

QUASI-ONE-DIMENSIONAL MODEL OF ELECTROCHEMICAL LOADING OF ISOTOPIC FUEL INTO A METAL

MITCHELL R. SWARTZ *Jet Technology*
16 Pembroke Road, Weston, Massachusetts 02193

Received January 17, 1992
Accepted for Publication February 13, 1992

COLD FUSION
TECHNICAL NOTE

KEYWORDS: cold fusion, isotope loading, deuterium

A quasi-one-dimensional model examines the electrochemical loading of isotopic fuel into a metal cathode. Both the competitive evolution of gas at that cathode and the ratio of the electric energy to thermal energy may control the spatial distribution and loading rate.

INTRODUCTION

In March 1989, electrochemically induced nuclear fusion reactions were reported^{1,2} but were initially very difficult to reproduce. By 1992, several experiments had demonstrated that anomalous nuclear and enthalpic processes occur in palladium that has been highly loaded with deuterium.³⁻⁵

This technical note discusses the electrochemical loading of a palladium cathode with an isotopic fuel (deuterium). A quasi-one-dimensional model was developed that suggests that both competitive gas-evolving reactions at the metal surface and the ratio of the applied electric field energy to thermal energy ($k_B \times T$) appear to be decisive in controlling the loading of the metal by the isotopic fuel.

QUASI-ONE-DIMENSIONAL MODEL

Classically, an electrode in a heavy water solution at equilibrium should measure potentials associated with the Nernst equation. However, during the loading of isotopic fuel or during the fusion reaction, the system may not be at equilibrium. Furthermore, such derived solutions may be less informative regarding the rates of such loading or fusion reactions. Therefore, a quasi-one-dimensional model has been developed in an attempt to describe the flux of deuterons toward and into the cathode.

The application of an electric power source generates an applied electric field intensity. The problem of a mathematical solution includes the fact that the electric field is itself altered as the solution and system each respond with complex conduction and polarization phenomena.⁶ The salient result, among other things, includes cation flux toward the cathode.

There also results in the pericathodic solution a buildup of both deuterons and other cations, as well as the development of a low dielectric constant (gas bubble) layer. Ionic drift, secondary space-charge polarization, propagation of solvated deuterons, deuterons in clathrates, and intra- and intermolecular deuterium transfer in the heavy water,⁷ and the formation of low dielectric constant (compared with water) bubbles abutting the cathode are the minimum expected.^{8,9}

Figure 1 shows the direction of the applied electric field and its effect on the spatial distribution of deuterons in the aqueous solution and cathode. Figure 1 shows the four regions of the electrochemical cold fusion cell. The first region

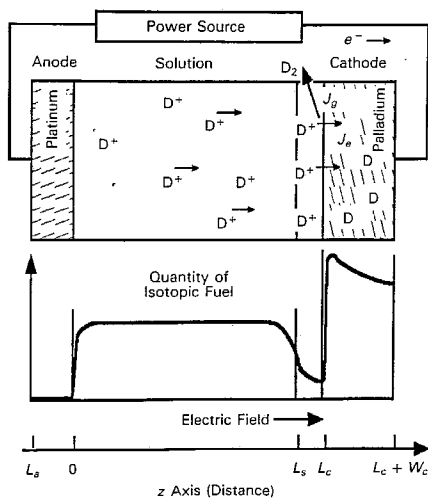


Fig. 1. Four-region cathode model.

is the platinum anode in which few deuterons reside. The second region is the solution, which is modeled as extending between $0 < z < L_s$. The third region is a double layer, whose width $L_c - L_s$ is greatly exaggerated in the figure. The last region is the palladium cathode, beginning at L_c and of width W_c . $L_c - L_s$ is so small that for most calculations, $z = L_c + L_s$ is simply taken as $z = L_c$.

Within the solution, the deuterons are distributed mainly tightly bound to oxygen atoms as heavy water. The drift induced by the applied electric field is shown schematically in Fig. 1; it does not mean that the deuterons actually are free to travel in such a simple fashion.

