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The Nature of the Energy-Active State in Pd-D

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ABSTRACT

Evidence is presented to show that the energy-active state is located within the surface of electrolyzed palladium. Although a high average D/Pd ratio is required to form this state, this is not the only condition. Several additional conditions must exist to cause a very high surface composition to form and to cause a conversion of the resulting material from β -PdD to another phase. The required high surface composition depends only in part on a high average composition. Absence of microcracks in the surface region, presence of surface and near surface impurities, and external energy application influence the eventual nucleation and growth of the required phase.

Cathode temperature is important because it influences the diffusion rates of deuterium and impurities consisting mainly of lithium. This property combined with the applied current and the eventual lithium content, determine how steep the deuterium concentration gradient will be between the surface and the interior. The steeper the gradient, the higher the surface composition for the same interior composition. This surface composition affects the amount and composition of the new phase. Both of these aspects determine the magnitude of power production.

I. INTRODUCTION

A major issue in understanding the cold fusion effect is to discover where the nuclear-active state (NAS) is located and its properties. Only with this information can proper models be developed and methods to enhance its formation be discovered. To complicate the situation, the NAS is different in different materials and when subjected to different conditions. This paper addresses the NAS that is produced in palladium when it is electrolyzed in an electrolytic cell containing LiOD-D₂O electrolyte.

I suggest the NAS exists just below the surface of the Pd cathode and that the material is not β -PdD. Therefore, the properties of β -PdD are irrelevant to any understanding of the phenomenon. The properties of the underlying β -PdD are only important to the extent that they support the necessary conditions at the surface. This paper will attempt to justify these suggestions.

Three major factors affect the production of the NAS. These are the presence of cracks within the palladium structure that communicate with the surface, the presence of a lithium alloy region below the surface, and the presence of a diffusion barrier on the metal surface. These conditions combine to determine the deuterium concentration in the surface region. The value and location of this composition gradient structure determine the overall amount of NAS that will form and its general location. Other factors such as local dislocations, local concentrations of impurity, and local crystal size and orientation

play a role in determining exactly where the NAS first forms. These latter variables will not be addressed in this paper.

Because the NAS is located on the surface and represents only a very small part of the total quantity of hydride, methods are needed that examine only the surface region. This work relies on the open-circuit voltage generated by the cathode with respect to a deuterium-saturated platinum electrode. This voltage is proportional to the average deuterium activity within the outermost region of the surface. In addition, the value is proportional to the deuterium content of this region. Unfortunately, the exact correspondence between the voltage and these quantities is not known. The work will address this problem.

The approach combines previously published information, newly obtained results, and proposed structures in order to suggest a new approach to understand processes that effect formation of the NAS. The experimental details and additional results will be published in subsequent papers.

First, let us examine the variables that influence how palladium reacts with deuterium within an electrolytic cell.

II. EXPERIMENTAL

II.1. Excess Volume

Most palladium contains defects that result in microcracks and voids upon its conversion to the hydride. The average volume associated with these cracks can be quantified by measuring the excess volume (EV)¹. Figure 1 compares the measured volume change with the expected volume change calculated using the published lattice parameter. EV is produced only after the hydride enters the β -phase. This excess remains when hydrogen is removed and increases each time the sample reenters the β -phase. No additional excess is produced if the sample is deloaded and reloaded while remaining in the β -phase. Most palladium produces 3%-7% excess volume. Only a small number of samples produce no excess. Once formed, this excess can not be reduced by high-temperature anneal.

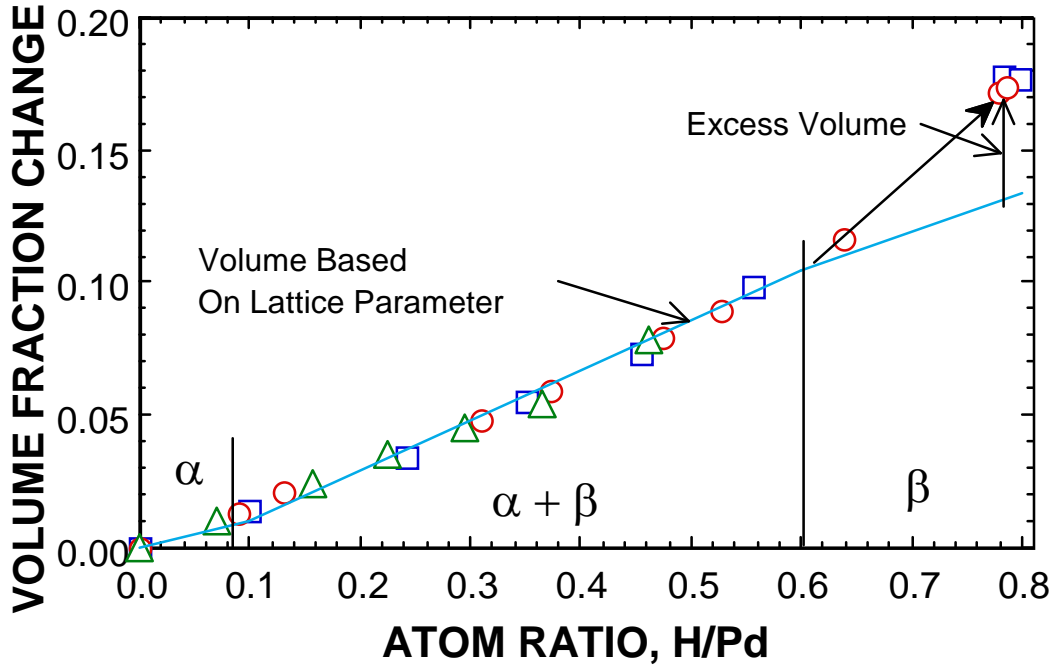


FIGURE 1. Volume fraction increase as a function of composition

Part of the EV consists of cracks that provide an escape path for hydrogen. This loss limits the maximum average composition that can be achieved. An example is shown in Fig. 2 where a sudden increase in EV resulted in a loss of hydrogen. Samples containing an initially high EV will not load to high compositions. This behavior can be seen in Fig. 3 where the relationship between EV and the maximum D/Pd ratio achieved after loading for 10 hr. at 250 ma is shown. These conditions are sufficient to produce a composition that is

