

ELECTROCHEMICALLY INDUCED NUCLEAR FUSION OF DEUTERIUM: THE EXISTENCE OF NEGATIVELY CHARGED DEUTERIDE IONS

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COLD FUSION

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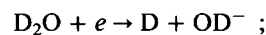
Cold fusion of deuterium by electrolysis of heavy water onto a palladium (or titanium) cathode has been reported. Contrary to the assumption of Fleischmann and Pons that electrochemically compressed D^+ exists inside the palladium cathode, the observations of Jones et al. can be partially explained by the simultaneous presence of deuteride D^- and the highly mobile positive deuterium ion D^+ . The opposite charges reduce the intranuclear distance and enhance the tunneling fusion rate. Furthermore, alloying of lithium with palladium can stabilize a negatively charged deuteride ion due to the salinelike character of lithium deuteride. The enormous pressure (or fugacity), achieved by the applied electrochemical potential (10^{30} atm), is a virtual pressure that would have existed in equilibrium with palladium deuteride (PdD_x). It is speculated that nuclear fusion occurs at the surface, and the PdD_x serves as a reservoir for the supply of deuteride ions.

I. INTRODUCTION

Apparent success at cold fusion has been reported by Fleischmann and Pons¹ and Jones et al.² Despite sketchy descriptions of the process, cold fusion involves the electrolysis of heavy water D_2O using a palladium cathode. Palladium can store very high quantities of hydrogen, or deuterium, in the form of palladium hydride (PdH_x) [or palladium deuteride (PdD_x)], where x is nonstoichiometric.³⁻⁹ Fusion occurs upon accumulation of a large quantity of deuterium, releasing significantly larger amounts of thermal energy than the amount of energy introduced for electrolysis.¹ Furthermore, these authors also may have detected tritium 3H and gamma-ray radiation that resulted from the absorption of the neutron in the heavy water, all supporting the apparent existence of nuclear fusion reactions. Jones et al.² detected a rate of fusion on the order of 10^{-23} per D_2 per second, well below the values reported by Fleischmann and Pons.¹

The electrochemical cell used by Fleischmann and Pons¹ consisted of a glass vessel filled with heavy water, containing 0.1 M LiOD + 0.5% H_2O , in which a platinum anode and a palladium cathode were immersed. Upon electrolysis, the

positively charged deuterium ions D^+ were reduced at the cathode and the resultant deuterium atoms diffused into the palladium metal to form PdD_x (equivalent to PdH_x if the electrolysis occurs in ordinary water). The fusion between the deuterium atoms occurred, according to Fleischmann and Pons, because the metallic lattice of palladium holds the deuterium atoms in such close proximity that a quantum mechanical tunneling occurs. An additional explanation has been reported by Fleischmann and Pons¹ in which they claimed that deuterium exists in palladium as positively charged deuterium nuclei, and the excess of electrons shield the positive charges of the nuclei from one another, thus reducing the enormous Coulombic repulsion between the deuterium nuclei, allowing them to fuse. The electrochemical generation of deuterium atoms can maintain enormous activity in the palladium cathode, as determined by the Nernst equation for the electrochemical reaction:



$$E = -\frac{RT}{F} \ln a_D .$$

Accordingly, an applied overpotential of ~ 2.0 V can maintain a deuterium activity of 10^{30} atm^{1/2} at room temperature. This huge activity hardly compensates for the enormous activation energy involved in a nuclear reaction between two deuterium atoms. The corresponding high pressure (or fugacity) of deuterium is a virtual pressure that can be defined as the pressure (or fugacity) that would be necessary to reach the deuterium concentration in the palladium that exists during the electrolysis.

The main question remains: How can two deuterium nuclei overcome the Coulombic repulsion between them? The explanations of high activity, close proximity, and shielding by the electrons are insufficient.

In this technical note, an explanation is presented based on the analysis that the deuterium exists as a negatively charged deuteride ion D^- , as a hydride ion H^- is believed to exist in PdH_x (Refs. 8 and 9). Furthermore, upon long electrolysis, Li-Pd alloying occurs, followed by the formation of lithium deuteride (LiD_x), which is ionic and in which the deuteride is negatively charged. Quantities of D^+ ions exist as well, as indicated by the high mobility and diffusion of hydrogen in palladium; thus, the Coulombic attraction between

the two opposing charges enables the two nuclei to reach sufficient proximity for subsequent fusion. Section II presents evidence that D^- (or H^-) is the dominant species in the PdD_x (or the PdH_x) system.

