Research Article

Reaction of the Hydrogen with Air During the Desorption of Palladium Hydride

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Abstract

Palladium cathodes can be loaded with hydrogen or deuterium by electrolysis. Sometimes, when a piece of loaded palladium is removed from the cell, it turns red hot. A simplified numerical model confirms that high temperatures can be reached. The process requires a catalytic metal surface. The combination of a detonation in the gas phase and of palladium self-heating may offer an alternative scenario to explain the meltdown of the Fleischmann and Pons cell operated with a 1 cm cube palladium cathode.
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1. Introduction

When a piece of palladium that has been loaded by electrolysis with hydrogen (or deuterium) is left in the air, it sometimes heats up on its own. On rare occasions, the piece of Pd becomes red hot. Because such experiments are most frequently conducted during the search for non-conventional energy, it is tempting to think that the heating is caused by such a reaction.

However, another explanation is possible: The oxygen from the surrounding air oxidizes the hydrogen seeping out of the metal. The chemical reaction between hydrogen and oxygen can be catalyzed by the metal surface.

Self-heating events have been observed by several researchers. A few examples are given here:

- F.A. Lewis wrote [1]: *"One related experimental observation is that the hydrogen contained in palladium wire electrodes which had been coated with palladium black could be so rapidly oxidized after the specimen had been dried out in the atmosphere that they were momentarily raised to red heat (J.A.S. Creen, unpublished). The atmospheric oxidation of the hydrogen in palladium had been noted, however, in his initial studies by Graham (1868) and also in other early work (see, e.g., Troost and Hautefeuille, I874)".*

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- Edmund Storms reports [2]: *"The behavior of PdD when exposed to air is very unpredictable. Some samples lose D_2 or H_2 rapidly and some lose none at all. Only a few get very hot when the D_2 or H_2 reacts with O_2 on the surface. Although some impurities on the surface are especially effective in catalyzing the reaction, such as sulfur, other samples react for no apparent reason. During my studies involving hundreds of samples, I have had no more than six that self-heated when exposed to air"*.
- Melvin Miles was experimenting in 1995 with a 2 cm long bar palladium cathode [3]. The electrode was clearly outgassing hydrogen in the cell because there were bubbles forming. The palladium electrode was lifted out of the cell and placed on the lab counter top overlying its electrical lead. Then, for an unclear reason, it started to heat up. It actually became cherry red. The electrical connecting wire, made of nickel, was welded to the palladium electrode and did not detach as it would if the connection had been made by solder. The electrode remained cherry hot for some considerable number of minutes. Miles imagined that, at that elevated temperature, the out-gassing must have been accelerated contributing to more vigorous combustion.
- Jean-Paul Bibérian relates similar experiences with Pd ribbons [4].

Based on these experiences, the heating of palladium samples is a rare event. However, the authors think that when the process starts the temperature reached can be high. The purpose of this paper is to show the results obtained by a simple model that simulates such effects. The numerical model uses a simple set of hypotheses in order to determine the temperature range that can be reached via the degassing/oxidation process. It does not predict the temperature evolution with great accuracy because too many parameters would have to be taken into consideration for that.

2. Hypotheses

2.1. General concept of the model

It is supposed in the following that the Pd sample has been loaded with H or D via electrolysis in H_2O or D_2O based electrolyte. At the start of the calculation, the piece of PdH_x contains x mole of H (or D) per mole of Pd. The piece is supposed homogenous, with a uniform distribution of H through the solid sample. At the beginning of the process considered here, the electrolysis is interrupted and the Pd cathode is removed from the bath, dried and exposed to ambient air at room temperature.

It is assumed that:

- The oxygen contained in the air reacts readily with the hydrogen that comes to the surface by diffusion.
- All the H (D) atoms at the surface are consumed so that the concentration of H (D) right on the surface is zero.
- The presence of oxygen on the surface is maintained by diffusion so that the oxygen concentration is not a limiting factor.
- The water vapor leaves the surface, so that the reaction rate is not hindered by an accumulation of the reaction product.

The heat of reaction between the hydrogen in the oxygen is dissipated via several mechanisms:

- Radiation from the solid surface into the environment considered as a black body at 300 K.
- Convection in the surrounding air.
- The balance contributes to the reheating of the metal.