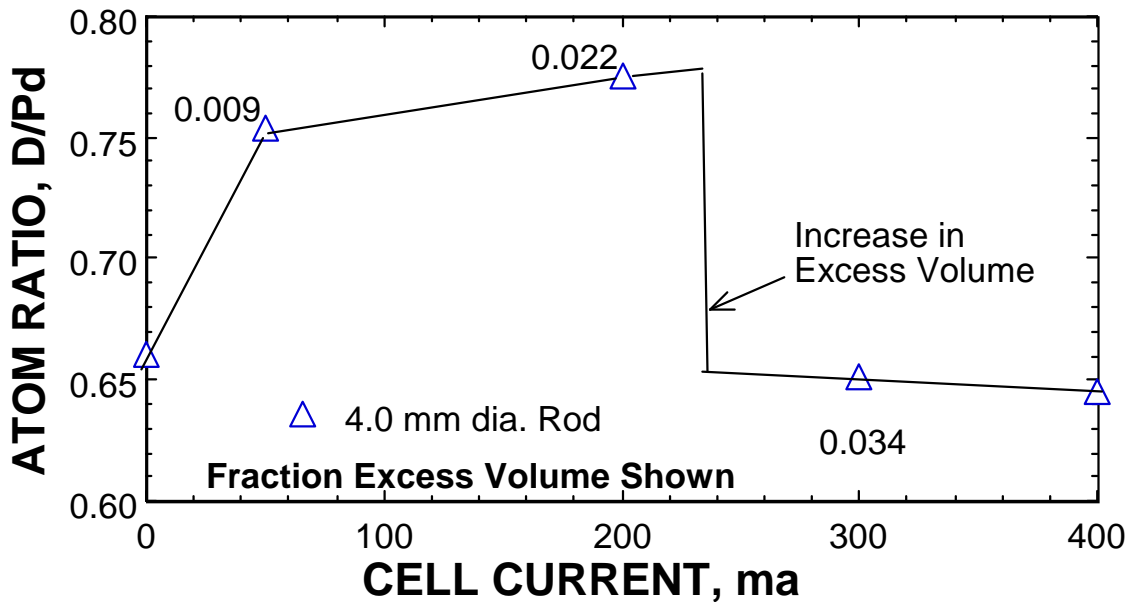


FIGURE 2. D/Pd Vs current with excess volume shown

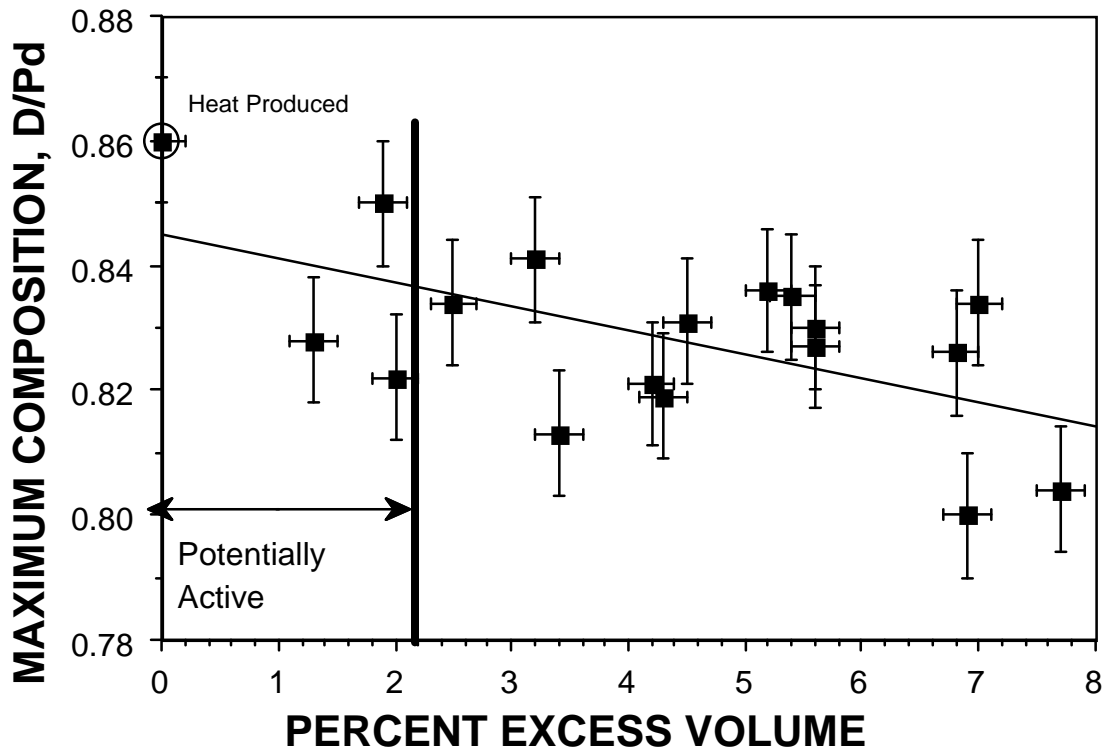


FIGURE 3. Maximum achieved D/Pd compared to the measured excess volume. The excess volume region proposed to allow excess energy production is indicated.

relatively constant with time. Although some samples will slowly go to higher compositions if electrolytic action is continued, this short-term loading condition is sufficient to show the effects being discussed in this paper. The relationship shows considerable scatter because the magnitude of the effect on the limiting composition depends on the fraction of the EV that communicates with the surface. This fraction is unique to each sample. In addition, this fraction frequently increases as the composition is increased. As a result, measurement of EV provides only a rough, but useful, method to identify potentially active samples.

