

Short communication

Reply to “Comment on papers by K. Shanahan that propose to explain anomalous heat generated by cold fusion”,
E. Storms, *Thermochim. Acta*, 2006

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Abstract

Dr. E. Storms has published a Letter [E. Storms, Comment on papers by K. Shanahan that propose to explain anomalous heat generated by cold fusion, *Thermochim. Acta*, in press] in which he argues that in a sequence of recent papers, the apparent excess heat signal claimed by Dr. Shanahan to arise from a calibration constant shift is actually true excess heat. In particular he proposes that the mechanisms proposed that foster the proposed calibration constant shifts cannot occur as postulated for several reasons. As well, he proposes Shanahan has ignored the extant data proving this. Because this Letter may lend unwarranted support to acceptance of cold fusion claims, these erroneous arguments used by Storms need to be answered.

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1. Discussion

The proposed explanation of the Fleischmann–Pons–Hawkins Effect (FPH or FPHE) proffered by Shanahan [3,5] consists of the following concepts: (1) an unrecognized calibration constant shift (CCS) during an experimental sequence can produce an apparent excess power signal, even when no excess heat source exists, (2) such a shift can arise due to a redistribution of heat sources inside a cell, and (3) such a redistribution can arise if recombination begins to occur at the electrode(s) under the electrolyte surface. At-the-electrode recombination can only occur if H₂(D₂) and O₂ bubbles unite on the electrode surface, and this requires transport of bubbles radially in a cell and the merger of said bubbles while at least one is attached to the electrode (otherwise the mixture lacks an ignition source, the clean metal surface).

It is worth noting that Storms does not dispute the mathematics of points 1 and 2 above. He does however dispute the likelihood of the chemical/physical processes postulated by Shanahan that would produce the heat redistribution and subsequent CCS, especially via the above postulated ‘bubble’ mechanism.

In summary, Storms’ arguments rest on four fundamental points: (1) O₂ and H₂ bubbles cannot mix on the electrode surface because all bubbles rise rapidly to the electrolyte surface, (2) recombination heat arising from any such possible recombination cannot account for the observed magnitudes of apparent excess heats (3) calibration studies of cold fusion calorimetric apparatus do not support any unexpected or unexplained phenomena such as the CCS, and (4) Shanahan misinterprets and/or fails to acknowledge said results. These points will now be addressed.

1.1. Storms point 1: mass transport in an electrolysis cell

It is a well documented fact that to obtain accurate calorimetric results, mixing in an electrolysis cell must be good. Otherwise stratification and hot spots will result that invalidate the calorimetry. As pointed out by Storms in his manuscript “Calorimetry 101...” (noted in [1]), this was especially true for the ‘isoperibolic’ calorimeter, and cold fusion calorimetrists moved to more integrating calorimeters, such as mass flow or Seebeck calorimeters, to alleviate this problem. The question is whether this approach has completely eliminated the problem, or if a residual still remains. It is this author’s contention that residual problems capable of explaining the apparent excess power measurements still remain. These residual problems arise

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due to some interesting surface chemistry and mass transport phenomena.

Fleischmann and Pons have previously reported $\sim 7\times$ faster radial transport than vertical transport [6] in a Fleischmann–Pons-type electrolysis cell, a claim echoed in a recent publication [4]. If radial transport of the cell liquid is rapid, then entrained solids or gases could be carried along. Visually observing this transport would be difficult in normal FPHE electrolysis cells, as the Pt anode is usually located completely around the central Pd cathode and the bulk of the gas flow would be upwards. However, *downwards* bubble flow in a gas/liquid system has been observed and was the subject of a Fluent computational fluid dynamics study which showed the feasibility of this phenomenon [7]. The stirring action of the rising gas bubbles leads to liquid motion. If gas bubbles are entrained in the liquid, they can be carried along with it in spite of buoyant forces and could potentially end up anywhere in the cell. The $7\times$ more rapid radial motion of the dye in the Fleischmann and Pons report clearly shows that adequate fluid flow to support such transport can occur. Thus Storms' assertion that such transport has never been observed is seen to be overly optimistic. It is more likely that such transport was not recognized as being relevant previously, and as such was not well studied.

This point however, is a key assumption of the Shanahan postulates, and if it could be shown that such transport absolutely does not occur, the physical/chemical basis of the Shanahan postulate would be severely challenged. While it is possible that changes in fluid or gas circulation patterns in the cell might also change heat flow paths, this is considered to be a less likely scenario than gas entrainment processes. However, we eagerly await such detailed and comprehensive studies.

