Miles, M., *Reply to "Mechanism of thermal runaway as a cause of Fleischman-Pons effect"*, LENR-CANR.org, Editor. 2025.

This is a critique of the paper: Galushkin, N.E., N.N. Yazvinskaya, and D.N. Galushkin, *Mechanism of thermal runaway as a cause of Fleischmann-Pons effect.* J. Electroanal. Chem., 2020. **870**: p. 114237. A preprint version of Galushkin's paper is here:

https://lenr-canr.org/acrobat/GalushkinNmechanismo.pdf

J. Electroanalytic Chemistry refused to publish Miles' critique.

Manuscript

Reply to "Mechanism of thermal runaway as a cause of Fleischman-Pons effect"

Melvin H. Miles
College of Science and Technology Dixie State University
St. George, UT 84790

Abstract

The major conclusions of this publication lack compatability with the basic laws of thermodynamics. In addition, there are electrochemical, chemical, calorimetric, and experimental issues with the authors proposed explanations for the Fleischmann-Pons effect. The major error with this publication is the assumption that D_{ads} or the deuterium in PdD_x is thermodynamically the same as gaseous atomic D atoms. The large endothermic enthalpy necessary for the formation of any atomic D must be considered in the calorimetric analysis. This new report of unusually large excess power effects for the Pd/D_2O system was apparently observed only in a single experiment and differs significantly from other reports of Fleischmann-Pons effects. The unusually large amounts of deuterium absorbed into the platinum anode and the palladium cathode are not supported by other experiments.

Introduction

The authors of this publication [1] propose that the thermal runaways observed in nickel-cadmium batteries are due to the exothermic recombination of accumulated atomic hydrogen. The authors then extend this explanation to the Fleischmann-Pons effect and proposed that the large experimental calorimetric excess heat effects for the Pd/D_2O system are due to the recombination of large amounts of accumulated atomic deuterium at both the platinum anode and the palladium cathode. The focus here will be on the Fleischmann-Pons effect and not on any battery issues

1. Thermodynamic Accountability

The enthalpy of formation for PdD_x ($\alpha + \beta$ phase) is exothermic (-35.1 kJ/mol D_2) [2,3] and should not be confused with the much larger endothermic enthalpy for the formation of atomic D atoms in the gaseous state (443.346 kJ/mol D_2). Atomic H or D atoms are very reactive [4,5] and would not be thermodynamically stable in either H_2O or D_2O solutions. For example, NaOH is reduced to Na + H_2O by atomic hydrogen [5]. The atomic D atoms would have to be absorbed (abs) within the metal electrodes and out of contact with the D_2O solution. The authors' equations, however, suggest atomic D adsorption (ads) at both electrodes.

There is no thermodynamic net energy source via atomic D atoms for a thermal runaway that could cause the Fleischmann-Pons excess enthalpy effect in the Pd/D_2O + LiOD system. The enthalpy required to form atomic D atoms from D_2 must exactly equal the enthalpy produced when these D atoms recombine to re-form D_2. The conversion of PdD_x back into Pd + D_2 is actually an endothermic reaction and not a source for any enthalpy production [2,3].

Enthalpy is a thermodynamic State Function which depends only on the initial and final states independent of any reaction pathways. Therefore, any cyclic process for the formation of atomic D from either D_2O liquid or D_2 gas by any mechanism, and its recombination back to D_2O liquid or D_2 gas will give a net enthalpy change of zero. Examples for this are given in the Appendix. Net energy production by any cyclic process would be an obvious violation of the First Law of Thermodynamics.

2. Electrochemical and Chemical Issues

The authors explanations for both the thermal runaways in batteries and the Fleischmann-Pons large excess heat effects are based on the assumption that H or D atoms on or inside metal electrodes are thermodynamically the same as atomic H or D gaseous atoms. This assumption is incorporated into the authors reactions 1, 2 and 3 as well as into reactions 8, 9, and 10, but how could reactive atomic H participate in both the anodic and cathodic reactions? Chemically, atomic H is a strong reducing agent similar to lithium and would readily become oxidized to H^+ or H_2O at the anode.