II.2. Mechanism of Hydrogen Loss

The mechanism of hydrogen loss can be identified and the loss rate can be quantified by using tritium as a tracer.

A piece of palladium is electrolytically loaded with hydrogen containing a known amount of tritium. The loaded electrode is placed in an electrolytic cell that contains no initial tritium. The tritium content of the electrolyte and the evolved H_2 is measured. As shown in Fig. 4, most of the tritium, hence dissolved hydrogen, appears in the gas.

The hydrogen isotopes have two routes by which they can leave the palladium, either through the electrolyzing surface or out of cracks that communicate with the surface. Any tritium that attempts to leave through the electrolyzing surface is expected

to quickly exchange with H^+ and OH^- ions in the solution and become trapped in the electrolyte. Only those hydrogen atoms that form HT or H_2 gas on an interior surface would be found in the gas. This behavior demonstrates that the evolving hydrogen gas is formed within cracks, out of contact with the electrolyzing surface. Thus, a hydrogen flux enters the palladium through the electrolyzing surface and leaves through interior cracks. Of course, a significant part of the available hydrogen does not enter the palladium at all but converts directly to H_2 at the surface. This hydrogen has no effect on tritium removal.

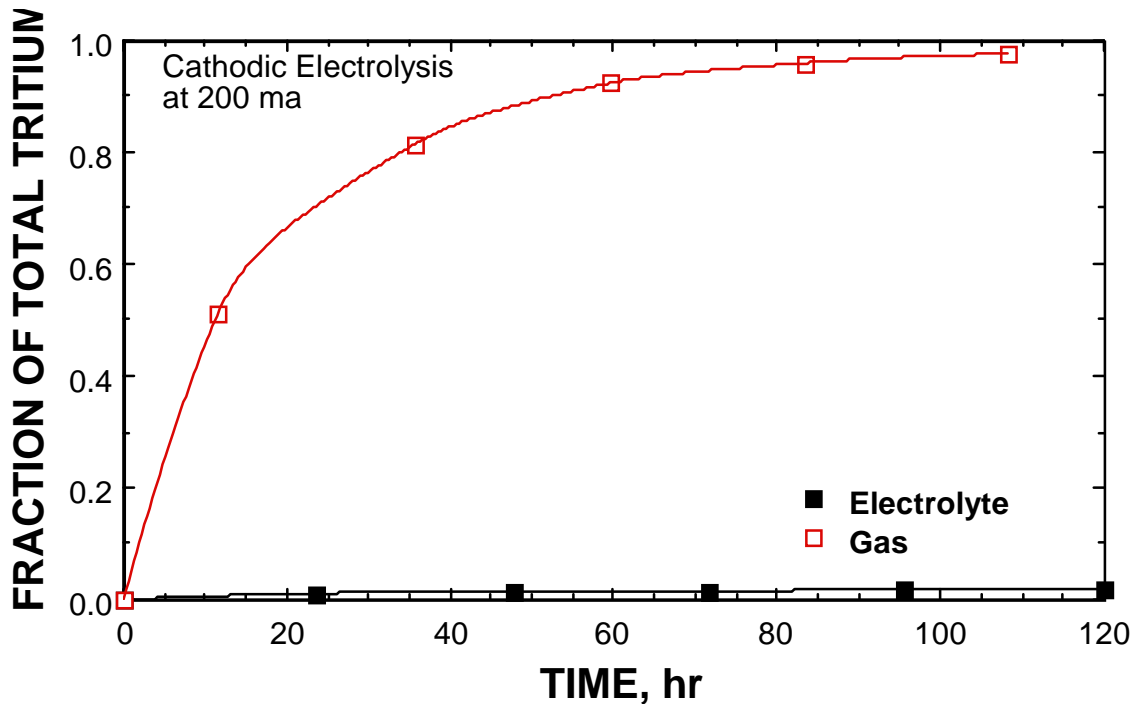


FIGURE 4. Fraction of tritium lost into gas and electrolyte during cathodic electrolysis

The data in Fig. 4 is replotted in Fig. 5 to show that tritium loss is a first order process, i.e. the loss rate is proportional to the tritium concentration. This behavior means that an average hydrogen atom resides for a definite time within the palladium. The half-life of a hydrogen atom in the palladium used during this study fell between 12 hr and 24 hr, depending on the applied current and the amount of EV. Temperature would also play a role but this variable was not explored.

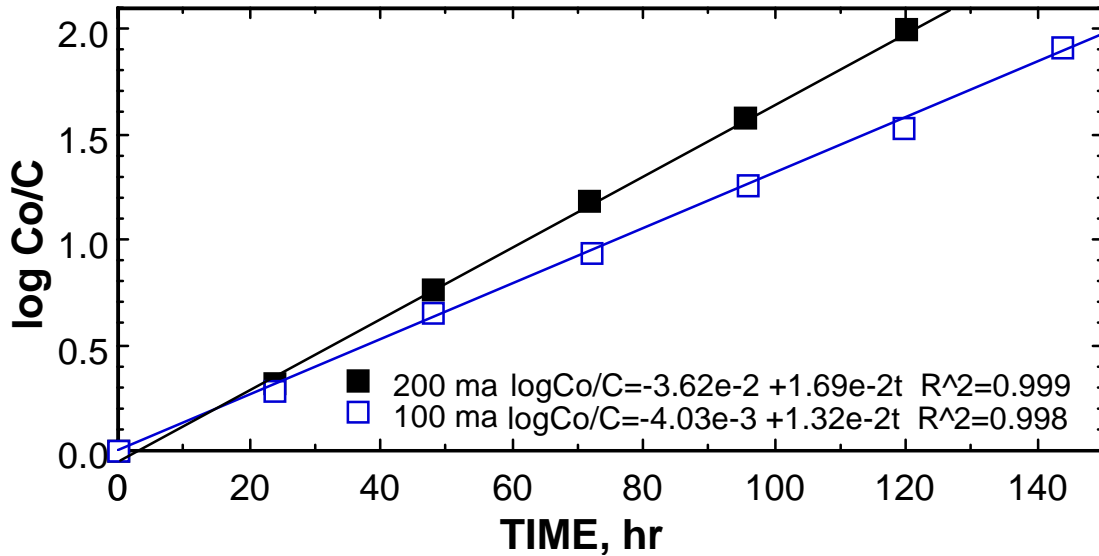


FIGURE 5. Plot showing first order loss of hydrogen from palladium being electrolyzed at two different currents.