In our prior publication, we contend just such an observation has been made in the Naval SPAWAR Research Laboratory [5]. Szpak and coworkers have recorded an active FPHE with an infrared video camera. While the images published from this study do not include a rule, the cathode size was reported to be a 4 cm^2 electrode. Assuming the field of view is $\sim 2\text{ cm}$ wide, the spot sizes of individual bubbles is on the order of 0.2 mm . There are many confounding factors in this estimate of course, such as the optical divergence from the source point, the focusing and magnification of the camera system, the field of view, etc., but the spot size is of the right order of magnitude of a typical bubble, which tends to be small in these systems. Further, one additional point is the observation from these video clips that no light spots seem to occur below the midpoint line of the electrode. This may suggest the effect of buoyancy, where the transported bubbles do rise during transport. Alternatively, this may be due simply to a localized special active state. Of course, that is purely speculative and would need to be confirmed by further experimentation.

1.2. Storms point 2: recombination heat cannot produce the observed excess heats

The point of the prior two publications was to show that this is a false contention. Electrolysis gases contain a power content (W) equal to the thermoneutral voltage (V) times the applied cur-

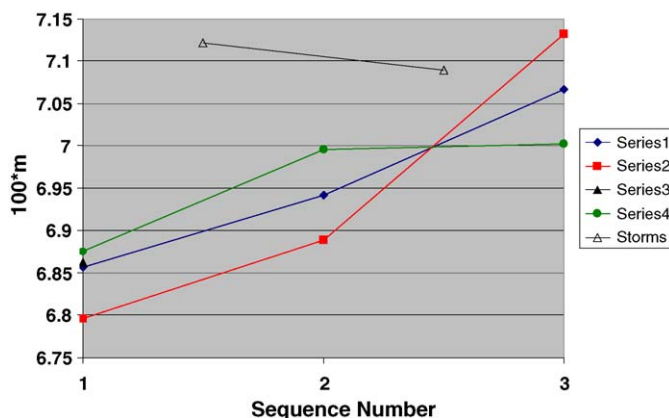


Fig. 1. Hundred times the calibration constant m reported in Table 1 of Ref. [3], plotted as time sequences separated by negative EP events. Four series are shown, and are broken up as follows by run number: {1,2,3}, {4,5,6}, {7}, {8,9,10}. Two calibration constants from the Storms' inactive electrode are also shown for comparison.

rent (A). For heavy water, the thermoneutral voltage is 1.54 V , and an applied current of 1 A could then deliver the potential of 1.54 W apparent excess power if the gases were to unexpectedly combine in the cell. If a CCS occurs the actual magnitude of the apparent excess power signal would potentially not be limited to that value, because the ratio of calibration constants can be greater than 1, producing a magnifying effect. Thus the observed apparent excess power signal magnitude need not be exactly the actual recombination heat being produced. However, with a potential of 1.54 W apparent excess heat coupled with a potential magnification, the vast majority of reported apparent excess heats can be well explained by the mechanism. The details of the electrolysis cell and calorimeter design will decide the potential magnitude of the effect.

Dr. Storms correctly notes that 1.54 W is potentially available and notes that this power is normally deposited at the recombination catalyst in closed cells (in open cells, the gases theoretically escape the cell without recombining), but then attempts to conclude that the amount of power deposited at the electrode is "very small" based on the data of his Fig. 1. The fraction recombined on an inert electrode, i.e. one that does not show the FPHE, is represented by the data in Storms' Fig. 1 (however see the next sections for more discussion), and is well fit by the Will model for the parasitic electrochemically driven oxygen recombination reaction that this author agreed was unimportant in his last publication [5]. The data would be quite different for an active FPHE electrode. Thus the data of Storms' Fig. 1 are not relevant to limiting the FPHE magnitude.

1.3. Storms point 3: cold fusion calorimetric studies have detected no CCS

This is perhaps the greatest area of confusion in Storms' attempted rebuttal of the Shanahan postulates. The purpose of the Shanahan publications was to outline a previously unconsidered mechanism for obtaining apparent excess power signals and show how it could be easily used to explain apparent excess heat. Clearly, if it was previously unknown, prior reports will not have

included it in their considerations. As proponents of a radical new explanation for the observed apparent excess power signals (namely the nuclear ‘cold fusion’ explanation), cold fusion researchers such as Dr. Storms should be well acquainted with this concept.