In this model, a double layer is present between the solution and the metal. The double layer is, in part, created by the cathode fall of ions and other polarization reactions of the solution and the solutes therein to the applied electric field. This boundary between the palladium cathode and the heavy water solution also may influence the loading rate of the metal by the isotopic fuel.

As Fig. 1 shows, at least three other deuteron fluxes must be considered. The model presented links the deuteron flux from the solution into the pericathodic volume, and then finally either into the metal or toward gas evolution. Not shown in Fig. 1 but considered in the model is the flux of deuterons lost in any and all putative fusion reactions (represented as J_f).

DEVELOPMENT OF THE QUALITATIVE MODEL

In the absence of solution convection, a quasi-one-dimensional model can be developed by considering that the flux J of any species (here the deuterons) results from both diffusion down concentration gradients and electrophoretic drift.⁹ For simplicity, solution convection and the impact of other conduction/polarization components are ignored for this analysis. Note that (see Nomenclature on p. 300)

$$J_D(z, t) = -B \times \frac{d[D^+(z, t)]}{dz} - \mu \times [D^+(z, t)] \times \frac{d\Phi}{dz}, \quad (1)$$

where

B = diffusivity of deuterons in each respective region considered (cm^2/s)

μ = electrophoretic mobility ($\text{cm}^2/\text{V} \cdot \text{s}$).

For this model, both material inhomogeneities and the anisotropy of the lumped parameters are ignored. Within the palladium, for example, there are great differences in B throughout the metal, especially between the lattice and grain boundaries.

Three additional components of deuteron flux must be considered. The first is the entry of deuterons into the bulk of palladium that constitutes the cathode. That flux is described as J_e , the rate at which deuterons physically enter the palladium cathode. The second deuteron flux is that component lost at the cathode to gas evolution and is described here as J_g . These deuteron flux terms are assumed to be present only at $z = L_c$. The term J_f is the flux of deuterons lost to fusion, which is assumed to be zero in the solution.

Adding the additional deuteron fluxes yields

$$J_D(z, t) = -B \times \frac{d[D^+(z, t)]}{dz} - \mu \times [D^+(z, t)] \times \frac{d\Phi}{dz} - \sum J_i(z, t), \quad (2)$$

where $\sum J_i$ is the sum of all deuteron fluxes at the cathodic surface and in the bulk metal and

$$\begin{aligned} \sum J_i(z, t) = & (J_e + J_g) \times u_0(z - L_c, t) \\ & + J_f \times \{u_{-1}(z - L_c, t) \\ & - u_{-1}[z - (L_c - W_c, t)]\}, \quad (3) \end{aligned}$$

where

u_0 = impulse function, located spatially at $z = L_c$

u_{-1} = step function; the superposition of two such step functions represents that the fusion flux may actually occur within the bulk of the metal.

Solution for the time rate of change in any given volume is thus determined by these fluxes. Gauss' theorem simplifies this to

$$\begin{aligned} \frac{d[D^+(z, t)]}{dt} = & \left[B \times \frac{d^2(D^+)}{dz^2} \right] + \left[\mu \times (D^+) \times \frac{d^2\Phi}{dz^2} \right] \\ & + \left[\mu \times \frac{d\Phi}{dz} \times \frac{d(D^+)}{dz} \right] + \left[\frac{d(D^+)}{dz} \times \frac{dB}{dz} \right] \\ & + \left[(D^+) \times \frac{d\Phi}{dz} \times \frac{d\mu}{dz} \right] - \frac{d \sum J_i}{dz}. \quad (4) \end{aligned}$$

For simplicity and to solve, a number of approximations can be made as follows:

1. The applied electric field intensity imposes a negligible energy [in relation to thermal energy at any molecular site of interest in the bulk solution (where the ratio of electrical to thermal energies is 10^{-4} to 10^{-6})]. Therefore, no free charge density in the solution is expected. Thus, the Laplacian of the electric potential [and thus the second term on the right side of Eq. (4)] is zero. This assumption may not be correct either in the vicinity of irregularities (such as spikes) on the cathode or in the double layer (see below).