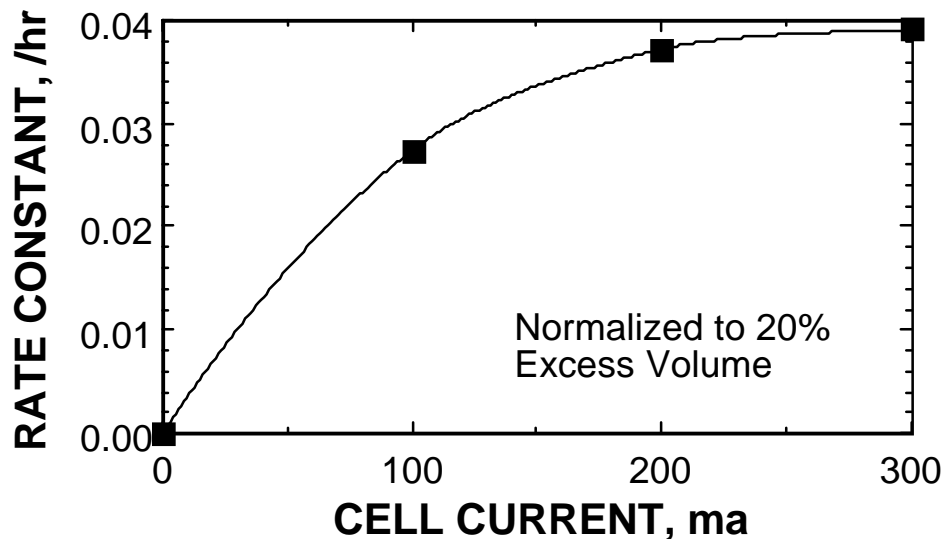


FIGURE 6. Effect of applied current on the rate constant at a fixed EV.

As the cell current is increased, the half-life decreases. However, as shown in Fig. 6, the loss process becomes saturated as the current is increased above a critical value. Apparently, the amount of hydrogen able to enter the palladium has a limit regardless of how many hydrogen atoms (ions) are presented to the surface. This saturation current and rate constant are expected to be smaller, the smaller the amount of EV.

The steady flux of hydrogen passing through palladium creates concentration gradients with the highest composition at the electrolyzing surface and the lowest composition at a crack surface. In addition, the higher the average composition, the higher is the surface composition, all else being equal. As a result, a complex concentration gradient pattern is created resulting in a very complex composition

structure on the surface. This structure has an average composition significantly greater than the average bulk composition. The challenge is to determine the surface composition.

II.3. Open Circuit Voltage Measurements

The open circuit voltage (OCV) developed between the cathode and a stable reference electrode is proportional to the activity (Gibbs Energy) of hydrogen dissolved in the surface phase. Accurate measurements can be made while the electrolytic current is interrupted for a brief time. Once calibrated, this quantity can give the actual composition of the surface. A rough calibration can be obtained by comparing the OCV to the average bulk composition. Provide the gradient is small, the relationship will show an upper limit to the voltage with respect to composition within the β -phase.

The relationship between the average composition, obtained from the weight change, and the voltage referenced to a deuterium-saturated platinum electrode is shown Figure 7. The phase boundaries are drawn to be consistent with published information. The data shown in this figure are preliminary and describe a sample that has been electrolyzed for sufficient time to acquire a surface layer of a Pd-Li-D alloy. Although the behavior does not represent the pure Pd-D system, it does describe a typical sample used to produce excess energy by this technique.

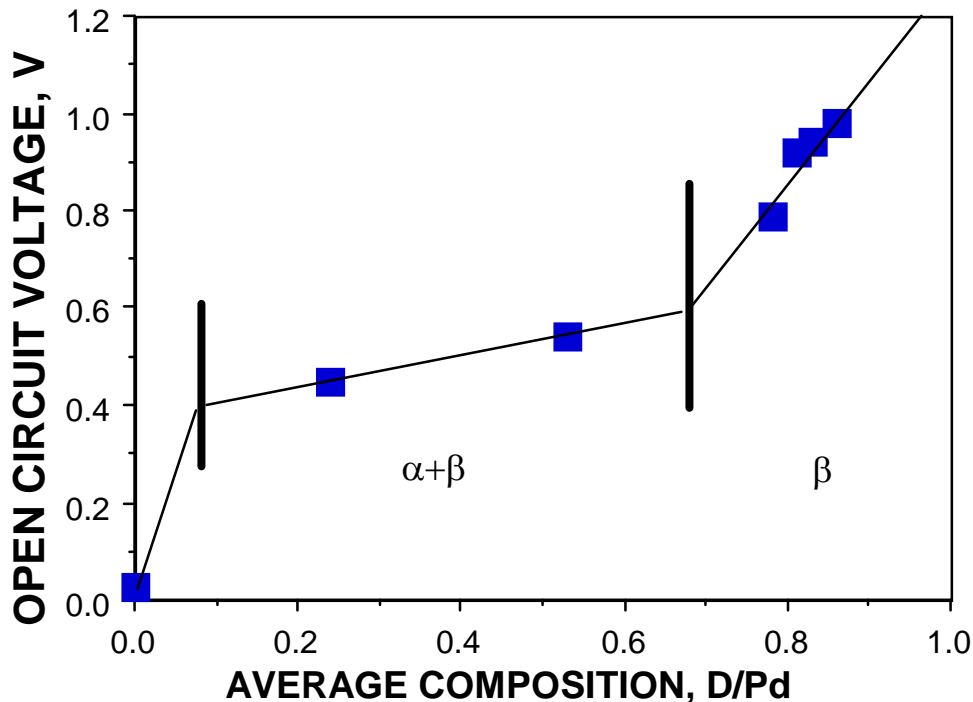


FIGURE 7. Open circuit voltage developed between the cathode and a platinum electrode located outside of the cell.