The heat diffuses by conduction within the solid. The temperature has an influence on the H diffusion rate, which is taken into account.

2.2. Heat of reaction

The hydrogen dissolved (absorbed) in the lattice is in atomic form. The heat of reaction of the gas that leaves the metal with oxygen can be calculated according to the first principle of thermodynamics [5], as illustrated in Fig. 1.

The initial state is: H absorbed (dissolved) in the Pd lattice.
The final state is: H_2O in the atmosphere surrounding the metal.

The overall reaction is sketched in Fig. 1 by the path 1. The path between these two states can be detailed along the paths 2 and 3:

Path 2:

- Adsorption of atomic H on the surface: $H_{abs} \rightarrow H_{ads}$.
- Recombination of molecules at the surface: $2H \rightarrow H_{2\,ads}$ (adsorbed on Pd surface).
- Desorption of the molecule into the air $H_{2\,ads} \rightarrow H_2$ (gas released in the atmosphere).

Path 3:

- Reaction with O_2: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ (vapor in air).

Each step is accompanied by an energy change. From the above reactions, the last one (path 3) is well known, because this is the combustion of hydrogen in air. The corresponding heat release is –242 kJ/mol H_2 or –249 kJ/mol D_2. In order to quantify the heat involved by the other steps, we can consider the reverse process that is following path 2 in reverse. When Pd is exposed to H_2, the following phenomena occur:

- adsorption of H_2 on the Pd surface,
- dissociation of the H_2 molecule into two atoms of H,
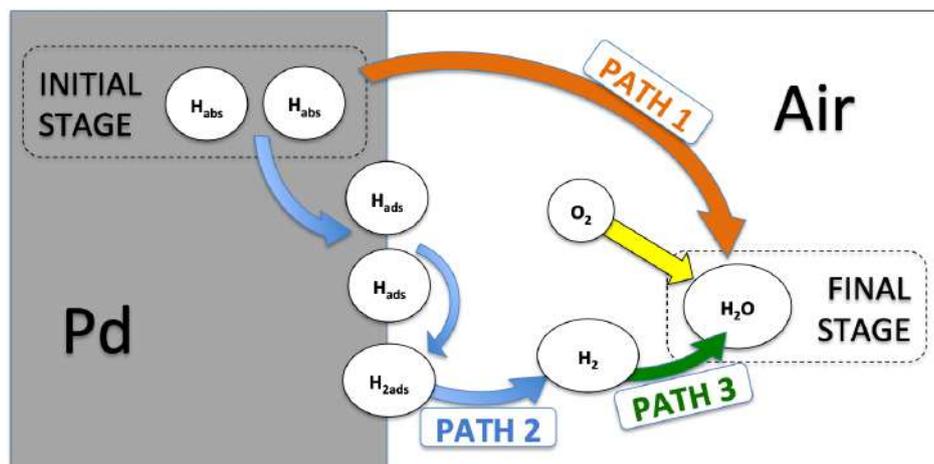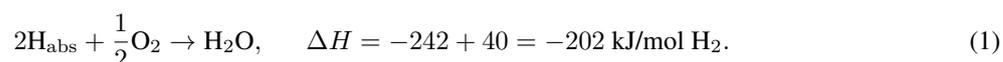- dissolution of the atomic H into the Pd.

Figure 1. Determination of the reaction energy involved in the formation of H_2O from H atoms dissolved in the metal according to the first principle of thermodynamics – The direct path 1 can be dissociated into the virtual paths 2 and 3.
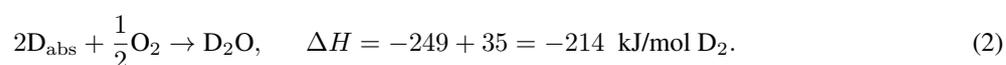
The dissociation of the H_2 molecule is highly endothermic (436 kJ/mol H_2). However, the dissolution is accompanied by a large energy release that more than compensates the energy required for the dissociation. The literature gives the enthalpy of the overall reaction: –40 kJ/mol H_2 (–35 kJ/mol D_2) [5].

