Research Article

The Enthalpy of Formation of PdH as a Function of H/Pd Atom Ratio

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Abstract

A Seebeck calorimeter is used to measure the bond energy between H and the lattice in the Pd–H system as a function of H/Pd atom ratio during electrolysis. The bond energy was found to become increasingly endothermic in excess of about $PdH_{0.75}$. This energy is found to be sensitive to repeated gain and loss of hydrogen and to the bond disruption caused by reduction in thickness. The study used Pd having various purities and in one case a single crystal. In addition, a new method is described to measure the H/Pd atom ratio during electrolysis, which is used to show how rapidly H reacts with Pd.

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1. Introduction

The bond energy between the PdH structure and the contained H atoms is directly measured in real time as a function of H/Pd ratio from zero to the maximum H content using an accurate calorimeter and the electrolytic method. This method is applied to several types of Pd including commercial Pd, extra pure Pd, and a zone-refine single-crystal of Pd after each is subjected to several treatments. These treatments include repeated loading–deloading cycles, annealing at 900°C, and reduction in thickness. The bond energy is found to be sensitive to purity, treatment, and H/Pd ratio. Good agreement is achieved with published measurements after certain treatments are used. This study supports the previous conclusion [1–4] that formation of beta-PdH(D) becomes endothermic at an unknown hydrogen content, as shown in Fig. 1. The partial enthalpy of formation as a function of H/Pd atom ratio shows that bonding between H and the lattice becomes repulsive at H/Pd atom ratios above about 0.75. This conclusion is important to correctly understand how PdH functions in many situations including when the low-energy nuclear reaction (LENR) occurs.

In order for the enthalpy of formation to be properly measured and understood, additional behaviors need to be measured at the same time. These include the effects produced when hydrogen reacts with Pd (loading) and as the H_2 is removed (deloading), which results in the formation of excess volume. Residual strain also has an effect. Each of these variables can affect the enthalpy of formation and is studied as part of this work.

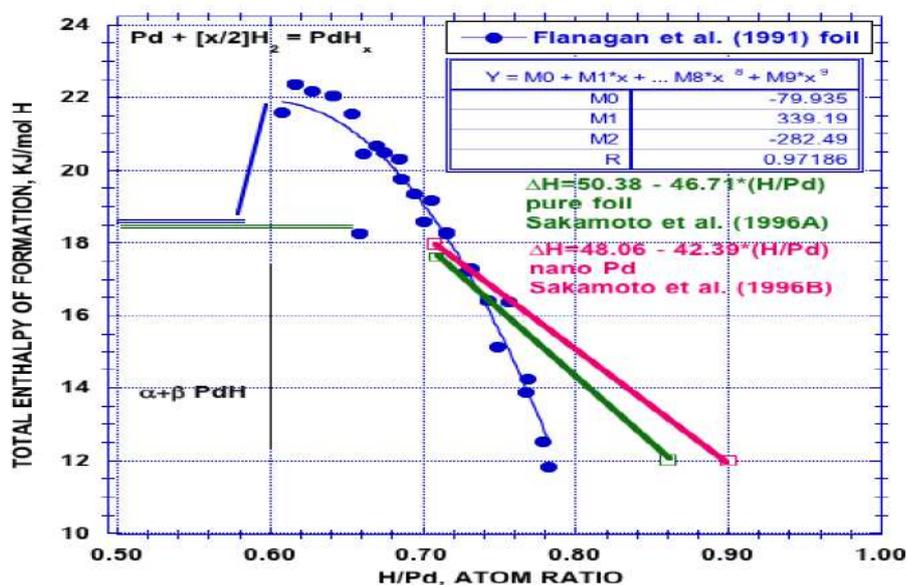*E-mail: storms2@ix.netcom.com.