The proposed anodic reaction in H_2O for atomic H is simply represented by $2H \rightarrow 2H^+ + 2e^-$ or $2H + 2\ OH^- \rightarrow 2\ H_2O + 2e^-$ for basic solutions. The cathodic reaction can also be expressed as $2H^+ + 2e^- \rightarrow H_2$ or $2\ H_2O + 2e^- \rightarrow H_2 + 2\ OH^-$ for basic solutions. There is no involvement of atomic H in the cathodic reaction. The authors cathodic reactions (Eqs. 2 and 8) are incorrect and apparently involve the addition of the net cell reaction to the correct electrode reaction at the cathode. For both acidic and basic H_2O solutions, the cell reaction is $2H \rightarrow H_2$ where two electrons are transferred per H_2 molecule formed rather than only one election as implied by the authors reactions 1, 2 and 3. These same errors are present in the authors reactions 8, 9 and 10 that involve deuterium in place of hydrogen.

The standard electrode potentials for the proposed reactions of atomic H or D are well outside the electrochemical stability range for H_2O or D_2O solutions. The standard cell potential for $H_2 \rightarrow 2\ H$ is -2.1065 V versus -1.2288 V for $H_2O \rightarrow H_2 + ½\ O_2$. A related standard cell potential of -2.1403 V is calculated for the $D_2 \rightarrow 2\ D$ cell reaction where D represents atomic D. Any atomic H or D produced electrochemically would not be stable in H_2O or D_2O solutions. Therefore, any accumulation of atomic H or D during the electrolysis of H_2O or D_2O solutions would have to be within the electrodes. However, atomic D would likely react with other accumulated D atoms within the electrode to form D_2 gas rather than undergoing any significant accumulation.

The Fleischmann-Pons electrochemical experiments generally used a palladium cathode with a platinum anode for D_2O electrolysis. Therefore, the platinum electrode surface during oxygen evolution would consist of platinum oxide rather than platinum metal, but atomic H reacts with metal oxides ($2\ H + MO \rightarrow M + H_2O$) [4]. There would not be any stable adsorption of deuterium (D_{ads}) or hydrogen (H_{ads}) atoms on this platinum oxide anodic surface. Even if atomic D atoms were produced at the anode in a Fleischmann-Pons electrolysis cell, they would likely soon be eliminated by their reactions with the electrogenerated oxygen gas [6]. Furthermore, unlike palladium (Pd), there is no significant absorption of hydrogen or deuterium into platinum (Pt) metal [7].

The Fleischmann-Pons excess heat effect usually requires a high deuterium loading of D/Pd = 0.85 or even higher [8]. Such high D/Pd loadings are difficult to achieve. From the authors Table 2, the D/Pd loadings can be calculated from the weight % deuterium reported for each experiment. The results give x = D/Pd = 10.5 for Electrode 71, x = 0.95 for Electrode 54 and x = 1.2 for Electrode 107. The results for Electrode 54 and 107 are somewhat high, but the result of x = 10.5 for Electrode 71 is completely unreasonable. Even for hydrogen pressures up to 100 GPa, a recent report states that there was no experimental evidence for hydrogen to palladium ratios greater than 1 [7]. Previous studies have reported that palladium can absorb up to 935 times its own volume of hydrogen gas (see Wikipedia). This corresponds to a composition of x = moles H/moles Pd = 0.676. The authors report of 2.525 L of D_2 accumulated in the palladium Electrode 71 (see Table 2) represents a D_2 gas volume that is 16,100 times the volume (0.157 cm^3) of this palladium cathode. This reported result by the authors simply cannot be correct. Accurate weighing methods show that the D/Pd ratios obtained by D_2O electrolysis are generally less than 0.85 in Fleischmann-Pons experiments [9,10]. Palladium cathodes that produced excess energy gave somewhat higher loading ratios ranging from 0.88 to 1.06 [8]. Cracks or other defects in palladium cathodes are generally detrimental for large loading ratios and excess heat effects [9,10]. Large excess volume measurements are a means of eliminating defective cathodes [10].