2. All of the fusion reactions are assumed to occur only at $z > L_c$ (i.e., no fusion occurs in the bulk solution).

3. Deuterium is neutral in charge and has insignificant electrophoretic mobility in comparison with that for D^+ . Deuterons also may migrate by dielectrophoretic forces⁶ by way of D_2 and by way of both intra- and intermolecular deuteron transfer, but such effects are ignored in this simple model.

4. It is assumed that no recombination of any generated D_2 gas occurs to form heavy water. Thus, for simplicity, J_r (for recombination) is ignored.

5. Deuteron penetration is modeled to occur only at the cathode-double-layer boundary (at L_c), and such flux ($J_e + J_g$) is assumed to be electron limited, with an efficiency (electrical transference) of η .

6. There is conservation of deuterons, with the exception of a small loss K_f to any fusion reactions. The value of K_f is extremely small compared with all other loading rates and/or gas-evolving reactions.

7. Neither solution convection, nor possible dielectrophoretic or other stabilization of that convection, is considered in this simple model.

8. Thermal effects are also ignored, but these could be especially significant across the double layer, especially in the

vicinity of irregularities such as spikes or near either temperature or material inhomogeneities.

Notwithstanding the foregoing, the steady-state general solutions are obtained by substituting

$$D^+(z) = \sum D_j \exp(\gamma \times z), \tag{5}$$

where γ can be complex.

By substitution, collection of terms, and the use of the binomial expansion, the homogeneous solution of Eq. (3) becomes, in the heavy water solution, of the form $\gamma = \mu E/B$. The particular solution of the differential equation is "driven" by the sum of the deuteron fluxes toward fusion, into gas, and into the metal cathode, where $\sum J_i = J_f + J_g + J_e$.

A simple solution can be developed with further approximations and linearizations.

9. It is assumed that there is no spatial gradient to the diffusion coefficient of deuterons B and/or their electrophoretic mobility μ . This is not true within the palladium cathode and is probably not true across the double layer. However, this approximation does permit a more simplified expression.

10. The generation of D_2 gas, the fusion loss of deuterons by the putative fusion reactions, and the loading of palladium are modeled to occur as first-order reaction rates proportional to the local concentration of deuterons. This is probably not true for gas evolution because it involves the formation of diatomic deuterium, and possibly not true for some of the putative fusion reactions.

11. Terms K_g and K_e are assumed to be zero away from the surface of the cathode in the solution. The only contribution to the spatial derivative of the first-order deuteron flux rates is thus proportional to the absolute value of K_f , K_g , and K_e at that cathodic location. Note that

$$J_f = K_f \times (D^+), \tag{6a}$$

$$J_g = K_g \times (D^+), \tag{6b}$$

and

$$J_e = K_e \times (D^+). \tag{6c}$$

For $0 < z < L_s$, the general solutions are thus

$$\gamma = 0, \left(\frac{qE}{2k_B T} \right) - \left(\frac{\sum K_i}{2B} \right) + \left[\left(\frac{qE}{2k_B T} - \frac{\sum K_i}{2B} \right)^2 - \left[\left(\frac{1}{B} \right) \times \left(\frac{d \sum K_i}{dz} \right) \right] \right]^{1/2}. \tag{7}$$

BOUNDARY CONDITIONS

The actual coefficients of Eq. (5) are determined both by the boundary conditions and by conservation of mass. The

condition of mass conservation of all deuterons at some time T requires

$$\int_0^{L_c + W_c} A \times [D^+(z, t)] dz = \int_{-L_a}^{L_c + W_c} A \times [D^+(z, 0)] dz - \int_0^T A \times \sum J_i(\tau) d\tau. \tag{8}$$

It is obvious that $D^+(t = 0)$ may not be uniform and that J_f , J_e , and J_g may not be time invariant. Furthermore, J_f and the possible addition of more deuterons to the system are also both ignored in this qualitative model.