Figure 1. Total enthalpy of formation for PdH as a function H/Pd ratio. A positive sign is used to indicate that energy is given off when PdH forms, as is conventional when energy is measured using a calorimeter. In each study the Pd was loaded and deloaded 10 times in order to increase its reactivity to H_2 gas before the measurements were made using a calorimeter and H_2 gas. The negative slopes within the beta-phase region show that while creation of the beta-phase releases energy, further addition of H absorbs energy. The tabulated values provided by Flanagan et al. [1] were fit by a quadratic equation in order to better define the behavior of the partial enthalpy of formation. The studies by Sakamoto et al. [2] fit their own values to straight lines, which are plotted here.

2. Experimental Method and Results

Three methods are used to measure the average H/Pd ratio during loading. These methods use weight gain (WG), orphaned oxygen (OO), and a new method using the recombiner temperature (RT). The weight of H in the PdH_x is measured every minute for seven minutes after current is stopped and the sample is placed on a 5-place balance. The weight is extrapolated back to zero time using the square root of time. The orphaned oxygen method measures the extra oxygen left behind after the H released from H_2O reacts with Pd. The volume of oxygen is measured by displacing oil on to a balance, from which is calculated the moles of H reacted with Pd. The temperature of the recombiner is used to determine how much of the decomposed H_2O is present as unreacted H_2 and O_2, which when compared to the amount of H_2O that is decomposed by applied current, results in a value for how much H reacted with Pd. A typical comparison between the three methods is shown in Fig. 2.

Many samples experience an initial time during which every H provided by electrolysis reacts with and enters the Pd, an example of which is shown in Fig. 3 for the high purity Pd sheet. The duration of this time is brief compared to the total loading process and is sample dependent. The rate of reaction slowly decreases, finally reaching zero when no further net addition of H to the sample is possible. This limit occurs when the rate of addition equals the rate of loss. Hydrogen continues to react and enters the structure at this limit but it leaves as H_2 gas just as rapidly from certain well-defined sites [5]. Many of these sites are cracks and other physical flaws in the surface.

Each sample was studied several times after repeated loading and deloading. This treatment causes the physical shape of the sample to change so that a plate increases in thickness while its length and width shrink after each
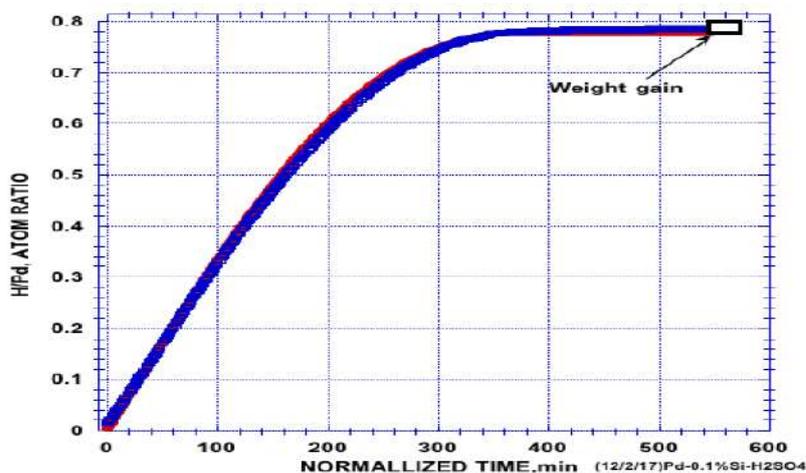
Figure 2. Comparison between the average H/Pd atom ratio obtained using the RT, OO, and WG methods with values measured every minute. The electrolytic current is 0.101 A. The delay caused by the calorimeter reaching equilibrium is avoided by applying power to a heater matching the electrolytic power. After the temperature in the calorimeter has reached constant value, heater current is turned off and electrolytic current is applied. This method allows the system to reach equilibrium within 5 min rather than after 60 min. Good agreement between the methods gives confidence in the value. Occasional lack of agreement reveals important information about the nature of the electrolytic process.

