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# Comments on "Thermal behavior of polarized Pd/D electrodes prepared by co-deposition"

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**Abstract**

Szpak et al. have published a report [S. Szpak, P.A. Mosier-Boss, M.H. Miles, M. Fleischmann, Thermal behavior of polarized Pd/D electrodes prepared by co-deposition, Thermochim. Acta 410 (2004) 101] that attempts to present more evidence for the nuclear nature of the Fleischmann–Pons (–Hawkins) effect, and in that process attempt to reject recombination as the alternative cause of their observations. Unfortunately, they have misunderstood the at-the-electrode, under-the-surface recombination issue. This paper presents the basics of this model, including what physical conditions could produce a calibration constant shift and what might cause those conditions to arise. The new evidences are discussed and it is shown that the possibility of at-the-electrode recombination cannot be eliminated; in fact prior photographic evidence is shown to be reasonable evidence of this phenomenon. Thus in the absence of definitive data, the conclusion that apparent excess heat arises from a nuclear cause is premature.


*Keywords:* Cold fusion; Excess heat; Recombination

## 1. Introduction

In [1], Szpak, Mosier-Boss, Miles, and Fleischmann, referred to as 'SMMF' hereafter, again propose that apparent excess enthalpy measurements obtained from the co-deposited polarized Pd/D electrodes is in fact real excess enthalpy caused by a new nuclear reaction. Their approach is an adaptation of the original work where three University of Utah chemists, Fleischmann et al. [2] claimed to have observed excess heat produced by D-loaded Pd in 1989. Apparent excess enthalpy is the predominant class of evidence offered as proof of a proposed room-temperature nuclear fusion process that leads to the so-called Fleischmann–Pons–Hawkins effect (FPHE) more commonly known as cold fusion.

Integration of observed signals has suggested that the cause must lie in the nuclear realm, because chemical sources are inadequate for the reported magnitude of apparent excess. However, if the apparent excess heat signal is not representative of a true heat source, but is instead an equipment/method malfunction, integrating the signal is of no value. This paper proposes that is the situation, and will therefore focus on examining the phenomenon of apparent excess enthalpy (sometimes called excess heat). Not addressed will be the myriad of other purported evidences of nuclear reactions. The apparent excess heat claims form the largest block of claims for a nuclear FPHE cause, and the correlation of apparent excess heat with apparent nuclear ash detection is often cited as evidence of the nuclear nature of the FPHE. For example, SMMF cite a study by Szpak et al. [3] where tritium production is monitored along with recombination efficiency as evidence that recombination is not relevant. But confidence in the validity of the apparent excess heat signal is of critical importance in validating a nuclear explanation. If the heat signal is erroneous, any correlation to nuclear ash production must also be erroneous, and the nuclear ash measurements likely spurious. This is a critical realization.

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## 2. Discussion

### 2.1. SMMF's objection to recombination

In Section 2.3 of their paper, SMMF contend that there is no experimental evidence for a significant contribution to apparent excess enthalpy from 'recombination', and cite the work of Szpak et al. [3] and Will [4]. Further they cite a calculation by Fleischmann and Pons [5] purporting to prove the heat generated by this recombination would be at most 6 nW per 'hot spot', and that heat would be rapidly dissipated in the metal electrode. Unfortunately, Szpak and his coauthors (in fact, most of their colleagues in the cold fusion research field) make a fundamental mistake exactly at this point. The references cited clearly deal with electrochemical oxygen reduction, a parasitic reaction whose impact is largest at low cell current. That reaction is mediated by dissolved oxygen. This author completely agrees with this point; electrochemical reduction mediated by dissolved oxygen is not significant to the apparent excess enthalpy issue. Thus SMMF's use of the three references to eliminate recombination as the apparent excess' source is irrelevant.

This author proposes the simple burning of hydrogen with oxygen to form water, as the source of the apparent excess. This is clearly not an electrochemically-mediated process, as it can occur anytime an oxidizable mix and a method to ignite that mix is present, the classic fire safety triad of fuel, oxidizer, and ignition source. The only unique aspect of this proposal is that this burning would occur at the electrode(s), under the electrolyte surface in bubbles. The chemistry invoked here is no different from the chemistry invoked to explain how a recombination catalyst works. No electrochemical concerns need be involved, other than to place a limit on the total available recombination heat at any point in time.