II. THE EXISTENCE OF NEGATIVELY CHARGED DEUTERIDE ION

Early models of metal hydrides, in general, and PdH_x in particular, assume that hydrogen is present as protons.³⁻⁷ This conclusion is based on several observations, especially the observed migration of hydrogen to the cathode during the electrolysis of filaments of metallic hydrides. However, strong arguments by Gibb⁸ indicate the possibility that H^- is the dominant form, and the palladium electrolysis results are explained by the presence of minute amounts of protons as an excited state. Because protons have enormous mobility relative to H^- , the net movement of hydrogen is toward the cathode. Furthermore, the metal-hydrogen distances in metallic hydrides are often very close to the sum of the radii of the hydride ion (1.15 to 1.4 Å, depending on the coordination number) and the metal ion in its highest oxidation state. Further evidence includes the hydride's crystallographic resemblance to fluorides and iodides. Hydrogen in the hydride can be regarded as having the radius of fluoride with the electronegativity of iodine. The standard potential of the electrochemical reaction $\frac{1}{2}H_2 + e \rightarrow H^-$ has been estimated by Latimer¹⁰ to be 2.23 V. Palladium hydride can be considered as saltlike with overlapping palladium orbitals that produce conduction bands to account for its electrical conductivity.

The existence of H^- (or D^-) in PdH_x (or PdD_x), and other metallic hydrides, is supported by the following arguments⁸: The internuclear distances d_{MH} are equal to the sum of the radius of H^- ($r_H = 1.15$ to 1.40 Å) and the radius of ionic metal of maximum oxidation number. This distance is always large enough to allow for the presence of H^- . Pauling's resonating covalent bond model gives good agreement with d_{MH} and implies that the electron distribution about hydrogen is greater than unity. The structural analogy between the hydrides and halides is further evidence that H^- exists in metallic hydrides and is not a proton.

A similar conclusion has been reached theoretically by Switendick⁹ using the solid-state counterpart of molecular orbital theory-band structure. Hydrogen plays an ambivalent role as it acts both as the alkali metal and the halide in its period. In the anion model, the hydrogen states are presumed to be below the metal states. In the proton model, the hydrogen states are higher than the metal states. Experimental evidence exists for both states, and theoretical calculations of band theory of solids indicate that the existence of hydride ion is preferred.⁹

The formation of Li-Pd alloy during the long electrolysis has been suggested both theoretically and experimentally.¹¹⁻¹³ Lithium forms alloys with various metals such as gold, silver, platinum, and palladium. Upon long electrolysis of heavy water, LiD_x can be formed as well; thus, both PdD_x and LiD_x coexist. Lithium hydride (LiH_x) is a member of the so-called saline hydrides,⁶ which are characterized by their ionic nature, where the hydrogen is definitely anionic. Hydrogen is evolved, upon electrolysis of a molten LiH , at the anode and molten LiH is a good electrical conductor, both indicating the saltlike nature of LiH_x .

The presence of LiD_x , within the electrochemically charged palladium deuteride, is another indication that negatively charged deuteride D^- coexists within the deuterated

palladium. The presence of lithium in the solution has been suggested as a necessary condition for the reproducibility of cold fusion.

A possible picture of the structure of PdH_x consists of the following: Some of the metal valency electrons are donated to the hydrogen to form H^- and the palladium-hydrogen bonds. The remainder valency electrons are used in bonding between the palladium atoms and occupy bands of permitted electronic states, as in free palladium. This picture explains the metallic character and the electrical conductivity of PdH_x , the observed palladium-hydrogen distances, and the lack of stoichiometric hydrides.

