

Research Article

Evidence Concerning the Mechanism of the Nuclear Reaction between Deuterium and Tritium

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Abstract

Both hydrogen and deuterium in their electrolysis on palladium gave linear Tafel lines but each had a kink in it at about 0.35 V overpotential (η). At this value damage begins to be seen in the SEM photographs of the interior of the electrodes. Tritium formation became detectable at an overpotential (η) of about 0.4 V. The reaction occurs in two consecutive steps: the first is a Volmer–Tafel reaction which occurs when the overpotential is less than 0.3 V. But as the measured coverage θ_D approaches unity, the deuterons begin to discharge onto the adsorbed deuterium (Heyrovsky mechanism). The second (consecutive) step leads to the tritium formation via a neutron transfer from the electrode to the Pd–D bond which at this stage (near to full occupancy by D) is relatively weak. The ready availability of neutrons in the surface region of the metal catalyst is rationalized in terms of the high electron concentration associated with the surface and the presence of D arriving from D_2O in the solution: $e^- + D^+ = 2 \text{ neutrons} + \text{a neutrino}$. The model is applied to two anomalies which have troubled this reaction. One is irreproducibility and also the long time (100 h or more) before any *nuclear* activity is seen.

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1. Introduction

This paper contains interpretive material of results in a paper published in 2000; the special nature of which was that it correlated the reaction deuterium to tritium with changes inside the electrode [1]. The experimental paper showed that a breakup of the internal structure of the palladium correlates with the beginning of nuclear activity.

The present paper begins with a brief summary of new facts recorded in the previous publication and then the mechanism is discussed in some detail. Thereafter, the model, which has been suggested, is applied to two outstanding anomalies of the tritium formation reaction, irreproducibility and the long latency period for tritium formation to begin on wire electrodes.

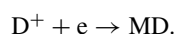
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2. Summary of Facts Previously Established

- (1) In respect to the two Tafel lines for the hydrogen and deuterium evolution, each showed [1] a marked change in slope at about 0.35 V (η) for the deuterium line. The lower slope of $d\eta/d \log i$ was 0.15 whilst the higher slope 0.22.
- (2) An examination of the pictures of damage taken at various overpotentials, time and temperature shows that the damage starts at $\eta = 0.35$ V for the room temperature measurements. The damage grows as the overpotential is increased. The information is available [1] up to 0.8 V (η).
- (3) Nuclear phenomena are observed when the “loading factor” is high.^a But the loading factor depends directly upon the surface concentration of the deuterium. In starting in an experiment up to, typically, 15–20 h, the transport of deuterium through the electrode is happening and building up the “loading.” The beginning of the damage is observed at about 0.35 V and the nuclear phenomena just afterwards (0.4 V) suggests damage precedes the onset of the second stage: the actual production of tritium.
- (4) An infrared spectrometer was equipped with Fourier transform mathematics and was used to indicate the presence or absence of adsorbed deuterium (or hydrogen) on the electrode surface [2]. The width of the spectroscopic peak for Pd–D spectra measures the occupancy with adsorbed hydrogen and its isotope. Here again, a break occurs at about 0.3 V (η). Above 0.4 V, little increase in the breadth of the spectroscopic peak occurs. Thus, the overpotential region of 0.3–0.4 is that at which the electrode coverage approaches unity. Thus, this potential region includes the internal loading coming up to, that which corresponds to $\theta \rightarrow$ unity, the beginning of damage, and slightly below the detectable production of tritium.^b
- (5) At higher θ s, there is no longer a smooth increase of permeation rate with time. The permeation decreases in a jagged fashion. Thus, damage evidently has begun and some of the deuterium which would have reached the other side of the membrane has been trapped in the damaged electrode material [1].
- (6) The stoichiometric number (ν) came out to be 1.11 at constant overpotential for conditions in overpotential greater than 0.4 V [3].

3. Mechanism of Tritium Formation

The parameters observed for the deuterium evolution reaction, in the lower Tafel line, were consistent with a rate determining deuterium transfer to an adsorbed site on the metal surface where the resulting MD could be observed spectroscopically:



Thus, for an η less than 0.35 V, the deuterium discharges with a Volmer–Tafel mechanism [5]. Above the η of 0.35 V, the surface is approaching complete occupancy with adsorbed deuterium. The course of the reaction now changes and the facts are consistent with a Heyrovsky desorption mechanism [4]:

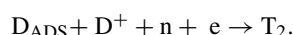


^aIt is important to determine the Tafel lines after the reaction has settled down. The delay before nuclear activity is observed (radioactivity of tritium!) was variable and could be as little as 10 h at low electrolysis current density (overpotential less than 0.3) then the second Tafel line began after a delay of as much as 50–100 h and the electrolysis continued with the higher slope and the production of tritium. The fact that one had to wait for the nuclear phenomenon to switch on is the direct cause of why so many experienced workers rejected the phenomenon in the years 1989–1991. Many switched on their apparatus and waited for some unusual phenomenon to happen. They saw no tritium so they switched off and concluded the phenomenon did not exist.