A synopsis of the nuclear explanation is that electrodes made from select materials can either be sometimes obtained or processed to show the ‘cold fusion’ effect. In these electrodes a ‘special active state’ forms which supposedly fosters some sort of nuclear reaction that serves as the source term for the apparent excess heat. The cold fusion field is split over whether the phenomenon is a surface or bulk effect.

Shanahan’s postulates have included the special active state concept, but have gone on to further specify that a surface contaminant derived from the electrolyte is the most likely candidate for what forms the ‘special active *surface* state’. The field of cold fusion research is littered with reports of both unexpected detection of deposited metals found on the cathodes, and with deliberate attempts to alter the surface state of the electrodes by addition of elements and compounds to the electrolyte. Sometimes these contaminated electrodes produce apparent excess heat and sometimes they do not. But clearly, the surface state of electrolysis electrodes is altered with time in these systems, and this aspect of the field has not been as well studied as this author thinks it should have been. The idea of a special active surface state has the useful properties of allowing the adhesive properties of bubbles to the surface to be altered and of being able to further easily alter the surface state by cleaning processes such as unloading, voltammetric stripping, acid washes, and/or flame cleaning, etc.

To obtain a FPHE then, one must have an electrode that has a surface which supports the effect. Clearly, this is not easy to obtain by accident and it was only the persistence of Fleischmann and Pons that led to the initial discovery of the FPHE (which was probably mistakenly attributed to nuclear causes due to apparent excess heat magnitude). Most cold fusion research makes no attempt to systematically define and control the surface conditions. Therefore the observation of the FPHE has been sporadic and irreproducible. The best recent research into reliably producing the effect has focused on high specific area surfaces such as those formed by chemical deposition of Pd on a base electrode, i.e. the Szpak studies. The high surface area would facilitate bubble entrapment and extraction of electrolyte contaminants, i.e. the formation of a special active surface state.

Within the context of the Shanahan postulates, most if not all of the reports of apparent excess power could arise due to the mechanism proposed, and not a nuclear reaction.

Furthermore, when a FPHE is in effect, simply pulsing a calibration resistor or the electrolysis current will not test for the calibration constant shift. The physical mechanism underlying the CCS requires a shifted source of heat, not just an additional one. An additional source of heat is expected to be accurately measured if it appears in a location that previously had a heat source such as a calibration resistor or electrolysis electrodes, or a recombination catalyst such as is used in closed cells.

In open cells, a recombination catalyst is not used. Recombination at the electrode should in theory therefore be reasonably

accurately measured. While that may be true, another complicating factor may be the dissolution of Pd or Pt and their deposition on the cell walls in the gas space effectively forming a recombination catalyst, even in an open cell (this could also occur in a closed cell). To test these theories, experimentalists must construct a cell that simulates the postulated processes adequately. Clearly this is another area of fruitful research to be pursued in order to understand the genesis of the FPHE.

Storms cites studies of inactive electrodes to show that the CCS cannot occur. Within the context of a special active surface state, the use of inactive (dead) electrodes is of no value. By definition, a dead electrode shows no FPHE, therefore it cannot be used to exclude the existence of the FPHE. Since there has been such confusion over this point, it bears repeating. A FPHE is expected to be observed only on an electrode that has been activated by processing to allow greater bubble adhesion and perhaps easier ignition. The greater adhesion would also facilitate the required merger of the separate H₂ and O₂ bubbles. ‘Dead’ electrodes and calibration resistors will not show a FPHE, by definition. Only when a heat source that previously was accounted for in a particular zone (i.e. the gas space or even flowing out of the cell) moves to another zone in the cell (i.e. in the electrolyte, perhaps at the electrode surface) with a different heat capture efficiency (or heat loss rate) will a FPHE be observed.

1.4. Storms point 4: Shanahan misinterprets or fails to understand extant results

Storms focuses his complaints on Shanahan’s use of the Storms data, and presents two figures to bolster his arguments. Unfortunately, the data presented by Storms’ actually supports Shanahan’s position better. Beginning with a discussion of Storms’ Fig. 1, it should be noted that the five leftmost points on this plot were produced by the Hansen and Jones research group [8]. At the time of their publication of this data, this author noted that there appeared to be one flyer point in the data set when compared to a straight line, but that with linear regression it was difficult to distinguish whether that was the fourth or fifth point. Will [9] has presented a mathematical modeling study of the Hansen and Jones data, and in Fig. 2 of that reference he illustrates the fit of that model to the data. (This fit shows the fourth point to be a flyer, lying roughly 8% above the theoretical line.) These models predict that higher current densities will produce no significant recombination via the parasitic electrochemical oxygen reaction which is controlled by dissolved oxygen, a fact that Shanahan affirmed was correct and not relevant to the excess heat issue in his last publication [5].

