

**Comments on “Anomalous effects in charging of Pd powders
with high density hydrogen isotopes” (U)**

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Comments on “Anomalous effects in charging of Pd powders with high density hydrogen isotopes” (U)

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Abstract

In Kitamura, et al [1], Pd-containing materials are exposed to isotopes of hydrogen and anomalous results obtained. These are claimed to be a replication of another experiment conducted by Arata and Zhang [2]. Erroneous basic assumptions are pointed out herein that alter the derived conclusions significantly. The final conclusion is that the reported results are likely normal chemistry combined with noise. Thus the claim to have proven that cold fusion is occurring in these systems is both premature and unlikely.

Introduction

In Kitamura, et al [1], (hereafter referred to as ‘Kitamura’) two Pd powders and a PdO/ZrO₂ powder are exposed to protium (H₂) and deuterium (D₂) in a flow calorimeter setup. Ostensibly the intent was to duplicate experimental results of Arata and Zhang [2] (hereafter referred to as ‘AZ’) that purportedly prove a nuclear process is active in deuterated Pd, the classic cold fusion argument. However, several assumptions are made in Kitamura that seem to be suspect. This comment addresses those issues.

In Table 1 of Kitamura, fourteen experimental sequences on the three types of Pd-containing powders are summarized. Kitamura arbitrarily divides the absorption process into two phases with the first phase ending when the cell pressure begins to rise from near zero. Most of the tabulated results refer to this first phase. Eleven of the experimental sequences described represent the results of exposing these powders to hydrogen isotopes for the first time, typically called the ‘first cycle’. Three results for subsequent exposures (2 ‘second cycle’ and 1 ‘third cycle’) are also reported. Kitamura does not explicitly state at what temperature the loadings are conducted. One possibility is that they maintained the reported bakeout temperatures during loading, but if true, that simply worsens their case, as discussed below.

In 9 of the 11 first cycles, loadings with H/M or D/M (generically referred to as ‘Q’/M) ≥ 0.79 at the end of the first phase are reported. In the case of the palladium black runs, one sample that reportedly loaded to Q/M=0.79 in the first cycle is also reported to have in subsequent second and third cycles only loaded to ~ 0.24 Q/M. Three runs with 0.1 micron Pd particles, one a second cycle, were reported to have loaded to Q/M ~ 0.44 .

Issue #1 – Pd loadings

The high reported loadings are inconsistent with known Pd chemistry. Pd-hydrogen isotherms are shown in Figure 3.4 of Wicke and Brodowski [3], and at 293 K and

~1MPa, an H/M value of ~0.78 is obtained. The Figure also illustrates that hydrogen content decreases with increasing temperature. Lasser and Klatt [4] present data for all three hydrogen isotopes, although they do not go below 323K in their studies. Since D is less soluble in Pd than H at a given loading pressure, the D/M value obtained will be lower, and D/M likewise decreases for a given pressure as the temperature increases. If Kitamura actually exposed their samples at the bakeout temperatures, expected loadings would be < .78. To obtain loadings of >0.78 would require either cooling below nominal room temperature, which is not indicated in the paper, or much higher loading pressures.

As well, Kitamura's loadings are for the first phase only. At the end of the first phase, the cell pressure is still very low or zero and has not approached the final pressure. Therefore the final loading of ~0.78 would not have been obtained, yet many values equal to or greater than this are reported specifically for first phase loading. Actual loadings that would be anticipated under equilibrium conditions at the end of the first phase would be closer to those expected at the plateau pressures (at best, ~0.6 for a nearly complete loading at the low pressure). (The estimated plateau pressures of H and D in Pd at 293K are ~7.3 kPa for D and ~0.8 kPa for H, based on the Lasser and Klatt's [4] Van't Hoff data.) The lower loadings reported for the 0.1 micron Pd particles and the second and third cycle of Pd black are more typical of loadings that remained in the plateau region, i.e. quarter- to three-quarters-loaded.

The loadings reported may be indicative of inadequate Pd activation, which would affect the results in two ways. Inadequate activation may greatly hamper absorption kinetics and potentially ultimate loading level, and may cause unexpected heat from side reactions. As received Pd normally has significant surface contamination (typically O, C, or S), and this contamination typically hinders the absorption of hydrogen into the Pd [5,6]. The usual procedure when studying hydrogen isotope chemistry in Pd is to 'activate' the material by cycling several times (often >3) in hydrogen to remove these contaminants, complete activation being indicated by rapidly obtained loadings (as expected from surface-to-volume ratio considerations) that are in agreement with literature values. Normally, the first few absorption/desorption cycles are not studied due to known difficulty with reproducibility. The differences reported by Kitamura between first cycle results and second and third cycle results are indicative of this problem. Any excess loading obtained in a first cycle by Kitamura above what is subsequently obtained in second and third cycles is more probably indicative of the extent of chemical reaction with these expected surface contaminants during the first cycle than indicative of cold fusion.