^bThe early runs in this work were analyzed for tritium in the nuclear engineering department at Texas A&M, but later runs were recorded within our group by an apparatus specifically designed to detect and measure tritium.

The SEM pictures published in the foregoing paper [1] show that the internal damage starts about $\eta = 0.35$ V [5]. Then with a higher surface occupancy with D, the deuterons in the double layer find the probability of discharge onto the adsorbed deuterium preferred. The stoichiometric number of 1.1 favors the Heyrovsky mechanism for the higher Tafel slope (for which theoretically the stoichiometric number should be 1.0).^c

The tritium formation occurs in two steps. The first is the deuterium discharge; firstly onto the palladium surface (Volmer) and then, with a change of slope, onto the adsorbed deuterium (Heyrovsky) with the direct evolution of D₂. In the second step, now with a high coverage of the metal with D, there are conditions suitable for a neutron transfer (high coverage corresponds to weak M–D bonding). The overall reaction becomes:



Here the n represents a neutron and T is for tritium. The neutron (see below) is suggested as joining the Pd–D bond when it is weak.

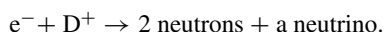
4. Neutrons: their Origin

Takahashi [7] hypothesized that there are free neutrons available inside the metal and they take part in the reaction stated. Fisher [8] supported this hypothesis suggesting that the neutrons inside metals exist in clumps. He obtained support from Oriani [9] who came into the picture because he had observed CO₂ with properties which seemed too heavy for a normal CO₂ molecule. This made him suggest that Fisher's clumps where in fact CO₂ carrying neutrons. Widom and Larsen [13] used neutrons in a number of their explanations of transmutation reactions.

Storms [10] hesitates in accepting neutrons as available for an electrochemical reaction. He points out that this would imply Pd¹¹¹ which is a β and a γ emitter, and such emissions have not yet been reported. This tritium is in fact deuterium to which a neutron has been added. So we have, finally, to have neutrons for the reaction to occur. However, tritium formation reaction is the most common reaction until the present examined up to around 100 individual papers of with Storms quotes 50 (the BARC team is responsible for many further replications).

We are dealing in a model, which sees the electrical double layer formed between the surface and the first layer of ions in solution as a main factor. Electric fields within this double layer region may reach as high as 10⁷ V/cm. Calculations [11] show the field distorts molecules, which come into its region. Reactivity in general has to be reconsidered in regions with such a high field strength. Adsorbed D comes from the solution, which contains the deuterium and gets adsorbed in the surface later undergoing electron transfer.

A suggestion made in a recent contribution by Widom and Larsen [14] is that neutrons are supplied at the surface by the reaction:



There is no supply of neutrons inside the electrode. They form on the surface. This formation in the strong electric field is part of the potential dependent of the rate of reaction.

The model is consistent with the dependence of the rate of these nuclear reactions upon potential. The D concentration on the surface is potential dependent and depends on the double layer field, as mentioned.

5. Latency Period in Commencement of Nuclear Activity

The tritium formation reaction is anomalously characterized by a delay in a start up of the appearance of the radioactive material. The delay is between 10 and 100 h for most papers, although occasionally a longer time is needed. Some

^cThe stoichiometric number is 2 for the Volmer–Tafel mechanism (lower slope) [5].

workers have found that the need to wait for such a time is too much and have given up after a few hours. However, they would be disappointed in most of the “tries” for the deuterium to tritium reaction, which seldom switches on under 10 h of low current density and therefore low overpotential.

The above mechanism will lead to tritium formation only in the presence of weak Pd–D bonds associated with a high θ . The time that is necessary for θ to increase and therefore the strength of the Pd–D bond to decrease, will new tritium form? The breakdown of the internal palladium which has been evidenced by the electron microscope photographs in reference [1] increases the number of possibilities for internal surfaces, which gradually increase θ s for provide slowly more sites, which produce the tritium. The solution will leak inside the electrode as and make active therefore the new sites, which are being formed by the breakdown.

This D–Pd bond on the surface of palladium electrode would add to the time needed for the appropriate condition for the neutron – Pd–D reaction to occur ($D + \text{neutron} = \text{tritium}$).