With the subsequent addition of the Storms’ data, the higher current density region of this fit can be filled in as well. It can be seen that the bulk of the high current density data agrees well with the Will fit, which is shown on the Storms Fig. 1 for high current densities. (In the Will Fig. 2, the fit extends back through the Hansen and Jones data almost perfectly, with the exception of the fourth point as noted.) There are actually several points that deviate significantly from that line representing an excess recombination beyond that expected by the electrolytic

model, and that is definitely relevant. The fourth Hansen and Jones point can be seen to lie ~ 0.08 units (8%) above the line. Of the first two points of Storms data, one lies nearly on the projected line, with the other being ~ 0.05 above that, which is probably within experimental noise. However, the next cluster of data points which includes several points at ~ 0.035 and ~ 0.07 A have only one point below the theoretical value at 0.0 fraction recombined. The remainder range from ~ 0.1 to 0.3 above the theoretical line. This is well beyond the experimental noise level present in the rest of the Storms data and is clearly unexpected recombination. This excess recombination could potentially be the recombination that is needed in the Shanahan postulate if said recombination occurred at the electrode.

In Fig. 2 of [1], Storms presents more calibration data, which just confirm the comments made by Shanahan. The figure presented here is the same as that used in Storms first publication [2], and thus was considered in Shanahan's reanalysis [3].

The initial and final electrolytic linear term calibration constant differ by $\sim 0.5\%$ in this case, and the Joule heater calibration is 1.7% higher than the final electrolytic calibration constant. In [3], Shanahan reports a span of about 5% total in the derived electrolytic calibration constants. The 1 sigma standard deviation of that data set is 1.5%. Thus all of Storms relative differences are within the statistical bounds defined by Shanahan.

Storms attempts to place the burden of proof regarding why and where a CCS would occur in his studies on this author by asserting that no explanation of the detailed behavior of the CCS has been offered. A detailed possible explanation has been presented above as an expansion of that presented in [5], and it is easy to speculate that the processes of forming and/or removing the 'special active surface state' could be time-dependent. This turns out to be particularly fruitful in this case.

In Ref. [2], Storms describes the experimental sequences used to study the active Pt electrode. (Note that the preprocessing required to make the Pt electrode active is not described, only the results from the activated electrode are presented.) He describes 3 A current sweeps and intermediate periods where less than 3 A were applied, followed by brief periods where the current was turned off. Storms discusses the repetitive behavior noted in his study and adds that one sequence of sweeps was not shown. In [3], Shanahan includes some of those missing sequences in the analysis, and analyzes the less than 3 A current applications as well, to arrive at a total of 10 current excursions (referred to as runs 1–10 herein).

In Table 1 of Ref. [3], the calibration constants derived under the $P_{ex} = 0$ assumption for those 10 runs are presented, and they clearly show sequence (time) dependent trends. This is presented here in Fig. 1, where 100 times the m calibration constant is plotted versus sequence number with the 10 runs divided into four sequences as described below. Also shown are the two electrolytic calibration numbers reported by Storms, arbitrarily placed on the plot in initial-final order to indicate the span of values for an inactive electrode (Storms' Fig. 2 in Ref. [1]). The sequences clearly show an increasing m trend as the electrode deactivates, where they approach the values determined by electrolysis with an inactive Pt electrode. (Note that Series 3 is a one-point series.)

Storms notes that current was briefly turned off after run 3 (Shanahan numbering, end of Series 1) and run 6 (end of Series 2), and that calibrations with the inert electrode and Joule heater were done at ~ 430 h (some time after run 9 presumably, but possibly after run 10, end of Series 4). These interruptions in current flow through the active electrode may be important, but the experimental description, especially regarding the latter runs, is somewhat lacking. However, examining Figs. 4–6 from Ref. [2] suggests another possibility associated with the occurrence of negative excess power (EP) production periods. This occurs five times in the figures, at approximately 88, 178, 300–333, 355–370, and 395 h. Two are confounded with subsequent "Current Off" indications (120 and 320 h). Two negative EP events (numbers 3 and 4) were only separated by a low current period that was not reanalyzed in [3] and will be counted as one combined event here. Thus, three of the four negative EP events correlate to the three break points in the sequences presented in Fig. 1.