As quoted in [1], this author has consistently proposed that entrained bubbles are the source of the effect, and it is intriguing that SMMF fail to differentiate between dissolved and entrained oxygen. SMMF report in point (viii) of Section 2.5 that radial mixing is ∼7× faster than axial mixing in their cell, so mass transport of bubbles to the other electrode should be facile. A simple calculation indicates the potential amount of heat available arising from one burning bubble in this proposed process.

If bubbles were an average of 1 mm in diameter, the gas content of one bubble at 350 K (a nominal cell temperature, note that SMMF's cell was operating at closer to 310 K) would be $1.82 \times 10^{-8}$ moles. The exact bubble composition is not known, but if an optimum 2:1 mixture of $H_2$ and $O_2$ and the 285.8 kJ/mole heat of formation of water is assumed, one bubble will produce ∼0.00347 J (milliwatts per bubble, not nanowatts), giving from 0.35 to 1.05 J for 100–300 bubbles. Of course, bubble size is critically important, as the volume of the bubbles is dependent on the cube of the radius, requiring a factor of eight more bubbles for a halving of bubble diameter to produce approximately equivalent heat output. SMMF report apparent excess heat output ranging up to ∼0.3 W, which, given the variability possible in this computation, represents good agreement between the computation and the results.

The Szpak group [6–9] has photographed 'cold fusion active' cathodes with an infrared video camera and have observed a large number of short-lived hot spots on the cathode during apparent excess heat production. SMMF contend that the hot spots observed photographically cannot arise from recombination. However, we have shown here that it is possible if enough bubbles of the right size and composition are ignited. The size of the hot spots in the pictures is consistent with small bubbles, probably of mixed $D_2$ and $O_2$ that ignite and burn. A rough estimate of the number of bubbles burning in a 1 s period can be made by counting the number of spots on the image. In [9], pictures of an active electrode show anywhere from zero to a few thousands of hot spots on the electrode in a given frame (each frame representing about 1 s of elapsed time). Presumably, the highest apparent excess enthalpy production correlates with the largest number of hot spots per frame. This number is consistent with the simple computation above.

This reaction occurring at an electrode would provide an additional heat source in an open cell, or would involve a redistribution of heat sources in a closed cell. In Shanahan [10], a set of cold fusion data supplied by Dr. E. Storms obtained from a closed cell apparatus was reanalyzed under the assumption that no excess heat was present. It was found that a variation of ±2.5% in calibration constants was all that was required to account for the apparent excess heat without invoking novel new nuclear processes. We now clarify how heat source redistributions in closed cells would produce calibration constant shifts and thereby apparent excess enthalpy.

### 2.2. Model of a heterogeneous calorimeter/closed cell

The standard approach to interpret calorimetric data usually assumes a homogeneous calorimeter, or at least that any inhomogeneities present are irrelevant. We will show below that a heterogeneous calorimeter model is more appropriate to understand the origin of apparent excess enthalpy.

For simplicity, this discussion will initially be restricted to the case of flow calorimetry. The flow calorimeter operates by flowing a fluid around a hot object whose power output is to be measured, and the fluid is thereby heated. The resultant temperature increase is measured, and with a constant fluid flow and heat capacity, the power output can be measured. The basic linear equation used for calibration of a flow calorimeter is:

$$P_{\text{in}} = P_{\text{out}} = m(C_p f\, \mathrm{d}T) + b$$

where $m$ and $b$ are the linear calibration constants, $C_{\text{p}}$ the calorimeter fluid's heat capacity at constant pressure, $f$ the fluid flowrate, and $\mathrm{d}T = T_{\text{out}} - T_{\text{in}}$, the temperature difference between the fluid entrance and exit points of the calorimeter. $P_{\text{in}}$ the highly controlled and well-known input power. For further simplicity, $b$ will temporarily be set to 0. This means that in practice $m$ would be determined via the equation:

$m = P_{in}/C_p f\,dT$, all of which are measured or known quantities. Once $m$ is determined, it will be used to translate data acquired from an experimental run into output power ($P_{out}$), and the apparent excess power ($P_{ex}$) will then be computed by subtracting the known input power ($P_{in}$) from the computed $P_{out}$, i.e.

$$P_{ex} = P_{out} - P_{in} = mC_p f\,dT - P_{in}$$

The key assumption in this analysis is one of homogeneity. The integrating characteristic of the calorimeter is assumed to negate any concerns about heat distribution and/or flow in or out of the hot object.