loading–deloading cycle. This process is known to result in significant changes in the physical and chemical behaviour [7–11]. An example of the increase in thickness is shown in Fig. 5. As shown below, this treatment affects the
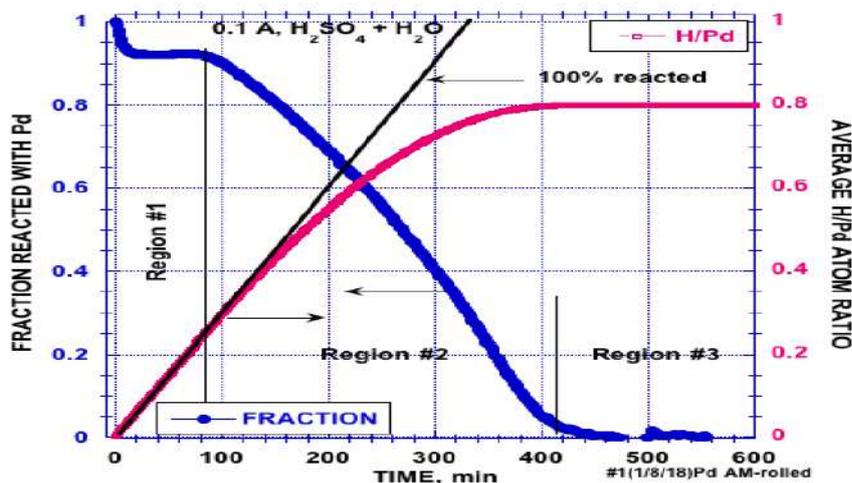

Figure 3. Example of fraction of H reacting as a function of time and the resulting average H/Pd ratio. Initially, nearly every H released from H_2O reacts with Pd (*Region* #1). Upon reaching the H/Pd ratio limit, the net amount of H reacting with the PdH is zero (*Region* #3) because H_2 leaves the sample as fast as it is applied by electrolytic action. Because every sample shows different behavior, the H/Pd ratio can not be obtained using the theoretical loading behavior as has been done by some researchers in the past.
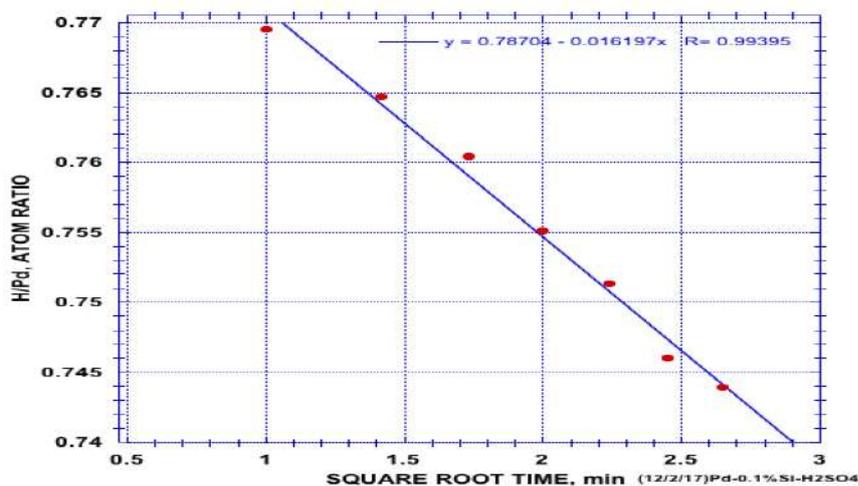
Figure 4. Example of loss of H after an electrolytic current of 0.101 A is stopped and the sample is allowed to lose H_2 in air. Weight is measured every minute using a 5-place balance with conditions of 0.75 atm and 20°C (lab pressure and temperature). The slope of this line is called the loss rate. This loss rate occurs in air, in acetone, and in the electrolyte when electrolytic current is stopped. Extrapolation to zero time gives the H/Pd ratio before electrolysis was stopped. This linear behavior continues for many hours and changes slope when enough H has been lost to cause the alpha phase to form on the surface.