The one that does not is at ~ 178 h. That excursion was followed by an exceptionally long period of operation (>100 h) at or below 1.5 A, as opposed to the 3 A excursions used by Storms to probe the EP behavior. Note that low but not negative EP was also produced after run 1, and that was also followed by a long period of lower current operation (~ 50 h) before a 3 A sweep was initiated. Both of the lower current-long time runs were included in the reanalysis [3] (runs 2 and 5). It would seem that long periods of operation cancelled the impact of the negative or near-negative EP events.

These observations should give impetus to Storms to further examine the chemical process information for the whole sequence of experiments to search for the key or keys to the observed time-dependent phenomena. Irregardless, there does seem to be a steady deactivation of the active Pt electrode with time in use that causes the observed calibration constants to approach that of an inactive Pt electrode. The loss and recovery of activity through chemical processing is a strong indicator of a chemically based activity.

1.5. Some final comments on optimum experimentation

The Storms work [2] shows a great deal of reproducibility in behavior when the time dependent features as discussed above are recognized. As such it represents an excellent material of choice for further experimentation aimed at resolving the origin of the FPHE. However, the field is still plagued by the assumption that bulk loading level (in reference to Pd) is a key parameter. So far, no one has reported that Pt can be made to form a bulk hydride, so clearly this is *not* a key parameter.

Further, use of Pd complicates the picture greatly when one focuses on the surface. When Pd hydrides (loads), the material swells, and this stress is relieved by a process called loop-punching, where dislocations are formed and often reach the surface of the electrode. The corrugation arising from this will produce active sites in the surface chemistry sense that are well-suited to absorbing impurities from the electrolyte. This whole process is highly uncontrolled, which would imply a good deal

of variability would result. Pt on the other hand should be much easier to control and monitor.

Additionally, the isotope effects present in these studies will make it quite difficult if not impossible to set up a classic control experiment, which has often been attempted by cold fusion researchers. Typically, light water cells have been presented as control cells. However, since the viscosity of heavy water is 25% higher than that of light water [10], it should be obvious that the bubble entrainment process will be highly impacted. As well, H and D load differently into Pd, so that choosing one set of electrochemical parameters for the control and experimental cells will not produce equivalent loading in the Pd electrodes. Thus, the extent of loop-punching, i.e. surface distortion, will not be the same in the control cells versus the experimental cells. If conditions are set so that equivalent loading is obtained, then different voltages or currents will be used in the cells, and if the chemical process that Shanahan postulates for the FPHE is considered, this will result in differing amounts and/or rate of development of the special active surface state.

The use of Pt cathodes avoids most of these issues. But instead of focusing on the simpler system presented with Pt, the trend is to go to more complex systems, such as codeposited Pd as was discussed in Ref. [4]. However, an explanation as to why the 'active' Pt electrode was active, and what was deactivating during the experimental sequences was never offered. Hopefully, these publications will stimulate some serious surface chemical research into what is causing the FPHE.

2. Conclusions

In summary we have shown that the Storms postulate that H₂ and O₂ bubbles cannot combine at the electrode surface in an electrolysis cell is premature, given the general state of knowledge of fluid dynamics and mixing in these cells. Also, Storms has shown that unexpected recombination fractions may easily reach 10–30%, and this does not prohibit even larger fractions, therefore the available recombination power (in W) can be up to the thermoneutral voltage (1.54 V for D₂O, 1.43 V for H₂O) times the current (A). For the 3 A sweeps Storms used, that allows up to 4.6 W. Storms observed about 0.8 W, which

would indicate a 17% recombination in the cell in the absence of the calibration constant shift ratio impact (which would nominally reduce the amount of recombination required to get the observed apparent excess heat). This is well within Dr. Storms own observations as shown in his Fig. 1. The issue of using the non-appearance of the FPHE in calibration and 'dead' electrode studies has been shown to be an incorrect logical procedure. And, it was shown that Dr. Storms' data was completely consistent with the error bands extrapolated from Shanahan's reanalysis study. Thus the four primary points used by Dr. Storms to rebut Shanahan have been rebutted themselves.

No one can ever prove nuclear cold fusion does not exist. However, the chemical explanation presented by Shanahan deserves an honest experimental test. If it turns out to have sufficient explanatory power, then it should be given the credibility it deserves as the potential explanation of apparent excess heat.

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