The molecular flux at each electrode must be considered so that just at the palladium cathode $z = L_c$,

$$J_D(L_c, t) = J_e + J_g. \tag{9}$$

Deuteron entry to the cathode is assumed to be electron limited (with all entry occurring only at the cathode-double-layer interface), and so

$$\sum J_i(L_c, t) = J_e + J_g = \frac{\eta \times I}{A \times F}. \tag{10}$$

Finally, it can be assumed that there is a negligible number of deuterons at the anode. This is reasonable because of the unstable nature of cationic deuterons at that location, where the anode is the site of oxidation. The applied electric field intensity would sweep the palladium cations away from the anode toward that cathode. The assumption is also reasonable because of the low solubility of deuterons for platinum. Note that

$$[D^+(0, t)] = 0. \tag{11}$$

The steady-state expression for the initial coefficient of the final spatial distribution at the pericathodic interface is proportional to

$$\frac{\langle D_i \rangle \times \left(\frac{qE}{2k_B T} - \frac{\sum K_i}{2B} \right) \times L_c}{\left\{ \exp \left[\left(\frac{qE}{2k_B T} - \frac{\sum K_i}{2B} \right) \times L_c \right] + \left(\frac{qE}{2k_B T} - \frac{\sum K_i}{2B} \right) \times (L_c - 1) \right\}}. \tag{12}$$

L'Hospital's rule may be used to determine the initial coefficient in the limit as either K_e , K_g , or K_f approaches infinity. That limit is 1.

POSSIBILITY OF A CRITICAL LOADING FLUX

Examination of Eq. (7) reveals that there may be a critical loading rate that occurs when the terms in the parentheses in Eqs. (7) and (12) go to zero. That occurs at $L = L_c$ when

$$K_e = (\mu \times E) - (K_g + K_f). \tag{13}$$

One implication is that the evolution of D_2 gas and loading of the palladium cathode are mutually exclusive. Another is that the critical loading rate appears to be related to the difference between the deuteron availability (secondarily produced by the applied electric field) and the loss of deuterons by gas evolution, loading of the metal, and the fusion reactions.

In fact, the ratio can be examined for its relation to thermal processes by substituting the Einstein relation:

$$\frac{B}{\mu} = \frac{k_B T}{q}. \tag{14}$$

At the beginning of an experiment involving the electrochemical loading of deuterium into palladium, J_f is zero because the palladium is not loaded. Therefore, the loading flux of deuterons into the palladium cathode is

$$J_e = \left(\frac{2B \times L_c \times \lambda}{\lambda + 1} \right) \times \langle D_i \rangle \times \left(\frac{1}{1 - \left[\exp\left(\frac{-qE \times L_c}{k_B T} \right) \right]} \right) \times \left(\frac{qE}{k_B T} \right)^2, \quad (15)$$

where

$$\langle D_i \rangle = \text{initial concentration of deuterons in the solution}$$

$$\lambda = \text{relative loading rate, the ratio of the fluxes, loading flux } J_e \text{ to the gas evolution flux } J_g.$$

Note that

$$\lambda = \frac{J_e}{J_g} \quad (16)$$

Thus, if λ is 0.01, most of the current goes to gas electrolysis, whereas $\lambda = 100$ would indicate a most efficient loading rate.

The substitution of Eq. (14) into Eq. (13) reveals that the loading is determined by two terms. The first term is controlled by the ratio of the organizing of the deuterons (by the applied electric field) to the random thermal disorganization. The second term is the mutually exclusive loss of deuterons at the cathode through gas evolution, represented by J_g [Eq. (13)] or by the loading factor in Eq. (16).

Figure 2 shows this relationship by plotting the relative loading of isotopic fuel into a metal based on the qualitative quasi-one-dimensional model described here. The loading flux of deuterons into the palladium at the cathode surface J_e is shown as a function of the electric field intensity parametrically for various rates of gas (D_2) evolution rates at the cathode (and resulting from J_g). The series of curves indicates that the loading rates may be critically dependent on the electric field energy as well as the competing gas-evolving reactions.

