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Preliminary note

Electrochemical fusion: a mechanism speculation

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INTRODUCTION

In recent months the electrochemical formation of tritium at Pd at a rate of ca. 10^9 atoms cm^{-2} s^{-1} has been observed [1–3]. Correspondingly, some surfaces of palladium, after prolonged electrolysis in D_2O, show dendrite formation under electron microscopy [4]. The protrusions consist of Ni, Fe and Cr.

GAMOW BARRIER

The probability of nuclear tunnelling is:

$$G = \exp\left\{-\pi e_0^2 \left(M_D/\hbar^2 E\right)^{1/2}\right\} \tag{1}$$

where M_D is the rest mass of the deuteron and E is the energy of an adsorbed deuteron incident on the electrode surface after passage from the solution.

Let it be supposed that fusion occurs at surface states associated with dendritic protrusions on the electrode surface.

It seems reasonable to assume that there is a Volmer–Heyrovsky pathway for deuterium evolution on palladium surfaces at high current density (i). Then, the electrode surface is fully covered with D and the rate of D–D collision (mol cm^{-2} s^{-1}) would be i/F (F is the Faraday constant). Should a certain fraction (Γ) of sites on the electrode surface be sites of abnormally high energy, and hence field strength, where the energy of the D–D collision is E, the following would be the rate at which the D–D barrier is penetrated:

$$\Gamma(i/F) \exp\left(-\frac{\pi\epsilon^2}{\hbar}\frac{M^{1/2}}{E^{1/2}}\right) \tag{2}$$

A SPECULATIVE MODEL

Time for development of sharply-pointed growths on an electrode surface

The time (5–100 days) needed to find tritium during Pd/D_2O electrolysis is ca.

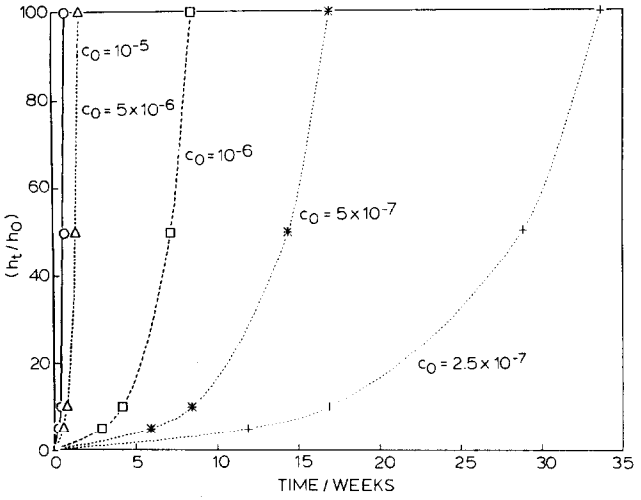

Fig. 1. The growth of surface promontories as a function of time and impurity concentration.

100 times that necessary to charge fully a 1 mm rod with D, and hence, diffusion as a cause of the initiation times is unlikely.

Promontories, some dendritic, grow gradually during prolonged electrolysis, upon electrode surfaces [5]. If the promontory growth occurs under diffusion control, then [6]

$$h_t/h_0 = \exp\left[(tVDc_0)/\delta^2\right] \tag{3}$$

where h_t is the height of the promontory after time t, and h_0 that at the commencement of high current density electrolysis, t is the time in s, V is the molar volume of palladium, 8.8 cm^3, D is the diffusion coefficient in $cm^2\ s^{-1}$, c_0 is the concentration of the hypothetical depositing entities in the solution in mol cm^{-3}, and δ is the diffusion layer thickness in cm. We take δ as 0.01 cm (mild stirring) and D as $10^{-5}\ cm^2\ s^{-1}$. Figure 1 shows h_t/h_0 versus time.

We hypothesize that the necessary preliminary event for tritium production is the substantial growth of the promontories described. Such a growth would be lengthy and irreproducible because the necessary impurites would arise as a result of, e.g., dissolution of the anode, diffusion from the glass, etc. A reasonable choice of parameters gives 10 to 100 days (Fig. 1) as the range of times to achieve exponential growth. Dendrite tips sharpen during growth [7]. The tips of such dendrites, emerging from the diffusion layer on the electrode, would be sites of abnormally high electric field strengths.

FIELD AT TIPS

Kolb and Franke [8] have concluded that locally, at surface states, there may be a metal–solution field strength of up to 10^9 V cm^{-1} for a silver–perchloric acid

interface. At dendrite *tips*, containing surface states, field enhancement over that found for surface states on planar surfaces will occur. In the absence of a simple way to calculate this enhancement it will be assumed here that the maximum Kolb–Franke value will be doubled (X_{tip}? 2×10^9 V cm^{-1}).