But in a real calorimeter, there are penetrations through the theoretical boundary that defines the calorimeter. These penetrations are due to sensor leads, and in the case of electrolysis-type cold fusion calorimeters, power leads that run the electrolysis. Typically these penetrations are concentrated in one area, usually the top of the cell, which is often constructed of a different material than the body. What this offers is the possibility that heat losses in the different regions of the cell might be well different. Specifically, the penetrations might well conduct some heat away from the integrating fluid, and that heat would be lost without causing a detected temperature rise at the calorimeter outlet. Further, objects can be heated non-uniformly by the chemical/physical process responsible, producing local 'hot spots'. This is known to be a problem in another type of calorimeter (commonly called isoperibolic) that does not integrate heat output with a surrounding jacket, but instead just measures temperature change at a single point. Thus, inhomogeneity is a recognized potential characteristic of a real calorimeter.

The question to be examined herein is whether a more realistic model of the calorimeter will provide an explanation for the experimental observations. What will be examined conceptually is the situation where the heat distribution inside the cell during calibration subsequently changed during experimental runs, i.e. a change in the steady-state conditions occurred. Note that this is fully equivalent to a change in heat loss patterns potentially induced by a change in experimental conditions. To do so, the complexity of the basic model must be increased somewhat to allow for, at a minimum, two regions. The basic assumptions are that the heat capture efficiency of one region is very high, and the other's, while being high, is not as high. Input power will be partitioned between the two regions arbitrarily to establish the base calibration condition and the partitioning changed to examine the impact of the change.

Initially consider the first region (1) to be of high heat capture efficiency ($e$), 99.9%, and the second region (2) to be of a lower ($e$), 90%, and that the calibration steady-state resulted in 50% of the input power being transmitted out through the high ($e$) region, and the other 50% through the lower ($e$) region. The actual power measured in the calorimeter will be lower than the true power input due to losses, so the actual input power terms will be decreased in proportion to the heat capture efficiencies to arrive at the actual observed power output. The calibration process will then adjust for the losses by determining $m$ by assuming the power out equals the power in.

Now if the postulated heat distribution changed to, say 75% in (1) and 25% in (2), then more of the total $P_{in}$ will be captured and $T_{out}$ will increase. Thus the calibration constant determined under this new set of conditions will be different in order to keep the computed $P_{out}$ equal to the known $P_{in}$. But note that all that has occurred is that heat losses have changed; no additional heat sources have been postulated. Yet the standard calibration constants computed for the two different steady-states will be different.

In [10], Shanahan pointed out that Storms reported a 1.7% difference in calibration constants between Joule heater calibration and electrolytic calibration, and a time dependent average calibration constant derived from electrolysis calibration. Shanahan reanalyzed the Storms data to show calibration constant variation of ±2.5% could explain the apparent excess heat (up to ∼0.8 W). As derived there, the apparent excess power has been computed (now including the $b$ terms) as:

$$P_{ex} = \left(\frac{m_c}{m_s} - 1\right)P_{in} + \left(b_c - \frac{m_c}{m_s}b_s\right)$$

where the 'c' subscripts refer to the original calibration condition, and the 's' subscript refers to the shifted steady-state.

Thus the actual $m$ value will vary depending on the partitioning and/or efficiency assumptions. In turn the $m$ variation will induce an apparent excess enthalpy. In usual practice, researchers assume no changes and compute output power with the initial $m$ determined from the original calibration conditions. This assumption of steady-state is the fundamental mistake that is being made.

This phenomenon is proposed as the root cause of the apparent excess heat signal in calorimetric data interpreted via a single region model. The two-region model efficiency factors are hidden variables incorporated implicitly in the one-region model calibration constants. Problems arise when the steady-state shifts due to unknown experimental reasons. Any experimental anomaly that would change the heat capture efficiency (such as an air bubble adhering to the external or internal cell wall) or alter the heat deposited in a particular region can be seen to potentially have a significant impact.

This model was developed for the flow calorimeter case with linear calibration as a convenience. In fact, the same problems should arise in any calorimeter calibrated via any type of calibration procedure when the steady-state shifts. This simply reflects the fact that it is impossible to calibrate an unstable system.

It should be noted that the use of a Joule heater for calibration will normally not allow a redistribution of heat source to occur, nor will the relevant physical/chemical processes that could alter heat losses be impacted by whatever apparently causes the FPHE at the electrodes. Therefore, calibration results obtained from a Joule heater are unlikely to show a FPHE.