When a sample has reached the conditions required to produce excess energy, the OCV rises abruptly from 1.1 V to near 1.4 V. The material having this voltage (D activity) can be decomposed by turning off the current. Figure 8 shows the voltage

change during the deloading process following current interruption. The behavior suggests the presence of a new phase (g) having a deuterium composition and activity significantly above that of the β -phase. A slight undershoot precedes decomposition of this phase into the b-phase. This behavior indicates that the g-b transition requires a significant activity difference to be initiated. An increase in activity is seen during the initial temperature drop indicating that the γ -phase becomes more stable as temperature is reduced. The structure and properties of this phase would be influenced by the proposed lithium content.

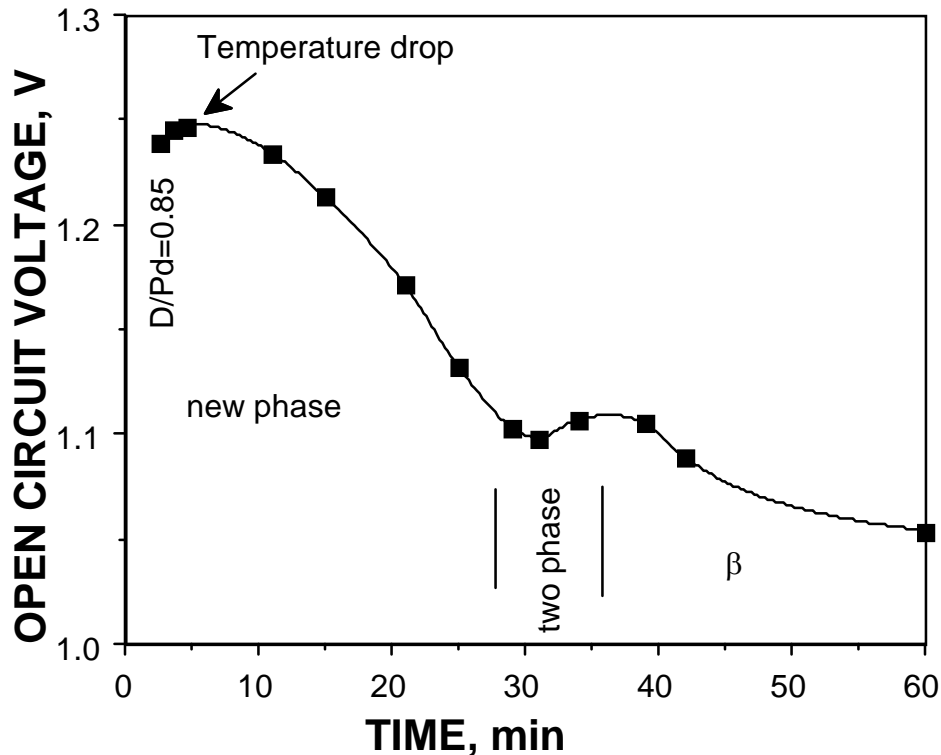


FIGURE 8. Voltage change during deloading in the cell. The temperature dropped from 22° to 9° C during the first 5 minutes. The initial average bulk composition is shown.

II.4. Proposed General Behavior

All of these observations can be explained if a gradient structure exists between the surface and the cracks. A diagram proposing how a crack affects the hydrogen gradient is shown in Fig. 9. Once established, this gradient would gradually change as lithium is deposited on the surface and is diffused into the interior.²³⁴ The slowly growing complex layer of various possible Pd-Li-D phases (Pd_7LiD_x , Pd_2LiD_x , PdLiD_x , PdLi_2D_x , and PdLi_3D_x) would lower the diffusion rate through this region resulting in a steeper hydrogen gradient. The hydrogen and lithium compositions within this region is proposed to gradually rise and eventually reach the critical value needed to form the NAS. Although evidence is not yet available to completely support this model, I suggest that a search for such evidence would be worthwhile.

A coating of other impurities also forms which blocks both deuterium entry and exit from the surface. These impurities include Zn, Cu, Fe, Pb, Ca, Na, Mg, Pt, Cr, Si, S, and

C , ⁵⁶⁷⁸ with a complex morphology and distribution. Formation of the NAS depends on which of these two blocking processes has the upper hand. Because the loss rate through cracks can not be blocked, the hydrogen content within a sample having a high EV will be reduced as hydrogen uptake is reduced by a blocking layer. Only samples having zero EV will be helped by this barrier as hydrogen loss is reduced.

Such layers have been proposed to affect the D₂ dissociation reaction by either preventing D recombination to the molecule or reducing the availability of D ions on the surface. The net effect of either process would appear as a net increase or decrease in the gross loss rate. This mechanism is not addressed in this study.

Localized cracks can grow in the surface region because of stress within the brittle impurity layers. These escape paths can result in a surface composition too low to form the NAS even though the average composition is high. Because of their limited range, an increase in the average EV would not be observed. Excessive deloading after the lithium containing layer has formed followed by reloading is expected to produce such cracks.