DIELECTRIC BREAKDOWN

When a water dielectric breaks down [9], a fluctuating gas film is formed at the surface of the charged interface concerned. As the gas layer grows, the charged surfaces (electrode–electrolyte surface) separate while maintaining constant excess charge over a time in the microsecond range. Under these circumstances, for a brief moment, the 2×10^9 V cm^{-1} field exists between the dendrite tip and the electrolyte surface. It seems reasonable to speculate that electrons are emitted from the dendrite tip into the gas layer ★. Then one might expect a reaction of the type:

$$D_2 + e^- \rightarrow D^+ + D + 2\,e^- \tag{4}$$

to occur.

The deuteron will be accelerated towards the tip (Fig. 2) to collide with a deuteron present on the dendrite surface.

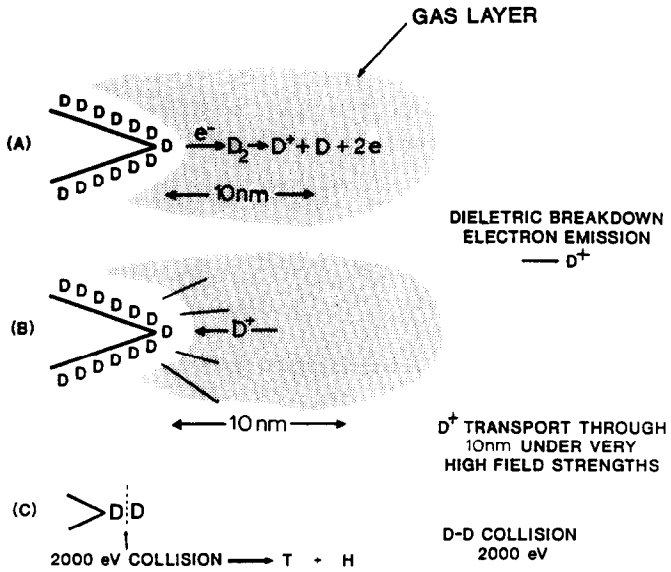

Fig. 2. The model.

★ On four occasions, sparks have been observed to be emitted from the cathode during D_2 evolution on Pd.

TABLE 1

The relationship between required energy and the fusion rate, f

E/eV	G	f ($i=1$ A/cm^2)	$f\Gamma$ ($i=1$ A/cm^2)
1000	2.63×10^{-14}	1.64×10^{5}	1.64×10^{2}
1500	8.18×10^{-12}	5.11×10^{7}	5.11×10^{4}
2000	2.50×10^{-10}	1.56×10^{9}	1.56×10^{6}
2500	2.59×10^{-9}	1.61×10^{10}	1.61×10^{7}
3000	1.44×10^{-8}	9.00×10^{10}	9.00×10^{7}
3500	5.52×10^{-8}	3.45×10^{11}	3.45×10^{8}
4000	1.62×10^{-7}	1.01×10^{12}	1.01×10^{9}

Application of this reasoning to eqn. (1) gives the results shown in Table 1. For an energy of 4000 eV (or that of 1000 with an effective mass of 1/2), agreement with experiment is achieved.

DISCUSSION

According to the model described, the electrical work done by the transient field on the deuteron would be $Xe_0\delta$ where X is 2×10^9 V cm^{-1}, e_0 is unity and δ is (say) 50×10^{-8} cm.

A potential difficulty in the acceptance of the model concerns the energy available to support fluctuating and occasional (ca. one collision in 10^{10}) D^+ transfer across a transient potential drop of ca. 1000 V in a cell driven at ca. 10 V. However, the hypothesis involves fluctuating potentials for short times at occasional sites. If such sites cover, for example, 10^{-4} of the interface at a given moment, the voltage requirement for a given cell is ca. 0.1 V. The hypothesis does not require a potential difference to occur in the electrode but across the gas layer, as in a similar hypothesis suggested by Klyuev [10].

The effective mass of the deuteron during a hypothetical fusion reaction in Pd has been predicted by Worledge et al. [11] to be 0.01 of the rest mass. If such reasoning were to apply here, the necessary field at the electrode would be reduced correspondingly (eqn. 2). Further, screening of Coulomb's repulsion due to the electron cloud in the double layer has been neglected in the present discussion and would further reduce the field needed (E) in eqn. (1).

The difficulty of the branching ratio much less than one may be interpreted on the model. When a D^+–D^+ collision occurs in a plasma, the direction of impact is random, and therefore either of the two pathways usually assumed would be equally favored. In the interfacial region under high electric field strength, the field will act vectorially on the quadrupole moment of the deuterons. Each deuteron–deuteron collision will occur with a fixed orientation, and thus may favor one pathway.

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