There should not be any significant accumulation of deuterium in the platinum anodes [7], yet the authors results in Table 2 yield x = D/Pt = 8.3 for Pt Electrode 71, x = 0.7 for Pt Electrode 54 and x = 0.9 for Pt Electrode 107. These errors regarding the large deuterium amounts accumulated in the palladium cathodes and even in the platinum anodes invalidates much of the following discussions in this publication (Sections 3.3 and 3.4).

3. Calorimetric and Experimental Issues

The calorimetric results from many Fleischmann-Pons type experiments are evidence that there is no significant formation of atomic D atoms during the electrolysis of the Pd/D_2O system [11,12]. Any formation of large amounts of atomic D atoms during electrolysis would require large endothermic enthalpy changes (see Appendix). For example, the reaction $D_2 \rightarrow 2\ D$ gives an endothermic enthalpy change of 443.346 kJ/mol D_2. If all the typical cell current of 0.200 A were used for this reaction for any period of time, then there would be a negative power production of -0.4595 W. Such a large and negative power effect would be easily detected by the calorimetry. Even if only 1.0% of this cell current was used for this formation of atomic D, then the negative power effect (-0.0046 W) could still be detected by many calorimeters. Finally, even the calorimetric results in this publication [1], do not indicate any observations of negative power effects that would support the formation of atomic D atoms. The only endothermic reaction in the Pd/D_2O calorimetric system is the electrolysis of D_2O to form D_2 and O_2 gases with a thermoneutral potential of $E_H = -1.5267$ V. The Fleischmann-Pons type calorimetry has been recently used to accurately determine the enthalpy of formation for D_2O liquid [13]. No additional endothermic processes were detectable.

The important results shown in the authors' Figure 3 [1] are not easily explained as Fleischmann-Pons effects. There is ~~a~~ an unusually close relationship in Figure 3 between the excess power peaks and the changes in the cell voltage. This cycle is apparently repeated twelve or more times over six hours as shown in Figure 3. This is not the normal behavior of the Fleischmann-Pons effect where the excess power often lingers after a decrease in the cell current and voltage or even after the cell is turned off [12]. There is no evidence for any atomic deuterium formation and recombination as the cause for the large type A Fleischmann-Pons effect because there are no negative power effects reported that would support the endothermic formation of atomic deuterium atoms.

The Fleischmann-Pons narrow cell design was based on providing effective stirring of the electrolyte by the generated gases. A typical cell had a small diameter of 2.5 cm and 25 cm in height [12]. The anode coil was positioned at the cell wall about 1.0 cm from the cathode with both electrodes near the cell bottom [12]. A more narrow gap between the anode and the cathode, as suggested in this publication, was never used by Fleischmann and Pons for actual calorimetric experiments. This narrow gap was only a suggestion for lowering the cell voltage by reacting the D_2 gas at the anode instead of the oxygen evolution reaction.

4. The Recombination Issue

The recombination of deuterium and oxygen was used by the authors as an explanation of small, type B Fleischmann-Pons effects (see Section 3.6). This is an old issue that was dismissed years ago by various experiments [11,14]. Furthermore, the Fleischmann-Pons calorimetric equations include a correction factor (γ) for any recombination where γ is the measured current efficiency [9,15]. If the current efficiency were less than $\gamma = 1.00$ as shown in Figure 4, then the excess power should be corrected by replacing E_H by γE_H where $P_{in} = (E - \gamma E_H)I$. This correction will eliminate the small excess power shown in Figure 4 and give $P_{out}/P_{in} = 1.00$. Measurements of the rate of gases exiting the cell as well as the rate of loss of the D_2O liquid generally show that there are no significant recombination effects in the Pd/D_2O electrolysis system [9,15,16].

A control experiment using a platinum cathode was conducted over a 16-Day period to accurately measure the extent of any recombination [11]. The detailed results at a cell current of $I = 0.200$ A gave a small and consistent excess power of 1.1 ± 0.1 mW [11]. This small excess power was attributed to the slight reduction of the electrogenerated oxygen at the cathode. There is no oxidation of hydrogen at a platinum oxide anode [17-19]. Furthermore, this accurate calorimetric experiment provides evidence that there was no endothermic formation of atomic D atoms during the entire 16-Day period.