bond energy in the material, which complicates interpretation of measurements made after repeated loading–deloading cycles are applied.
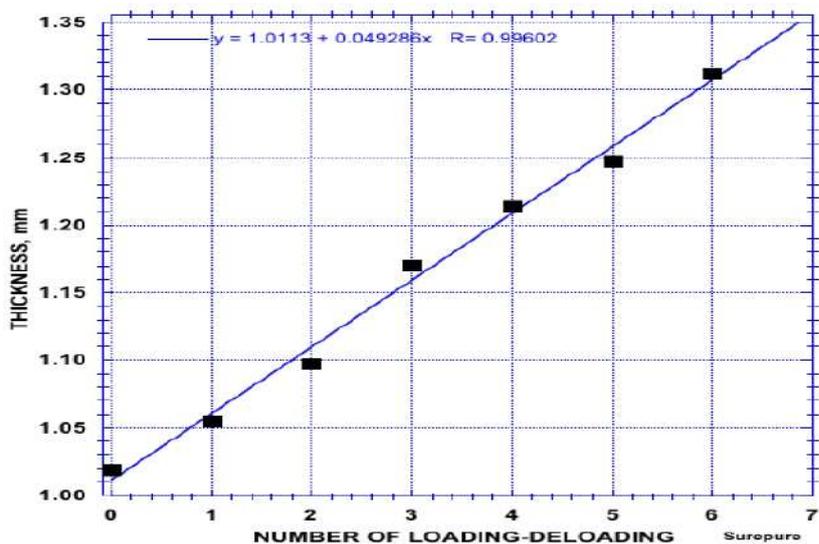

Figure 5. Effect of loading–deloading cycles on the thickness of palladium sheet. Although the other dimensions are reduced in value, the average volume increases. Each sample shows a different amount of expansion.

Figure 6. Picture of the opened calorimeter with the orphaned oxygen apparatus for measuring the H/Pd atom ratio of the cathode. The calorimeter contains a sealed Pyrex electrolytic cell and a fan. All insides of the box are covered by 54 thermoelectric convertors that are maintained at a constant reference temperature of $15 \pm 0.01°$C by flowing water. Measurements are made using NI hardware and LabView. Water enters and leaves the top though the hinges.

Once the H/Pd ratio reaches the saturation limit, most H_2 is lost from cracks or flaws that penetrate the surface [6]. This loss rate was measured by weighting the sample in air as a function of time immediately after electrolytic current is stopped. An example is shown in Fig. 4. This loss rate provides another way to evaluate the variables that limit the amount hydrogen the beta phase can acquire.

A Seebeck-type calorimeter [12], shown in Fig. 6, is used to determine the amount of net heating power involved in the electrolytic process. This calorimeter has a measured uncertainty over the full range of applied power (0–25 W) of ± 0.010 W. At the same time, the rate of reaction between H_2 and Pd is obtained by measuring the temperature of a catalyst used to convert excess H_2 and O_2 to water within the electrolytic cell. This novel method allows the moles of H_2 that have not reacted with Pd to be determined, hence are available to react with O_2. The number of moles of hydrogen that have reacted with Pd is calculated by subtracting this number from the number of moles made available by the electrolytic current.

Figure 7 shows a comparison between the power measured by the calorimeter and the rate of reaction between hydrogen and the Pd cathode based on using the temperature of the recombining catalyst.

Values for the total enthalpy of formation measured after a series of loading–deloading cycles are compared in Fig. 8. Values for the alpha phase show a steady and dramatic reduction in value as result of the treatment.

In contrast, the values measured at higher H contents show a tendency to become only slightly smaller as result of loading–deloading. The effect of loading–deloading cycles on the behavior of the beta phase is not obvious when the data are viewed this way because the behavior of the alpha phase affects subsequent values. Nevertheless, addition of H to beta-PdH shows the expected downturn (Fig. 1) in values as H/Pd is increased from 0.6 to 0.8.