In the case of the PdO/ZrO₂ powder additional complications arise. Kitamura correctly notes the PdO reaction with hydrogen to form water. Another complicating factor with metal oxides present is the observation that absorbed hydrogen can migrate onto the ZrO₂ to form surface hydroxylated material, i.e. ZrO₂H_x, where x is indeterminate and difficult to control, in a process typically known as spillover. Kitamura rejects this possibility but without specifying why. But for example, this laboratory has measured hydrogen uptake on a powder consisting of well-activated ~5nm Pd nanoparticles supported on α -alumina, and we have detected significant spillover as indicated by the initial portion of the

absorption isotherm where all hydrogen introduced is absorbed (see Fig. 1). Only after completing the spillover reaction is the typical Pd isotherm observed, now displaced on the millimoles absorbed axis by the spillover. Note that the amount of H absorbed to the alumina in this case was approximately equivalent to that of the Pd. Any metal oxide can potentially absorb hydrogen from Pd particles, and PdO/ZrO₂ has been specifically studied in this regard [7]. Failure to consider these processes lead Kitamura to partition the absorbed hydrogen incorrectly as noted above, obtaining loadings much too large for the conditions used, but consistent with those presumed to be required to obtain cold fusion.

The observed heat will be the combination of the heat of hydriding and any hydrogen reactions with contaminants, plus oxide decomposition and whatever heat of reaction with the support is to be expected based on the chemistry in the case of PdO. These reactions can potentially continue into the second phase depending on the quality of the activation process used. Heat could also continue to be generated by hydriding reactions during the second phase depending on the actual loading level at the arbitrary end of the first phase. (Loading from 0.6 to 0.78 will produce less heat than that from 0 to 0.6.) The large E_{1st} values reported in Kitamura's Table 1 for materials which presumably loaded to greater than $Q/M=0.7$ seem too large due to these considerations. Kitamura note this but postulate unlikely scenarios to explain this. The standard considerations noted above should be the first assumed causes for any real excess heat over that expected from simple Pd hydriding chemistry.

Issue #2 – Baseline noise vs. signal?

Kitamura presents graphical results for their powders in Figure 3, showing the output power obtained as a function of time while loading these samples. Both the 0.1 micron Pd particle sample and the Pd black sample evidence baseline deviations occurring after the hydriding reaction heat has subsided (the second phase) that Kitamura consigns to noise. However in Figure 3c they present results for the PdO/ZrO₂ samples which they conclude represent anomalous excess power and thus replicate the AZ results. However, they also acknowledge that there has been a thermocouple malfunction in the hydrogen trace of Figure 3c, resulting in a negative baseline shift. This has the immediate effect of making the baseline deviation in the deuterium trace in Figure 3c look more significant, since now it is unobscured by the hydrogen trace as in found in Figures 3a and 3b. The period running from ~ 200-500 minutes seems relatively flat and offset positively by approximately the same amount that the hydrogen trace is offset negatively, perhaps suggesting some cross-talk in the signals. Furthermore, there appears to be a large and abrupt baseline shift at t~1350 m., where the baseline now goes negative. The maximum deviation of the deuterium trace from the offset baseline of 200-500 m. is only about 0.1 W, which is equivalent to those observed in Figures 3a and 3b, where it is assigned to noise. The conclusion would seem to be that the deviations in Figure 3c should likewise be assigned to noise, but instead Kitamura claims they are true excess power signals and indicate a replication of the AZ work, i.e. cold fusion. This seems unlikely.

Issue #3 – Replication or not?

The underlying intent of the Kitamura paper seems to be to declare that a replication of the AZ results has occurred. However, this is only true in the most general of senses, as the two experiments produced significantly different *classes* of results. In AZ material was loaded and the heat of hydriding followed as it slowly flowed out of the system and the temperature returned to ambient. The internal temperature of the experimental apparatus evidenced a continuous and uniform offset from the external temperature over a span of 3000 minutes, where the presented data ceases. In the Kitamura case however, the positive deviations in the output power are erratic both in duration and in intensity, sometimes even going to negative values. This would translate via the mass flow calorimeter equation to an equally erratic internal temperature signal in the AZ case, sometimes even going below the reference external temperature, which is not what was observed by AZ. Thus the extent of the Kitamura ‘replication’ seems to be that anomalous (but different) signals were observed in similar experimental configurations, which is a typical of results in cold fusion research. Unfortunately, the reasons for the anomalies in both cases are unknown and cannot be equated without independently determining them, and attempting to do so represents a fundamental logical flaw. One anomaly does not replicate another *different* anomaly unless the causes of both are known, and the differences can be analytically explained. True replication requires the ability to nearly exactly reproduce the behaviors noted.

Conclusions

The Kitamura paper represents an archetype of cold fusion research results, with poor understanding of the related chemistry and directed assumption-making aimed at confirming unlikely explanations as the norm. As well, the idea that any anomalous result confirms another, even when grossly different in behavior, is a rampant problem in cold fusion research. Because of the issues brought up herein, the conclusion that observation of anomalous energy emanating from a Pd-containing material seems premature. What seems more likely is that activation issues caused significant underloading of the Pd materials, and side reactions caused significant heat generation in several cases. Failure to recognize this caused misassignment of Pd loading levels, which in turn lead to incorrect energetics calculations. The actual signals presented as true anomalous excess power are more likely just baseline drift. Thus, no evidence for an anomalous nuclear reaction has been presented in Kitamura, and thus no replication of AZ has occurred, leaving the AZ result as another unsupported anomaly claimed to prove cold fusion.

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Figure 1. 353K Hydrogen Absorption/Desorption Isotherm from Nanoparticulate Pd on Alumina