Our model sees the critical tritium formation step as that which a neutron formed on the surface as explained above “breaking into” the weakened Pd–D bond. Information becomes easier; activation energy becomes lower and its rate faster. The tritium formation stops and gets a lower activation energy and hence faster rate.

6. Irreproducibility

Experience suggests that there are no electrodes, which are simple failures. All electrodes produce tritium but all need different amounts of waiting time, which may be too much for some experimentalists. These are the ones, which the latter may call “failures.” Investigators who have experience of this reaction also suggest that there are no failures for investigators who wait.

One factor bearing on the variability of the waiting time may lie in the origin of the palladium samples. In the first two years of work on the tritium work reaction with wires of 1–2 mm, the *origin* of the palladium was varied. It was seldom that one run used palladium from the same manufacturer. One of the principal factors of a metal in the manufacturing phase is the mode of crystallization from the liquid and how much time is given for annealing. Few manufacturers anneal at all (i.e. cool on a known scientifically established schedule). This is a factor, which would give rise to different properties and feedback on the strength of the D–Pd bonds.

It is also noteworthy to record here that just before the heat starts evolving (i.e. the tritium forming), there is a period of cooling at constant current density that lasts for a short time such as 10 min, but nevertheless, the endothermic reaction implied involves a change of internal structure of palladium and is significant in any considerations of the extent of latency.

7. Dendrites Falling off

The author has experience with dendrite formation and its behavior [6]. Some of the break-off is visible. The presence of the dendrites is accelerative because of the high fields at the dendrite tips leading to a higher rate of D aggregation on the surface. When these high electric field points are removed, the reaction slows. If the removal were complete, one would see about a 10–100 times reduction in the reaction for the same applied potential. An observer would likely conclude the reaction has stopped functioning; whereas, it has just been reduced a considerable amount.^d

^dAs to the presence of copper and whether it is critical, we detected that after the electrode of special longevity had a copper impurity in the solution, we added copper in another solution but could find no further effect.

8. Water in D₂O?

In 1992 in collaboration with Nigel Pakham, experiments were carried out on water absorption from the atmosphere, which contains up to 15% water vapor. D₂O in an open beaker was put on the bench for up to two weeks and analyzed for water at regular intervals. It was found to continue to absorb water until 26% of the D₂O was diluted H₂O. Little variation in rate of the reaction was observed before 15% water.

9. Comparison with Non-electrochemical Performance of Similar Cold Fusion Reactions

Many reactions may be carried out electrochemically or chemically over the whole field of chemistry. However, all interfaces bare electric charges so that if in an attempt to carry out the reaction without electronic control, one has to take into account that charges are still there although undetermined.

The virtue of the electrochemical case is that the use of a potentiostat, allows one to control the potential and thus the concentration of electrons at the interface. The rate of the reaction is therefore under control and this provides a warning for those who carry out nuclear reactions in the cold but do not know what the potential is, other investigators may try the same reaction but under different circumstances also without control and these two reactions will not be comparable as far as their rate is concerned. It is only possible to compare a reaction with another investigator if the rate of overpotential is known. It is noteworthy that about 2 to 1 from ICCF 16 papers chose the electrochemical method of carrying out the reaction.

The excess surface charge is positive or negative. There is a potential of zero charge but that is difficult to maintain without electronic control.^e

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I acknowledge helpful discussion with Ed Storms and with Nigel Packham who was the first to find tritium, and also with Ramesh Kainthla who was a senior post doc working for me but who proved his experience in research particularly in the early years by helping me with the supervision of the large number of coworkers who were in the group studying tritium formation.

Appendix

Tritium is created from deuterium under electrochemical conditions for the most part and with more than 100 papers in support. Writing it as $d + n \rightarrow t$, has to take into account the bonding d–pd and the t–pd. Although we have no means of determining their bond strengths these bonds at the moment (separation factors), it is clear that the t to Pd should be stronger than the d–Pd. Although neutrons would have some small exchange force in respect to palladium, it would be too little to concern us. So I think the overall reaction would be somewhat ΔG° negative taken in the usual way of the right–left.

As the reaction fundamentally depends on neutrons, it is necessary to explain their existence and this has been done by Widom and Larsen [14]. According to them, the d in the presence of an electron rich surface will give two neutrons. This is easy to understand.

On the other hand, a more complex series of reactions might be necessary and these would be: $d + d + e + n \rightarrow t + 2n$

The main point of the paper is the switch on of the nuclear reaction when damage shows up inside the structure.

^eA number of laws had been set up long ago for electrochemical reactions. One knows, for example, that a Tafel slope (the gradient of the overpotential-log current density relationship) has a certain mechanistic meaning.

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