Many experiments for the Pd/D_2O system have used closed cells where the D_2 and O_2 gases are intentionally recombined inside the cell [8,20]. The excess heat results reported are very similar to those measured for open cells [9]. Furthermore, no Fleischmann-Pons effects are observed with the Pd/H_2O or $Pt/D_2O/Pt$ systems where recombination would be equally likely. Another important argument against recombination is that the correlated heat and helium-4 production, as reported by several groups [9,16,21], cannot be explained by recombination.

5. Conclusions

This Galushkin publication [1] contains many significant scientific errors. Reactions involving atomic deuterium do not provide a correct explanation for the Fleischmann-Pons effect. No actual calorimetric data was provided, and the only calorimetric information was that the Fleischmann-

Pons Dewar cells and methods were used. It should be mentioned that the English language was poor, and it was often difficult to understand in this publication.

The large amounts of deuterium contained in both the palladium cathodes and the platinum anodes have never been reported for any other Fleischmann-Pons type experiments. The close relationships between P_{out}/P_{in} and the large cell voltage changes in Figure 3 are unlike any other reported studies of the Fleischmann-Pons effect. This was apparently a single experiment that needs to be replicated by the authors, as well as by other groups, before attempting any explanations.

Other scientific studies of hydrogen and deuterium absorbed into platinum and palladium metals [7] do not support the reported results for this Galushkin publication. Even under high hydrogen pressures, there is no significant absorption of hydrogen into platinum metals [7]. For palladium, the hydrogen/palladium ratio never significantly exceeds 1.0 [7]. The negative overvoltage at the palladium cathode in the electrochemical cell acts thermodynamically as a high fugacity effect that drives the D_2 gas into the palladium. There is no such fugacity effect for D_2 at the platinum anode.

Palladium or palladium alloy cathodes for use in Fleischmann-Pons type experiments are generally carefully polished and examined for cracks or other defects [12]. Defective electrodes are rejected for experimental use because they do not produce the Fleischmann-Pons effect. This does not fit with the Galushkin conclusions that electrodes with a very significant number of micro-defects should be used in these Fleischmann-Pons experiments. Recent experiments suggest that boron may be an essential impurity in palladium for reproducible Fleischmann-Pons effects [3,12].

Research on cold fusion continues in various countries, but most scientific journals and even preprint servers such as arXiv and ChemRxiv automatically block most manuscript submissions about this research. Most cold fusion research today is published in our own electronic journal (see Ref. 3). Cold Fusion (or LENR) obviously remains a very controversial topic, but there are now many scientific experiments that have confirmed the Fleischmann-Pons excess heat effect [22, 23].

Is it not time for a new look at cold fusion when the world has need for a new energy source to replace carbonaceous fuels [23]? A starting point could be replications by other scientists of these Fleischmann-Pons type experiments. The extensive calorimetric data available in Reference 12 that was also obtained using a Fleischmann-Pons Dewar calorimeter should be evaluated by other scientific groups. It should be noted that even today no actual scientific errors have been found in the comprehensive 1990 publication by Fleischmann and Pons concerning their electrochemical calorimetry [15].

References

[1]. N.E. Galushkin, N.N. Yazvinskaya, D.N. Galushkin, Mechanism of thermal runaway as a cause of Fleischmann-Pons effect, J. Electroanal. Chem. 870 (2020) 114237, 8 pages.

[2]. J. Balej, J. Divisek, Energy balance of D_2O electrolysis with a palladium cathode. Part 1. Theoretical relations, J. Electroanal. Chem. 278 (1990) 85-98.

[3]. M.H. Miles, The thermoneutral potential in electrochemical calorimetry for the Pd/D2O system, J. Condensed Matter Nucl. Sci. 33 (2020) 74-80.

[4]. H.C. Urey, G.I. Lavin, Some reactions of atomic hydrogen, J. Am. Chem. Soc. 51,11 (1929) 3286-3290.