The disruption of bonds produced by change in shaped produced by rolling to reduced thickness also causes significant reduction in enthalpy of formation, as shown in Fig. 9. This effect is eliminated by deloading at 200°C in air after which the sample is again reacted with hydrogen. Deloading and annealing at 900° C caused no significant
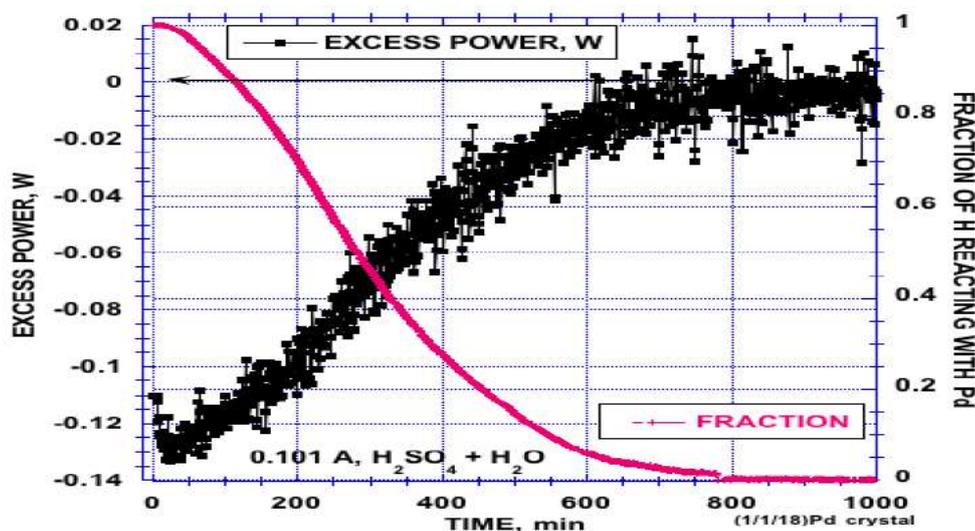
Figure 7. Variation of measured power and the fraction of H reacting with Pd based on the recombiner temperature using a single-crystal rod of Pd. The points taken during the initial 5 min are ignored because the calorimeter is close to but not at steady state. Values are measured every minute.

change in behavior. The apparent phase boundaries may not be real because the samples are expected to suffer from non-uniform hydrogen content.

Initially, each of the samples showed a slightly different behavior but remained in basic agreement with the behavior reported by Flanagan et al. [1] as shown in Fig. 10. This basic agreement

indicates that the composition gradient expected to be present in the samples studied here is not having a serious effect on the measured values for the enthalpy of formation at the composition limits. Nevertheless, the behavior between these limits is expected to show an unknown effect caused by this gradient.

The partial enthalpy of formation can be calculated for each H/Pd ratio by using the values measured during each 1 min interval. These values are equivalent to the slope of the enthalpy of formation, such as potted in Figs. 1, 8–10. This value can also be considered a measurement of the bond energy between the lattice and each H atom. The bonding behavior is more easily seen in Fig. 11 where the energy involved when H is added at each H/Pd ratio is plotted as a function of average H/Pd ratio for the initial and final loading–deloading cycles of the sample described in Fig. 8. This sample has a lower limit to the beta phase boundary that is apparently much smaller than the accepted value ($PdH_{0.6}$), perhaps because the H content is not uniform. Nevertheless, the transition to the endothermic behavior near H/Pd = 0.75 is consistent with the behavior all the samples studied here.

3. Discussion

Loading followed by deloading has very little effect on the bonding within the beta phase, with the alpha phase experiencing the greater effect. In addition, the behavior shows no evidence for formation of the proposed stable phase described as Pd_3vacH_4 by Fukai [13,14] or the phases proposed by Long et al. [15] based on complex calculations. Nevertheless, the apparent increased rejection of H by the lattice would suggest eventual formation of a less stable structure as the H/Pd ratio is increased beyond the range studied here.