Palladium hydride occupies a special position among metal hydrides. It is capable of absorbing large quantities of hydrogen, which is, in effect, compressed to extremely high pressures. Furthermore, hydrogen can easily diffuse through palladium, and its diffusion coefficient is similar to that in water. Palladium expands very slightly upon conversion to PdH_x . The lattice parameter for face-centered-cubic (fcc) palladium metal is 3.891 Å while α - $PdH_{0.03}$ has a lattice parameter of 3.894 Å, which increases to 4.026 Å for β - $PdH_{0.6}$ and 4.08 Å for $PdH_{0.8}$, obtained by electrolysis.⁶ The alpha phase represents a solid solution of hydrogen in palladium, which is an endothermic process. The beta phase represents a distinctive hydride phase with higher H/Pd ratios and is usually an exothermic process. The expansion of PdH_x with increasing hydrogen content is due simply to the effective metal and cation radii. The lattice distortion in hydrides (or deuterides) is partially caused by the repulsion of nearest hydrogen atoms, as shown by calculations of the Coulombic interaction by Hauck.¹⁴ Hauck et al.¹⁵ analyzed the short-range-order parameters for the nearest and next-to-nearest neighbor Z/Z interactions in interstitial alloys MZ with $Z =$ hydrogen, deuterium, carbon, nitrogen, oxygen, etc. With $n = 0.5$; $0.8 PdD_n$ was found to have repulsive interactions closed to the borderline of maximum separation, which is characterized by Pauling's electrovalence rule, postulating an equal distribution of charged metal ions within the octahedra. Entin et al.¹⁶ proved that ordering of hydrogen atoms in a metallic lattice is strongly affected by optical vibrations so that the transition temperatures of hydrides and deuterides of the same composition differ significantly. Entin et al.¹⁷ found by neutron diffraction of PdH_x that the low-temperature transition from the random distribution of hydrogen atoms among octahedral interstices in the fcc lattice of palladium is caused by the precipitation of a solid solution and the redistribution of hydrogen atoms in the metal matrix. This suggests considerable local inhomogeneities. Similarly, Brodowsky¹⁸ suggested the formation of clusters of stoichiometric composition. The average number of hydrogen atoms per cubic centimetre is given by

$$N_H = 6.02 \times 10^{23} \frac{n}{V},$$

where

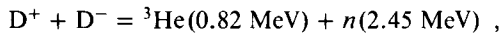
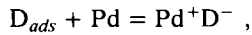
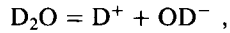
$n =$ number of hydrogen atoms per formula

$V =$ molar volume.

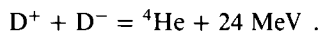
For $PdH_{0.6}$ the density is 4.0×10^{22} , which is similar to that of solid hydrogen at its triple point, which is 4.6×10^{22} . This indicates that the hydrogen is quite compressed within the PdH_x , especially when it is subjected to redistribution and clustering. The bonding in PdH_x is partly ionic with residual metallic bonds. A correlation exists between the ability of a

metal to form a hydride directly and its electronegativity. Palladium has electronegativity of 1.35, which is unique in its immediate neighborhood, thus explaining its large capability for hydrogen absorption.

Nuclear fusion apparently occurs when D^+ , which participates in the electrochemical reduction of heavy water D_2O , accumulates and reacts with the oppositely charged deuteride D^- , which is the dominant form in the PdD_x electrode:



and



The opposite charges reduce the intranuclei distance and enhance the tunneling rate for nuclear fusion. The formation of molecular D_2 according to $D^+ + D^- \rightarrow D_2$ is unfavorable because the electrons are shared with the palladium metal and are unpolarizable.

III. COMMENTS ON THE OBSERVATIONS OF JONES ET AL.²

The electrolysis of heavy water was conducted in 160 g of D_2O containing various salts in 0.2-g amounts each: $FeSO_4 \cdot 7H_2O$, $NiCl_2 \cdot 6H_2O$, $PdCl_2$, $CaCO_3$, $Li_2SO_4 \cdot H_2O$, $Na_2SO_4 \cdot 10H_2O$, $CaH_4(PO_4)_2H_2O$, $TiOSO_4 \cdot H_2SO_4 \cdot 8H_2O$, and very small amounts of $AuCN$. The pH was adjusted to ~ 3 by HNO_3 . The cathode consisted of 0.5 g of 0.25-mm-thick palladium foil, or 5 g of mossy palladium, or a 3-g titanium pellet. Gold foil was used as the anode on which oxygen gas evolved. The applied voltage varied from 3 to 25 V, and the corresponding current was 10 to 500 mA. The distance between the cathode and the anode is estimated to be ~ 2 cm. The roles of the various supporting electrolytes, beyond the usual task of providing electrolytic conductivity, might be to increase the overpotential for deuterium and to accumulate D^+ for subsequent fusion with D^- . It is possible that the role of co-deposition of the various metal ions is to increase the overpotential for hydrogen reduction and to build a high concentration of deuterium ions in the cathode. Furthermore, in light of the present explanation of the coexistence of deuteride D^- (or anionic H^-) in the palladium (or titanium) hydride, it is quite possible that the presence of alkali and alkaline earth metals can further stabilize the negatively charged deuteride or hydride ions. The conductivity of the heavy water can be estimated to be about $\kappa = 10^{-2} \Omega^{-1} \cdot \text{cm}^{-1}$ because the total molality of the solution is estimated to be on the order of 0.1 M. The ohmic drop through the cylindrical cell can be estimated to be