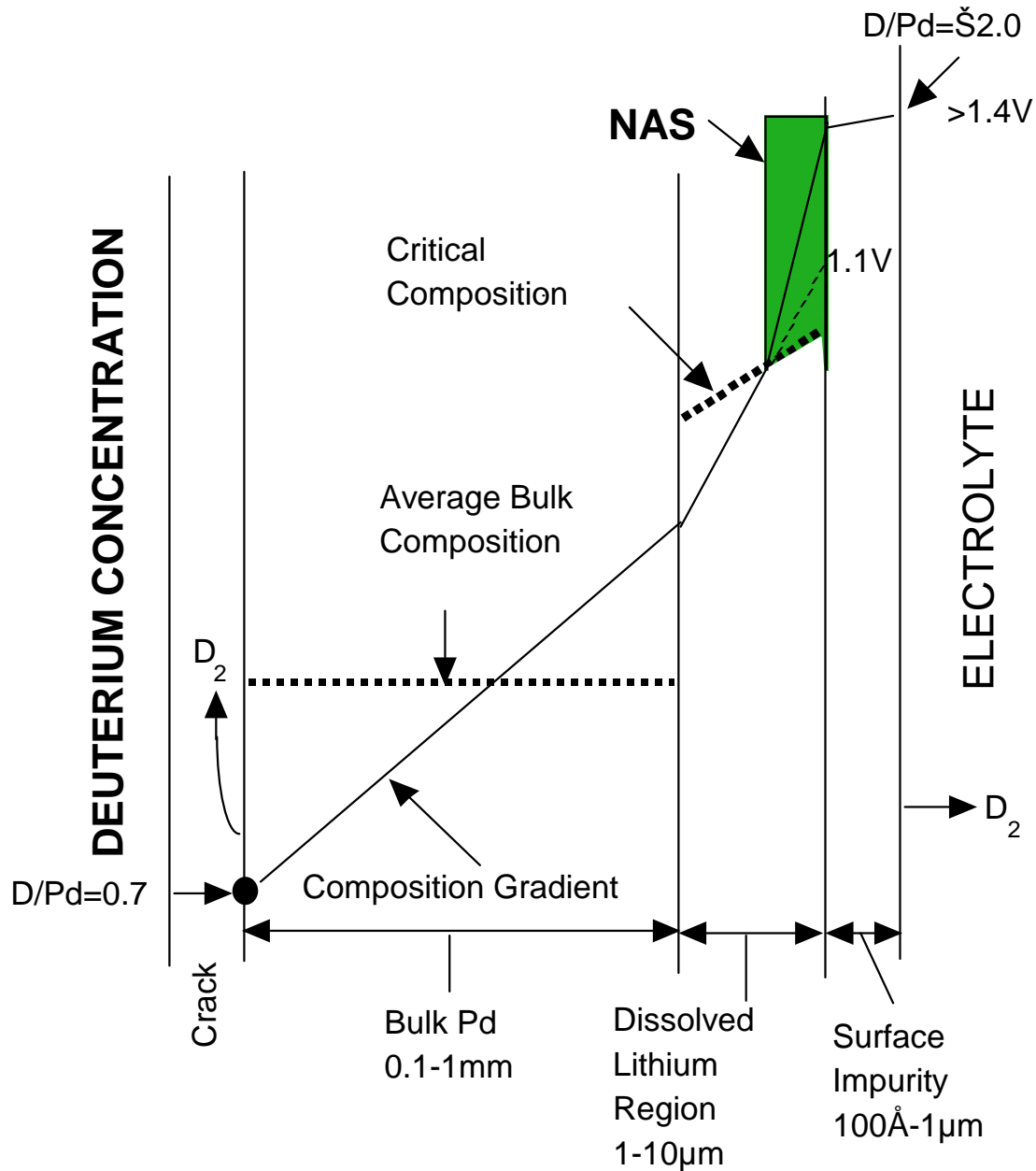


FIGURE 9. Concentration gradients in the various regions between the electrolyzing surface and an interior crack. The various measured OCV are shown. The nuclear-active state is designated by NAS. The thickness and composition scales are arbitrary. The complex phase structure within the “dissolved lithium region” is not shown.

II.5. Deloading Rates

It is possible to measure the deuterium loss rate through this barrier by assuming that this loss rate is independent of electrolyte action. If this assumption is correct, the barrier effect can be measured by allowing PdD to deload in air or within the cell.

An example of such deloading is shown in Fig. 10. A change in deloading rate is seen when the bulk composition reaches a value that allows a-phase to form on the surface. Only the loss rate within the b-phase is of interest here.