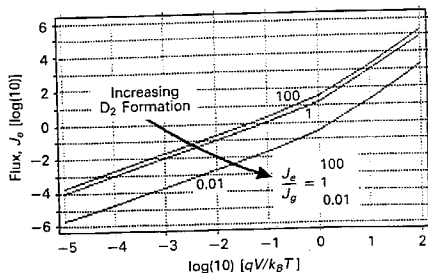


Fig. 2. Loading rate of palladium.

WITHIN THE CATHODE

Intermolecular deuterium transfer from the solution to sites within the palladium may dominate the rate of loading. Within the metal and across the double layer, the diffusion has been considered by several models. Defects, grain-boundary dislocations, and fissures may greatly influence the deep loading of the metal, and "zeolite"-like diffusion has been described.¹⁰

POSSIBLE IMPLICATIONS REGARDING SPIKES ON THE CATHODE

A corollary is obtained by inverting the equation, which indicates that the electric field must be greater than

$$E > \frac{\sum J_i}{\mu \times \langle D_i \rangle \times \left[2 + \left(\frac{\sum J_i \times L_c}{2B \times \langle D_i \rangle} \right) \right]} \quad (17)$$

One interpretation is that spikes and irregularities on the cathode may be crucial to obtain adequate filling of the cathode. This effect may occur by way of the large electric fields that occur at such sharp points on a metallic surface such as the palladium cathode.

STEADY-STATE FUSION RATES

When the filling of the palladium with deuterium is complete, a "steady state" (to the degree such might exist) of fusion might be expected. At that time because the electrode is already fully loaded, then J_e would be expected to be small and J_f to be relatively more significant. J_e would be on the order of J_f , and so at that time,

$$J_f = \frac{B \times L_c \times \langle D_i \rangle}{\left[1 - \exp\left(\frac{-qE \times L_c}{k_B T} \right) \right]} \times \left(\frac{qE}{k_B T} \right)^2 - \frac{J_g}{2} \quad (18a)$$

or

$$J_f = \left(\frac{2\lambda}{2\lambda + 1} \right) \times \left(\frac{B \times \langle D_i \rangle}{L_c} \right) \times \left[\frac{1}{1 - \exp\left(\frac{qV}{k_B T} \right)} \right] \times \left(\frac{qV}{k_B T} \right)^2 \quad (18b)$$

Equation (18a) uses the two deuteron fluxes at the cathode to define the approximate fusion flux. Equation (18b) substitutes the transolution voltage, and thereby assumes a simple distribution, neglects contact potentials and overvoltages, and uses the simplification of λ as the relative loading rate factor. The Einstein relation is used to put the equation back in terms of the original parameters.

POSSIBLE IMPLICATIONS FOR CODEPOSITION AND OTHER THEORIES

Because palladium cations in solution can be modeled similarly to deuterons (with the exception of intra- and intermolecular deuterium transfer and their different roles in clathrates), such palladium nuclei will also drift toward the cathode in an applied electric field. For palladium, there is

obviously no K_g or K_f term, but K_c does exist, and the palladium cations can electrodeposit on the cathode. The model was examined to consider this further. Coupled equations, considering both charge carriers, were used to determine the final distribution of deuterium species in the bulk solution. An equation similar to Eq. (12) was used to determine the ratio of deuterons to palladium just at L_c . This is the local loading ratio.

The derivations for the spatial distribution of palladium nuclei undergoing codeposition from the solution indicate that the physical deuterium/palladium ratio near the cathode surface is significant and nonzero shortly after the electric field is applied to the solution.

The model indicates that the distribution of codeposited palladium and deuterons onto the cathode should theoretically yield excess energy more quickly than simple electrodeposition of deuterons onto palladium. This advantage accrues because a local high fractional saturation of the deposited phase occurs at L_c . This analysis indicates that the active medium would be very close to fully charged as it is created, enabling it to function immediately.

In cold fusion experiments, full loading appears to be a prerequisite, but possibly insufficient requirement, before fusion occurs. Therefore, as compared with simple electrodeposition of deuterium onto a palladium cathode, codeposition may surmount at least one rate-determining step.