All samples, regardless of their nature or treatment, exhibit endothermic behavior when the H/Pd ratio exceeds
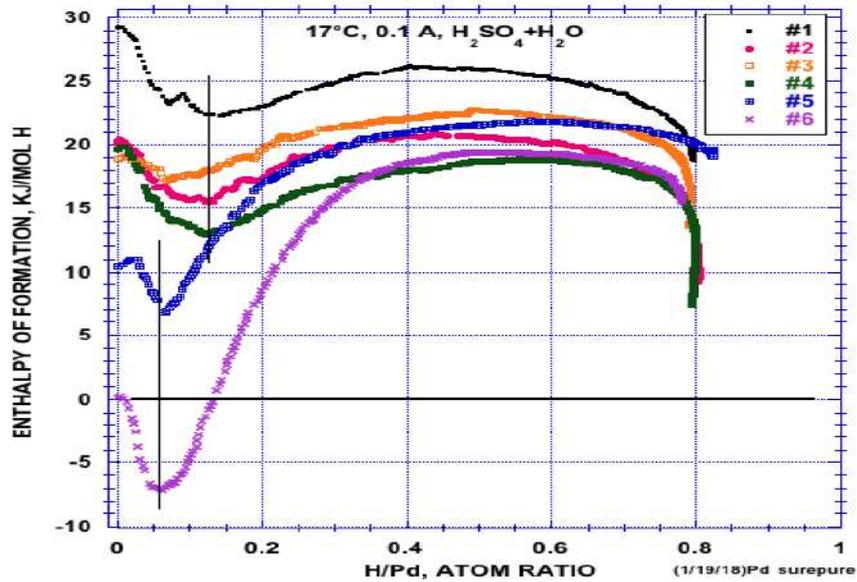
Figure 8. Total enthalpy of formation as a function of H/Pd for the various loading–deloading cycles that resulted in the thickness change shown in Fig. 5. The values apply to the reaction $Pd + (x/2)H_2 = PdH_x$.

approximately 0.75. This behavior can be compared the resistance ratio (Fig. 12), which starts to decrease near this composition. These two behaviors may have a relationship as proposed below.

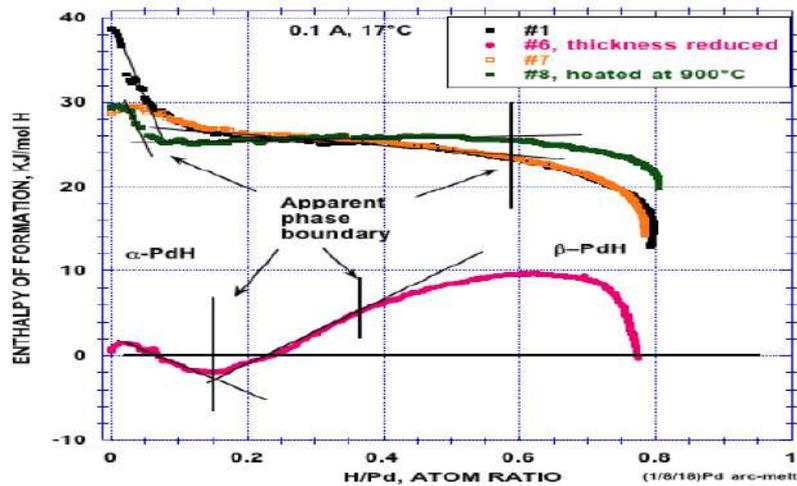Conversion of the alpha to the beta phase requires all the atoms of Pd to move further apart and 60% of the resulting