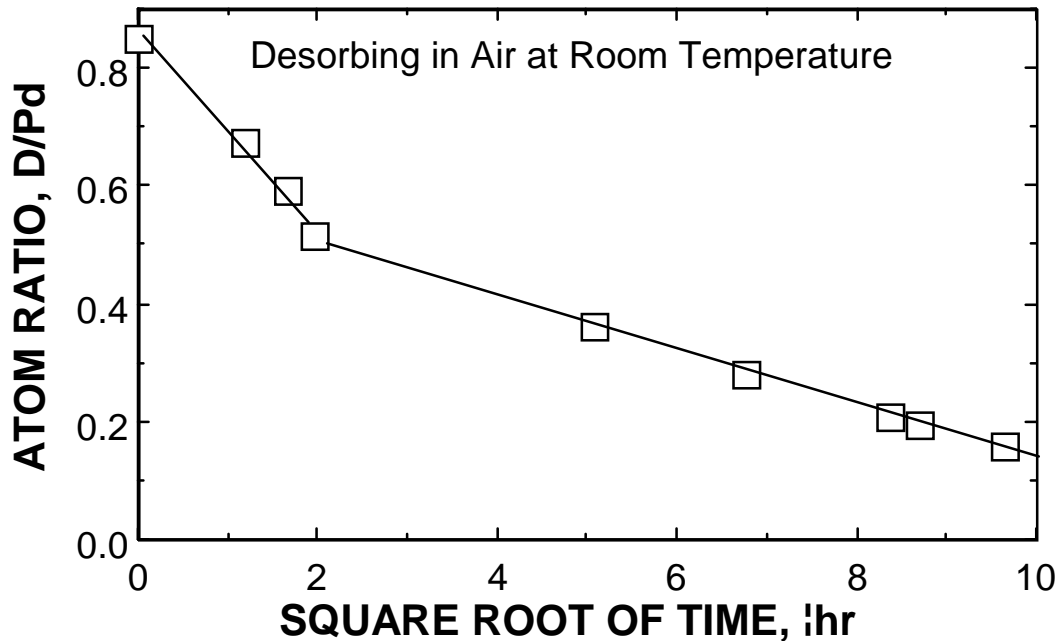


FIGURE 10. Composition of a typical PdD sample shown as a function of $\sqrt{\text{time}}$ while deloading in air.

The deloading rate is influenced by the amount of EV, as shown in Fig. 11. To make this comparison, the final composition is shifted in time so that the final composition-time relationship falls on the line. In this way, a compensation can be made for the tendency to deload faster at higher compositions. The figure shows that a rapidly increasing deloading rate as the composition is increased prevents samples having high EV from achieving a high composition. Apparently, the cracks become more effective as the composition, hence internal pressure is increased.

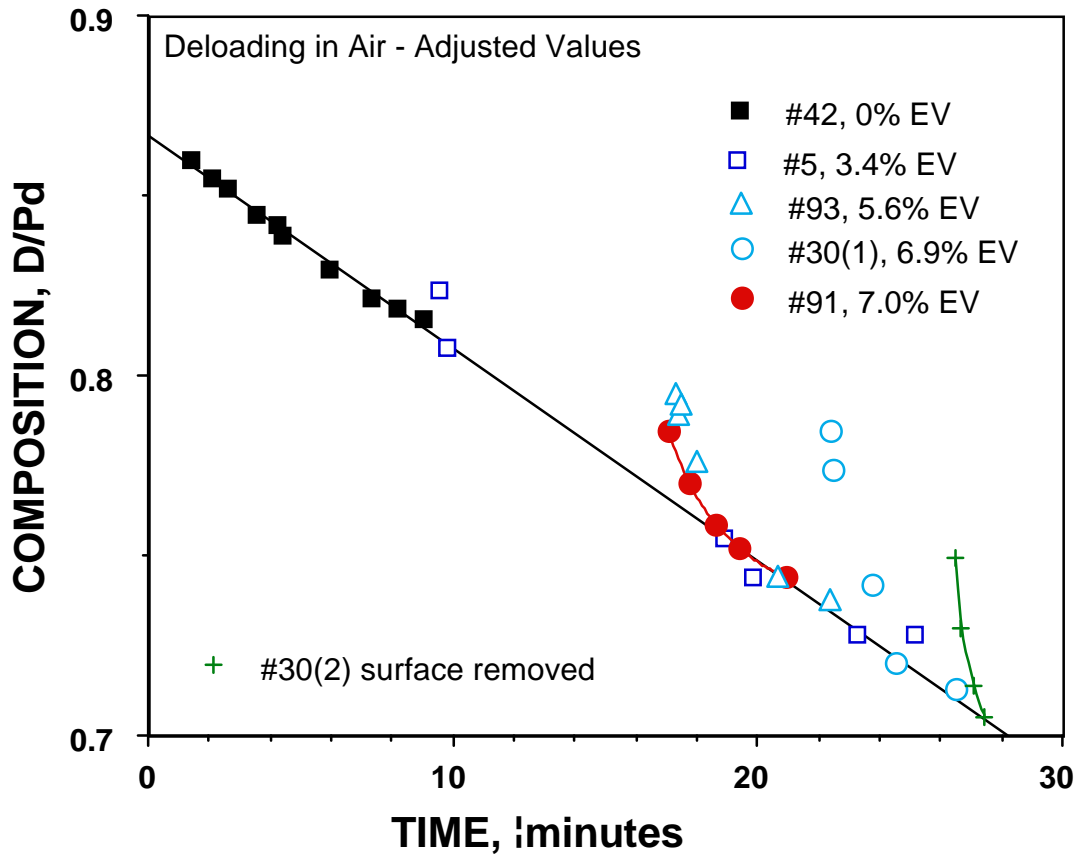


FIGURE 11 Deloading rate in air compared. The composition is adjusted in time to make the final deloading slope fall on the line. The curves terminate at the highest composition achieved during loading.

III. CONCLUSION

III.1. Speculation About the Nature of the NAS

The NAS involves a phase having a higher composition and a much higher hydrogen activity than found in β -PdD. Although a variety of phase structures are available to explain this phase, I propose that the new phase relates to the β -phase as shown in Fig. 12. The new phase, designated gamma (γ), is formed as single deuterium atoms within the fcc structure of β -Pd (Li)D are replaced by D_2 dimers. A cut through the [100] plane of the proposed fcc structure is shown in Fig. 13. In addition, the dimers may interact to produce an ordered structure leading to a slight modification of the cubic lattice. Ordering of the Li atoms would have the same effect.

