$J_{Pd}$	= palladium flux onto cathode ( $\text{mol}/\text{cm}^2 \cdot \text{s}$ )
$K_{Pd}$	= first-order palladium flux rate onto cathode ( $\text{cm}/\text{s}$ )
$\sum K_i$	= first-order deuteron flux rate to all fusion, gas, and loading reactions ( $\text{cm}/\text{s}$ )
$k_B$	= Boltzmann constant (J/K)
$L_c$	= length of cell (cm)
$[Pd]_{init}$	= initial palladium concentration ( $\text{mol}/\text{cm}^3$ )
$[Pd(z,t)]$	= palladium concentration ( $\text{mol}/\text{cm}^3$ )
$q$	= electric charge (C)
$T$	= temperature (K)
$\Delta t$	= time increment (s)
<i>Greek</i>	
$\lambda_{D,Pd}$	= loading ratio (nondimensional)
$\mu_D$	= electrophoretic mobility deuterium ion ( $\text{cm}^2/\text{V} \cdot \text{s}$ )
$\mu_{Pd}$	= electrophoretic mobility palladium ( $\text{cm}^2/\text{V} \cdot \text{s}$ )
$\Phi$	= potential = $-V$ (voltage)

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