Figure 9. Effects of various treatments on the energy released by the total amount of H reacted at the average H/Pd atom ratio. The distortion in bond angles and distance caused by the rolling process caused an especially large reduction in bond energy between the lattice and the H ion.
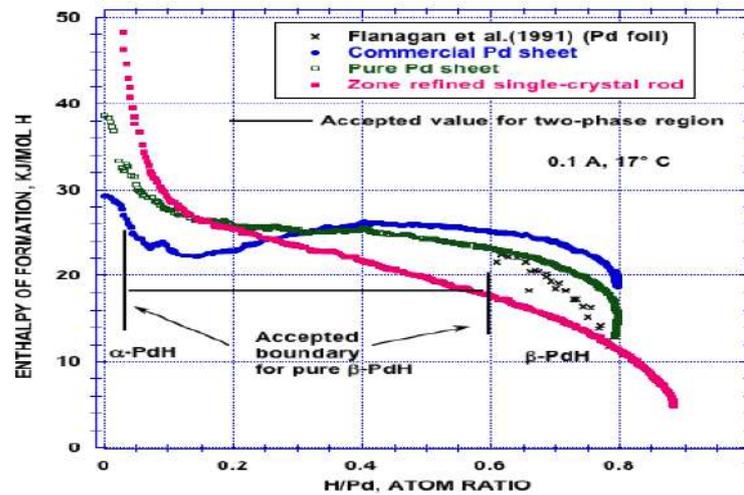
Figure 10. Enthalpy of formation measured before loading and deloading treatment was applied compared to values obtained by Flanagan et al. [1]. when a composition gradient was not present.

octahedral sites to be occupied in a random way by H. This process causers the resistivity to increase. This change in resistivity is proposed to result from electrons being moved from the conduction band to the bonding energy state. As result, the bond energy initially increases between the H and the lattice.

This behavior changes when the ratio exceeds 0.75. Thereafter, added electrons are proposed to enter the conduction band as free electrons because the energy states associated with the Pd atoms would have filled. Consequently,
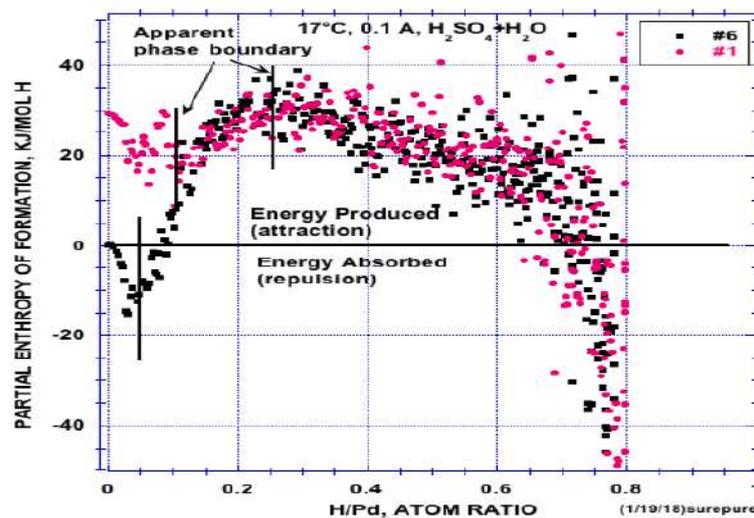

Figure 11. Partial enthalpy of formation for the first loading compared to the behavoir after the final loading–deloading cycle.
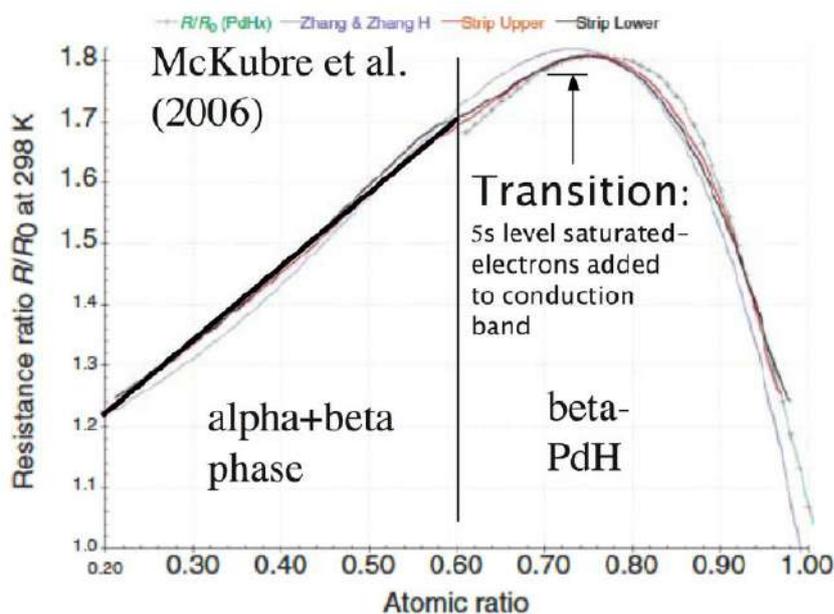
Figure 12. Resistance ratio ($R_{(PdH)}/R_{(Pd)}$ for PdH as a finction of H/Pd atiom ratio [18]. The region in the $\alpha + \beta$ two-phase region needs to be described by a straight line, as is added here, because the behavior results from the combined average of two phases having two different but constant resistances.