### 2.3. The open cell case

In the case of open cells such as SMMF use, an at-the-electrode recombination represents an additional heat source in the cell, as opposed to a heat source redistribution. Nominally, such an additional heat source would be located in the same region as the calibration Joule heater or electrodes, and we should expect a more accurate measure of actual heat deposited, as the calibration conditions would be nominally the same as would be currently extant. Slight modifications might occur, however, due to the physical impact of a percentage of the bubbles igniting subsurface. This would likely change the mixing patterns slightly, and might even cause a slight increase in fluid entrainment in the exiting gas stream.

SMMF cite Ref. [3] to assert that no such recombination occurs in their cells. That work reports apparent tritium levels in the electrolyte and gas phases and recombiner efficiency, but no actual excess enthalpy values. The authors do not address accuracy issues, which as shown below, are significant. In fact, if there really was no excess enthalpy, that work is probably a good indication of problems with the tritium detection technique being used, as the signal would seem to be spurious in that case.

SMMF report an apparent excess enthalpy time plot with several significant excursions, which can be divided up into two large blocks. The first occurs during the charging and co-deposition period, and the second occurs in the later third of Fig. 3 after an extended low current period. SMMF report that the first large block of such excursions is suspect because of other possible chemical reactions. During the second block of apparent excess enthalpy activity, they apply three-heater pulses. Interestingly, all three-heater pulses show impacts in the excess enthalpy curve, although the first seems to be confounded with what may well be an actual FPHE. A Joule heater will not have a FPHE, so the excess enthalpy response is actually indicative of a calibration problem. When the heater causes the cell temperature to rise, the power output is miscalculated by the calibration equation producing a positive excess enthalpy. This evidence implies that the excess enthalpy curve must be carefully interpreted. A response is expected under these conditions whenever the electrolysis current is changed, but this is confounded with a possible FPHE in the later period.

SMMF integrate the apparent excess enthalpy signal and report that 75 kJ excess enthalpy was detected over the experiment span. However, as noted previously, if the signal is computed erroneously, the integration of that signal is valueless. Further, SMMF seem to include the first block of events even while concerned that the signal may be spurious for other reasons. Thus the level of apparent excess enthalpy actually is unclear.

SMMF report that their $D_2O$ consumption was 7.7 $cm^3$ instead of a computed 7.2 $cm^3$, a 6.5% deviation, and claim this is within experimental error. As was noted in [10], a 2.5% error was able to produce a ∼0.8 W apparent excess enthalpy signal, suggesting that the 0.5 $cm^3$ error is more than enough noise needed to produce the reported ∼0.3 W apparent excess enthalpy. The variation between actual and expected consumption suggests a slight problem with knowing how much power was passed through the cell (more water electrolyzed than expected), and that in turn would also lead to a slightly inaccurate calibration. This is in agreement with the observation that heater pulses register apparent excess enthalpy peaks.

Use of the applied current ($I$) and thermoneutral voltage can estimate the available thermal energy arising from recombination as ∼1.54I. Szpak reports up to 0.4 A current in Fig. 2, but that is in a brief transient. The largest current sustained for an appreciable time is 0.3 A. This equates to an available actual excess enthalpy of ∼0.5 W.

This value is a typical value of absolute excess heat measurements (even in light of the calibration constant shift error). SMMF report an average excess enthalpy in that period of ∼0.27 W (which may be overstated due to the aforementioned calibration error concerns), well below what is allowed.

Thus even assuming the reported excess is accurate, the recombination extent is at most ∼50%, but is probably much less. The reported 0.5 $cm^3$ discrepancy in collected water volume is an excess, whereas recombination should produce a deficit. An excess of collected water could arise from entrainment of electrolyte droplets in the gases flowing to the recombiner. This entrainment might well mask any recombination effect. As well, entrained electrolyte in the condensate could easily lead to interference effects in other techniques, such as liquid scintillation counting (used to detect tritium). (These difficulties can exist in concert with the apparent calibration problems).

SMMF point out in Section 4.1 that the apparent excess enthalpy events occurring during the charging/co-deposition period are potentially spurious, yet they attempt to analyze said data in Fig. 5 as evidence of ‘heat-after-death’. The decay curve presented in their Fig. 5 shows a decay taking approximately 6–7 system time constants, which is actually within the span often associated with system stabilization periods in other work. It is even reasonable to assume some chemical process active in that time period is slowly expiring. As SMMF indicate, this region of the apparent excess energy curve is highly suspect, and their attempt to derive ‘proof’ of heat-after-death, and thereby cold fusion, needs much more explanation before being accepted.