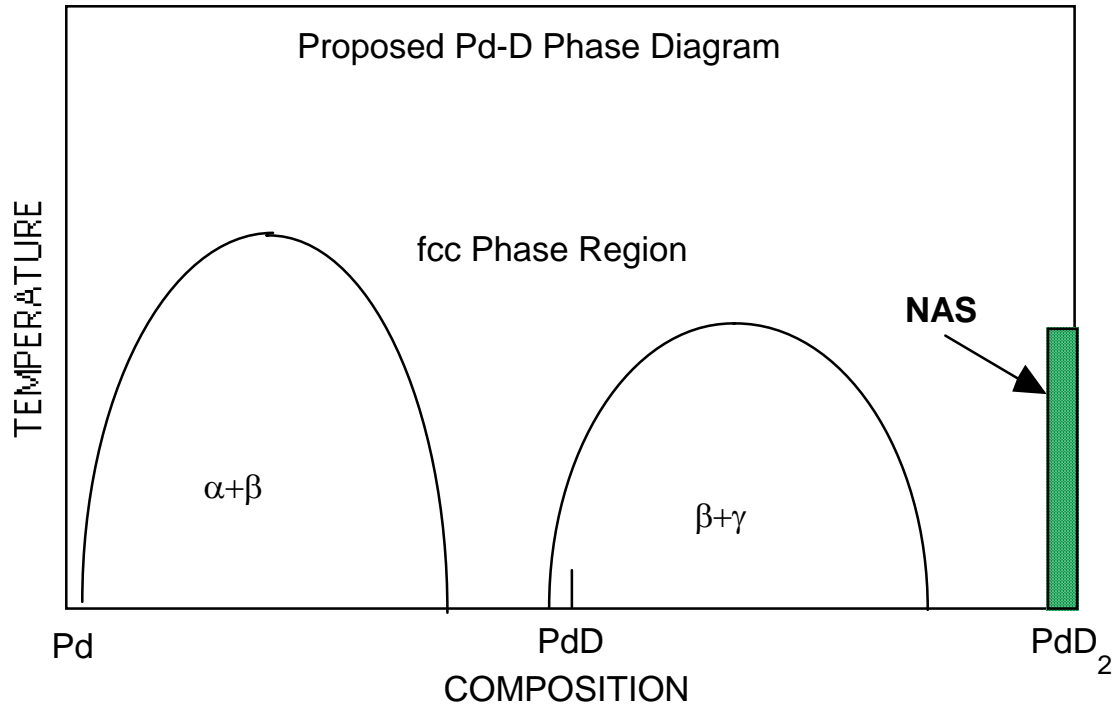


FIGURE 12. Proposed phase relationship in the Pd-D₂ system.

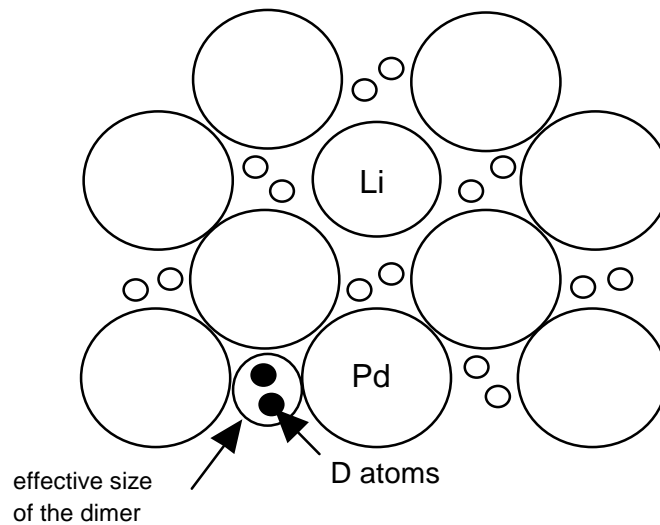


FIGURE 13. Diagram of the {100} face of fully occupied (fcc) γ -Pd(Li)D₂.

This dimer structure is proposed to form by covalent sharing of 1 electron between two deuterium atoms. The other electron is contributed to the conduction band of the palladium structure. This phase is expected to have a very low diffusion rate for hydrogen as well as other unusual properties.

In an electrolytic cell, the NAS also contains Li atoms. The resulting structure will be modified by the presence of this impurity. How this modification affects the stability or structure of the γ -phase is unknown. These lithium atoms are not proposed to participate in the nuclear reaction but only aid in creating the necessary chemical

(electron) environment in which nuclear reactions might occur. This is not to say that the Li atoms as well as other impurity atoms would not participate in a nuclear reaction once the NAS forms.

III.2. General Conclusions

Formation of the NAS in a Pd-D electrolytic cell is affected, at least in part, by the following factors:

1. Concentration of microcracks in the cathode. (The palladium purity has a direct effect on this factor.)
2. Applied current between limits. (These limits will be affected by the number of cracks that reach the surface.)
3. Temperature of the cathode. (This factor can be influenced by the amount of applied current.)
4. Presence of surface barriers on the cathode. (The effect will depend on the number of cracks that reach the surface.)
5. Presence of lithium within the surface region. (The loading time and temperature have a direct effect on this factor)
6. Crystal size and orientation. (Annealing has a direct affect on this factor.)
7. Application of energy to the lattice to aid in the β - γ conversion. (This energy can take various forms including RF, magnetic, sonic and optical.)

All of these factors impact on the ability to achieve high, local concentrations of deuterium. The presence of impurities unrelated to producing a high deuterium concentration have unknown but probably important influence on the stability of the γ -phase.

Because of a very low diffusion rate, once formed, the NAS can remain metastable for a period of time after the electrolytic current is stopped. It lasted for about 60 min in this study. However, it will eventually decompose when the surrounding deuterium concentration drops below a critical value. The lifetime will depend on how fast the NAS loses deuterium, on the presence of nucleation sites to allow γ to β conversion, and on the amount of lattice destruction caused by nuclear energy release while at the nuclear-active composition. These factors give some hope for an eventual determination of the crystal structure for this phase.

Because the NAS is not within the β -phase, theories and models based on the atom environment or thermochemical properties of the β -phase have no merit. The proposed phase offers the possibility of fusion involving 4 atoms of deuterium, i.e. 2 dimers, as suggested by Takahashi.

Minor variations in the NAS would appear to have important consequences because a variety of nuclear reaction products are occasionally seen. Consequently, the proposed model adds an unanticipated complexity to any theoretical approach.

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