further addition of H and its electrons would require energy in order to promote them to the Fermi Energy, thereby making the process endothermic as is observed. The added electrons would then enter the conduction band where they would reduce the resistivity, as is observed. In fact, these electrons are found to be superconducting at low temperatures [16].)

It is important to note that the loading and deloading process affects both the bond energy as well as the resistance [17]. This correlation in behavior suggests the resistance is influenced by the same condition and mechanism that affects bond energy. Consequently, these two behavious appear to be related as result of the proposed electron transfer.

This need to apply energy to achieve high loading hinders the ability to achieve greater H contents and helps to explain why high pressure H_2 is required to reach greater H contents. This goal is further hindered because crack formation, which results from stress produced when H reacts with Pd, creates avenues from which H_2 gas can easily escape without being hindered by the electrolytic process. The number of such cracks is apparently related to the amount of excess volume a particular sample will experience when it reacts with hydrogen, as demonstrated by Storms [19–21]. His work shows that the more excess volume produced by the loading and deloading process, the less hydrogen a sample would retain at the upper limit. This excess is related to the amount of thickness expansion experienced by a sheet of Pd, an example of which is shown in Fig. 5. Consequently, this measurement can be used to test whether a piece of Pd can be expected to achieve high loading.

Storms [9,19,22] showed how the LENR process is favored when only a small amount of excess volume is produced when β-PdD forms. In other words, LENR is less likely to occur when many large gaps are present in the material as revealed by the excess volume measurement. How is this observation relate to the Storms theory [23,24] of nano-cracks being the site of LENR? Samples having a large concentration of large cracks or gaps cannot form the required small gaps because the large cracks would dissipate all the stress that is required to cause additional crack formation

having the required small gap. Consequently, absence of excess volume means that large cracks are not present, which reduces the loss rate of H_2, thereby allowing a greater H/Pd atom ratio to be achieved. Consequently, the increased probability to cause LENR is actually related to the absence of large cracks, not to the ability to achieve a high H/Pd ratio. In other words, it is easy to reverse the cause and effect relationship between these two variables that apparently affect LENR, thereby placing emphasis on the wrong variable for improving the ability to cause LENR. Unfortunately, the conditions that affect excess volume formation are not known and, consequently, cannot yet be controlled.

4. Conclusions

This work reveals how the bond energy between H and the PdH structure changes and becomes endothermic when the hydrogen content is increased above a critical value. This bond energy is sensitive to loading–deloading cycles and to distortions caused by reduction in thickness using the rolling method. The work shows the relationship between bond energy and electrical resistance, both of which might be affected by the same variables.

A new and very effective way to measure the H/Pd ratio during electrolysis is described using the temperature of the recombiner catalyst. This method can be used with other methods to measure the H/Pd ratio in order to achieve better accuracy.

Many attempts have been made to extract additional details about bonding and atom arrangement in PdH by using various theoretical models, but without considering how the partial enthalpy of formation changes with H/Pd ratio or the effect of the loading and deloading process on the behavior of the alpha phase. This work shows the importance of these variables.

Various issues about how to cause LENR are explored. Achieving a high D/Pd ratio is shown not to be as important as preventing formation of large cracks and flaws in the structure.

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