[5]. J.C.G. Martin, C. Seaton, M.P. deMiranda, J.M.C. Plane, The reaction between sodium hydroxide and atomic hydrogen in atmospheric and flame chemistry, J. Phys. Chem. A, 121, 40 (2017) 7667-7674.

[6]. E.J. Badin, The reaction between atomic hydrogen and molecular oxygen at low pressures, J. Am. Chem. Soc., 70, 11 (1948) 3651-3655.

[7]. (a) B. Guigue, G. Geneste, B. Leridon, P. Loubeyre, An X-ray study of palladium hydrides up to 100 GPa: Synthesis and isotopic effects, J. Applied Physics, 127, 075901 (2020), https://doi.org/10.106311.5138697. (b): V.E. Antonov, I.T. Belash, V. Yu Malyshev, E.G. Ponyatovsky, The solubility of hydrogen in the platinum metals under high pressure, Platinum Metals Rev. (1984) 28 (4), 158. (c) Z.M. Geballe, M. Somayazulu, N. Armanet, A.K. Mishra, M. Ahart, R.J. Hemley. High pressure synthesis and thermodynamic stability of PdH up to 8 GPa, Phys. Rev. B, 103, 024515, 19 January 2021.

[8]. M.C.H. McKubre, Electrochemical loading to produce the Fleischmann-Pons heat effect (FPHE), in Cold fusion: Advances in Condensed Matter Nuclear Science, Chapter 3, Jean-Paul Biberian (Ed.), Oxford, 2020, pp. 37- 54.

[9]. M.H. Miles, B.F. Bush, K.B. Johnson, Anomalous Effects in Deuterated Systems, NAWCWPNS TP 8302, China Lake, CA (September 1996), 98 pages.

[10]. E. Storms, The Science of Low Energy Nuclear Reactions, World Scientific Singapore, 2007, pp. 24-33.

[11]. M. Fleischmann, M.H. Miles, The instrument function of isoperibolic calorimeters: Excess enthalpy generation due to the parasitic reduction of oxygen, in Condensed Matter Nuclear Science, ICCF-10 Proceedings, P.L. Hagelstein and S.R. Chubb (Eds.), World Scientific (2006), pp. 247-268.

[12]. M.H. Miles, M. Fleischmann, M.A. Imam, Calorimetric analysis of a heavy water electrolysis experiment using a Pd-B alloy cathode, Naval Research Laboratory Report, NRL/MR/6320-01-8526, March 26, 2001, 155 pages.

[13]. M.H. Miles, Electrochemical isoperibolic calorimetry for D_2O electrolysis, ChemRxiv, November 17, 2019. DOI: 10.26434/chemrxiv.10269713.

[14]. F.G. Will, Hydrogen + oxygen recombination and related heat generation in undivided electrolysis cells, J. Electroanal. Chem. 426 (1997) 177-184.

[15]. M. Fleischmann, S. Pons, M.W. Anderson, L.J. Li, M. Hawkins, Calorimetry of the palladium-deuterium-heavy water system, J. Electroanal. Chem. 287 (1990) 293-348.

[16]. M.H. Miles, R.A. Hollins, B.F. Bush, J.J. Lagowski, R.E. Miles, Correlation of excess power and helium production during D_2O and H_2O electrolysis using palladium cathode, J. Electroanal. Chem., 346 (1993) 99-117.

[17]. J. Bao, D. Macdonald, The oxidation of hydrogen on oxidized platinum, ESC Mect. Abstr. MA 2005-01, 1613 (2005).

[18]. J. Bao, D.D. Macdonald, Oxidation of hydrogen on oxidized platinum: Part 1: The tunneling current, J. Electroanal. Chem. 600 (2007) 205-216.

[19]. S. Tahmasebi, A.A. McMath, J. van Drunen, G. Jerkiewicz, Catalytic duality of platinum surface oxides in the oxygen reduction and hydrogen oxidation reactions, Electrocatalysis (2017) 301-310.