Finally, some theories of cold fusion are reported to involve the putative requirement of a pericathodic or intracathodic role for second-row elements during the fusion reactions.¹¹ This quasi-one-dimensional model could be used to similarly determine both their buildup and loading parameters.

SUMMARY

A simple qualitative quasi-one-dimensional model is derived to consider the loading of deuterium into palladium. Both competitive gas-evolving reactions at the metal surface and the ratio of the applied electric energy to thermal disordering energy ($k_B \times T$) may be decisive in controlling the loading of the metal by the deuterons obtained from heavy water. There appear to be possible implications for the shape of the cathode and for codeposition methods of loading the cathode.

NOMENCLATURE

A	= area
B	= diffusivity of deuterons (cm^2/s)
$(D)_{\text{tot}}$	= total deuterium concentration (used within the metal)
(D_+)	= deuterium concentration (used within the solution)
$D(t=0)$	= initial deuterium concentration (at time $t=0$)
E	= electric field
F	= Faraday
I	= electrical current
J_D	= flux of deuterons in solution
J_e	= flux of deuterons entering into the palladium cathode
J_f	= flux of deuterons lost in putative fusion reaction(s)

J_g	= flux of deuterons at the cathode evolving to gas
K_c	= first-order deuteron entry rate
K_f	= first-order deuteron fusion rate
K_g	= first-order deuteron gas evolution rate
k_B	= Boltzmann constant
L	= length
q	= electric charge
T	= absolute temperature (K)
V	= transsample voltage
z	= distance variable
<i>Greek</i>	
ϕ	= potential
μ	= electrophoretic mobility ($\text{cm}^2/\text{V} \cdot \text{s}$)
η	= electrical transference ratio
λ	= relative loading rate

ACKNOWLEDGMENTS

The author wishes to thank several individuals for their helpful comments and suggestions regarding this manuscript, including M. Zahn, S. Baer, I. Straus, J. Tolleson, and C. McCue.

REFERENCES

1. M. FLEISCHMANN and S. PONS, "Electrochemically Induced Nuclear Fusion of Deuterium," *J. Electroanal. Chem.*, **261**, 301 (1989).
2. S. E. JONES et al., "Anomalous Nuclear Reactions in Condensed Matter," *J. Fusion Energy*, **9**, 199 (1990).
3. E. F. MALLOVE, *Fire from Ice: Searching for the Truth Behind the Cold Fusion Furor*, John Wiley & Sons, New York (1991).
4. M. SRINIVASAN, "Nuclear Fusion in an Atomic Lattice: An Update," *Curr. Sci.*, **143** (1991).
5. J. O'M. BOCKRIS, G. H. LIN, and N. I. C. PACKHAM, "A Review of the Investigations of the Fleischmann-Pons Phenomena," *Fusion Technol.*, **18**, 11 (1990).
6. J. R. MELCHER, *Continuum Electromechanics*, MIT Press, Cambridge, Massachusetts (1981).
7. A. VON HIPPEL, D. B. KNOLL, and W. B. WESTPHAL, *J. Chem. Phys.*, **54**, 134 and 145 (1971).
8. *Dielectric Materials and Applications*, A. VON HIPPEL, Ed., MIT Press, Cambridge, Massachusetts (1954).
9. M. R. SWARTZ, "Charge Transfer to Methemoglobin and Oxygen Using Methylene Blue, Light and Electricity," ScD Thesis, Chap. 5, Massachusetts Institute of Technology (1984).
10. S. SZPAK, C. J. GABRIEL, J. J. SMITH, and R. J. NOWAK, "Electrochemical Charging of Pd Rods," *J. Electroanal. Chem.*, **309**, 273 (1991).
11. P. HAGELSTEIN, "Coherent and Semicoherent Neutron Transfer Reactions," *Proc. 2nd Annual Conf. Science of C.F.* (Cuomo), p. 205, T. BRESSANI, Ed. (1992).