As well, both the ‘proof’ of a positive feedback relationship and that of a heat-after-death condition are singular examples. Replication is required to prove the observed events are not random coincidences. Replication would also demonstrate control of the effect, which is missing to date.

### 2.4. The possible chemical cause of the FPHE

It is likely the unique characteristics of the electrode surface state that offers the possibility of initiating at-the-electrode, under-the-surface recombination, altering heat

source distributions in a closed cell and introducing additional heat inside an open cell. The ability of SMMF to alter the apparent excess enthalpy curve by severe current changes was mimicked by Storms using only Pt electrodes [11], and the observation of apparent excess enthalpy on Pt electrodes by Storms [11] and Dash [12] is a critical observation. Obviously, since Pt does not form hydrides, bulk loading is not the relevant number. Instead, some special surface state must bring on the FPHE. This surface state can apparently be adversely impacted by voltage excursions, which suggests it may be electrochemically formed.

A highly sensitive surface state is already acknowledged as a relevant factor in cold fusion research. What is not acknowledged is that the primary impact of such a state could be to promote at-the-electrode recombination, though Szpak et al. have photographed just such a process. It seems reasonable to assume that some surface modification occurs to the electrode with time in service that forms this special state. The co-deposition process used by Szpak et al. to prepare their electrodes seems to achieve this state most readily, yet is susceptible to disturbance, as was shown in their current work by the impact of the current transient between heater pulses Q2 and Q3, where the apparent excess enthalpy level was approximately the same, even though the current was different before and after. The co-deposition process produces a high surface area electrode surface, and it seems reasonable that such a surface would be more efficient at extracting electrolyte contaminants, which are suggested to form the active surface state.

## 3. Conclusions

SMMF attempt to present more data as proof of the nuclear nature of the FPHE, and in that process attempt to reject recombination as the alternative cause of their observations. Unfortunately, they have misunderstood the recombination at the electrode, under the surface issue. This paper has attempted to clearly present the basics of this model, including pointing out what physical conditions could produce a calibration constant shift and speculating on what might cause those conditions to arise. A prior publication [10] describes the direct impact of a calibration constant shift on the apparent excess enthalpy signal. SMMF's evidences are discussed and it is shown that they do not eliminate the possibility of at-the-electrode recombination, in fact their prior photographic evidence is shown to be reasonable evidence of just that.

As well, the observation of excess enthalpy peaks arising from heater pulses suggests a calibration error, which is supported by the disagreement between expected and observed recovered water. Comparison of the purported excess enthalpy signals with those analyzed in [10] suggests that all observations are well within the noise parameters and possible recombination heat availability. Thus the conclusion that a nuclear process has been proven is premature. Clearly, the calibration process is of prime importance to these studies, and determining the true noise level (not just baseline fluctuation) should be a primary task of cold fusion researchers. Uncontrolled steady-state shifts produce a non-random noise component in the studies.

If the proposed surface state is in fact the cause of the FPHE, until researchers control the formation and extent of that state, apparent excess heats will likely remain uncontrolled and highly variable. Once the possibility of unsteady states is allowed, any kind of apparent excess heat profile could be obtained in a given experiment. This severely limits expectations of reproducibility, as reproducibility requires control. But control is not expected if no actions are taken to limit the degree of change associated with the proposed surface state formation. Clearly, further research focused on the surface conditions of cathodes that are showing apparent excess heat is required to define the actual catalytic surface state. Unfortunately, the co-deposition process produces a highly heterogeneous structure, which may complicate that task. Of more promise is the work on platinum electrodes when combined with modern surface science.

The prior work [10] showing the impact of calibration constant shifts, combined with the problems evident in the current SMMF work [1] indicate that cold fusion researchers have also not appreciated the difficulties in obtaining calibrations that would result in a reliable excess enthalpy computation. In general, the raw data presented by most cold fusion researchers is of high quality. However, those researchers then exceed the reliability of the data by computing excess enthalpies as they do. This is nothing but a reflection of the inability to calibrate an unstable system combined with the classic analytical problem of accurately detecting a small difference between two large numbers.

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