[20]. M.C.M. McKubre, S. Crouch-Bakers, R.C. Rocha-Filho, S.I. Smedley, F.L. Tanzella, Isothermal flow calorimetric investigations of D/Pd and H/Pd systems, J. Electroanal. Chem. 368 (1994) 55-66.

[21]. M.H. Miles, Production of Helium in Cold Fusion Experiments, in Cold Fusion: Advances in Condensed Matter Nuclear Science, Chapter 1, Jean-Paul Biberian (Ed.), Elsevier, Oxford, 2020, pp. 3-15.

[22]. Cold Fusion: Advances in Condensed Matter Nuclear Science, Jean-Paul Biberian (Ed.) Elsevier, Oxford, 2020, 377 pages.

[23]. R. Carat and M. Howerth, Discover Cold Fusion, Curtis Press, Great Britain, 2020, 32 pages.

Appendix

Any proposed cyclic sequence of reactions that start with D_2O or D_2 and form atomic D atoms followed by recombination reactions that reform the D_2O or D_2 will always have a net enthalpy change of zero. The simplest example is $D_2 \rightarrow 2\ D$ followed by $2\ D \rightarrow D_2$. The standard enthalpy change is 443.346 kJ/mol D_2 for the endothermic formation of atomic D atoms and -443.346 kJ/mol D_2 for the exothermic recombination back to D_2. The net enthalpy change is obviously zero for this cyclic process (see Eq. A-4 below). This large recombination enthalpy for atomic D is essentially what is proposed by Equation 10 of this publication as the explanation for the large Fleischmann-Pons excess heat effects. Expressing these reactions as $D_2 \rightarrow 2\ D$ (metal) and followed by $2\ D$ (metal) $\rightarrow D_2$ will alter the value of the enthalpy change, but the net enthalpy change will still be zero. The authors, however, use the thermodynamic values for atomic D gaseous atoms which are quite different from D atoms on or inside platinum or palladium electrodes.

A more complicated reaction sequence that starts and ends with D_2O (liquid) and makes use of reported standard formation enthalpies follows:

$$D_2O \rightarrow D_2 + 0.5\ O_2 \qquad \Delta H = 294.600\ \text{kJ/mol}\ D_2 \qquad \text{(A.1)}$$
$$D_2 + 4\ Pd \rightarrow 4\ PdD_{0.5} \qquad \Delta H = -140.400\ \text{kJ/mol}\ D_2 \qquad \text{(A.2)}$$
$$4\ PdD_{0.5} \rightarrow 4\ Pd + 2\ D \qquad \Delta H = 583.746\ \text{kJ/mol}\ D_2 \qquad \text{(A.3)}$$
$$2\ D \rightarrow D_2 \qquad \Delta H = -443.346\ \text{kJ/mol}\ D_2 \qquad \text{(A.4)}$$
$$D_2 + 0.5\ O_2 \rightarrow D_2O \qquad \Delta H = -294.600\ \text{kJ/mol}\ D_2 \qquad \text{(A.5)}$$

Reactions A.1 and A.3 are endothermic while the other three reactions are exothermic. The net enthalpy change for all five reactions for this cyclic process is zero as expected from the First Law of Thermodynamics. If atomic D formation and recombination reactions were actually the cause of the large Fleischmann-Pons excess heat events, then the calorimetric excess power episodes would have to be balanced by negative power effects. This has never been observed in any Pd/D_2O calorimetric experiments.

The reaction of atomic deuterium with oxygen is highly exothermic: $2\ D + ½\ O_2 \rightarrow D_2O$, $\Delta H = -736.746$ kJ/mol D_2O. Could this recombination reaction be a source for the large Fleischmann-Pons effect? Again, the answer is NO because this is another cyclic process where exactly the same magnitude of endothermic enthalpy is required to form the reacting D atoms and oxygen gas from the D_2O solution.

The palladium lattice assisted fusion of deuterons to form helium-4 provides a valid thermodynamic process for excess enthalpy production in Fleischmann-Pons type experiments [21]. Based on $dG<0$ at constant T and P, deuterium fusion to form helium-4 is thermodynamically possible at room temperatures.