$$V_\Omega = \frac{I}{2\pi H\kappa} \ln \frac{r_a}{r_c} ,$$

where

I = total current

H = height of the electrodes, i.e., 4 cm

$\kappa = 10^{-2} \Omega^{-1} \cdot \text{cm}^{-1}$ = electrolyte conductivity

r_a, r_c = estimated radii of the anode (2 cm) and the cathode (0.5 cm), respectively.

For $I = 10$ to 500 mA, the ohmic voltage drop is estimated to vary in the range $V_\Omega = 0.1$ to 8 V. These rough estimations indicate that the majority of the applied voltage was consumed by the overpotentials at the electrodes and not by the ohmic resistance of the electrolyte. An overpotential of 1.6 V, for example, can generate deuterium activity on the order of $a_D = 10^{27} \text{ atm}^{1/2}$, as can be calculated from the Nernst equation for hydrogen electrode at room temperature. However, because the Nernst equation applies only to equilibrium, this is only a virtual pressure. The high overpotential at the cathode also indicates the possibility of accumulation of D^+ during the electrochemical reduction and its subsequent fusion with the negatively charged deuteride D^- within the palladium.

The time needed to charge the palladium cathode can be estimated by solving the diffusion reaction equation inside the palladium.¹⁹ It varies from hours to weeks, depending on the diameter of the palladium cathode. Nevertheless, it is suspected that fusion occurs on the surface, and the bulk PdD_x serves as a reservoir for the supply of deuteride ions.

IV. COMMENTS ON THE OBSERVATIONS OF FLEISCHMANN AND PONS¹

The electrochemically induced nuclear fusion experiments of Fleischmann and Pons¹ gave significant energy output, far beyond the detected amount of neutrons, which has been observed indirectly by gamma-ray emission caused when the neutrons plunged into the water bath. They also detected tritium, one of the products of the assumed fusion reaction. It appears that either the energy balance is in error due to the prior, lengthy buildup of deuterium inside the palladium or other unknown processes occurring within the palladium. The lengthy buildup and charging of the PdD_x could have been responsible for this additional release of energy.

The neutron flux claimed by Fleischmann and Pons,¹ using a 0.4×10 -cm palladium rod polarized at 64 mA/cm^2 , is $4 \times 10^4 \text{ s}^{-1}$, which is still in serious disagreement with the reported rates of 10^{11} to 10^{14} s^{-1} , as calculated from the excess enthalpy measurements.¹ Several explanations for the vast disagreement have been attempted. For example, Bresnani et al.²⁰ indicated that in condensed matter, the interaction between the quantized radiative electromagnetic field and the nuclei and electrons can provide screening of the Coulombic repulsion between deuterons and also a mechanism for absorbing the excess energy of the deuterium-deuterium (D-D) fusion in a very short time. Hagelstein²¹ proposed a coherent fusion theory in which virtual neutrons are produced and are captured by deuterons and protons yielding heat. Ragheb and Miley²² raised the possibility of deuteron disintegration in condensed matter due to polarization in the Coulombic field. Horowitz²³ suggested that the width of the fusion barrier for deuterium in palladium must be reduced to 0.1 Å for the fusion rate to reach 10^{-25} per D-D pair per second. Burrows²⁴ discussed the enhancement of cold fusion by screening of the deuteron or proton charge in the lattice cages. Nevertheless, none of the above theories, including the present one, can account for the large energy reported¹ or the absence of fusion products.

V. SUMMARY

In both experiments,^{1,2} the dominant presence of anionic deuteride D^- in the PdD_x and the formation of LiD_x , together with small amounts of cationic D^+ accumulated during

the electrochemical reduction, are suggested as the main reason for the apparent discovery of detectable rates of nuclear fusion at room temperature of electrochemically produced deuterium within palladium. This approach can possibly be extended to other metal deuterides.

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