The phenomena that take place during the dissolution of H_2 in Pd are exactly opposite to steps 1–3 discussed in the above (path 2). Therefore, the enthalpy associated to path 2 is the opposite of the enthalpy released during the dissolution. As a conclusion, the heat of reaction when the gas dissolved in the metal escapes and burns in air is:
Hydrogen:

$$2H_{abs} + \frac{1}{2}O_2 \rightarrow H_2O, \quad \Delta H = -242 + 40 = -202 \text{ kJ/mol } H_2. \tag{1}$$

Deuterium:

$$2D_{abs} + \frac{1}{2}O_2 \rightarrow D_2O, \quad \Delta H = -249 + 35 = -214 \text{ kJ/mol } D_2. \tag{2}$$

2.3. Diffusion of hydrogen in palladium

The coefficient of diffusion of hydrogen in palladium depends on the temperature but also on the hydrogen loading ratio. In this simplified model, the diffusion law is represented by the following relationships. According to [6] we have:

$$D_H = 2.5 \times 10^{-7} \exp(-21\,800/RT)(m^2 s^{-1}), \tag{3}$$

$$D_D = 1.7 \times 10^{-7} \exp(-19\,900/RT)(m^2 s^{-1}). \tag{4}$$

These values are for solid pieces of palladium.

2.4. Properties of palladium

The model supposes that the piece of metal behaves as if it were pure palladium. The presence of hydrogen in the lattice is not taken into account on the properties listed below [7]. The role of temperature is also disregarded.

Specific mass: $12\,030$ kg m^{-3},
Heat capacity: $c = 0.24$ J g^{-1} K^{-1} or 2952×10^6 J m^{-3} K^{-1},
Thermal conductivity: $\lambda_{Pd} = 75$ Wm^{-1}K^{-1},
Normal spectral emissivity: $\varepsilon_{Pd} = 0.49$.

These values valid for Pd are also considered for PdH$_x$ to simplify the problem. Hydrogen concentration: For a hydride corresponding to the formula PdH$_x$, the equivalent standard volume of molecular di-hydrogen contained in the metal is:

$$C_0 = x\,1294 \text{ Nm}^3 H_2/\text{m}^3\text{Pd}. \tag{5}$$

For $x = 0.7$ we find $C_0 = 906$ volumes of gas per volume of metal, a value frequently noted in the literature.

3. Model of the Cylindrical Configuration (2D)

The numerical model uses a finite difference method and works as follows:

The cylindrical metal rod is subdivided into concentric layers (see Fig. 2). Initial temperature is $T_a = T$ ambient in the whole piece of metal. The initial H concentration is uniform along the radius and corresponds to the loading ratio PdH_x selected as input. H concentration at metal/air interface is considered zero at all time. There is therefore a concentration gradient that drives the H out of the metal. H_2O concentration on the surface is zero at all time. The model calculates by time steps, sufficiently small to guarantee the numerical stability.

All the hydrogen flowing out of the surface reacts with oxygen. Oxygen availability for the reaction is supposed sufficient without further analysis. The time constant of the reaction of the hydrogen adsorbed at the surface with oxygen is supposed to be negligible compared to the rate of diffusion of hydrogen towards the surface, so that the process is governed by the diffusion rate of hydrogen in the lattice. The heat of reaction Q_0 is split into several fluxes.

- Q_1: radiation loss to the environment,
- Q_2: convection in the surrounding air,
- Q_3: the balance modifies the temperature of the outermost metal layer.

The heat flow is computed in each layer to obtain the new temperature distribution. The coefficient of diffusion is recalculated at each step in each layer according to the new temperature.

The heat conductivities of palladium λ_{Pd} and air λ_{air} are constant, as well as the Pd heat capacity c. A more accurate model should revise these hypotheses, taking into account the influence of the temperature on the heat capacity and the heat conductivity. Another improvement would be to take into account the influence of the temperature and the hydrogen concentration on the heat of dissociation of the hydride, as shown for example in [8]. This sophistication is not introduced here.

This set of equations is introduced in the numerical model. The model gives the distribution of the temperature and hydrogen content in the rod at each time step. The evolution of the temperature along the time is also obtained.

The model is a finite difference explicit method written in Visual Basic. It is known that numerical errors introduced by this method are proportional to the time step and the square of the space step [9]. On the other hand, if the space step is diminished in an attempt to improve the accuracy, the time step must also be reduced, otherwise the numerical model is unstable. In our case a space step $\Delta x = 5 \times 10^{-4}$ m is sufficient to obtain a valuable result. The corresponding time step is $\Delta t = 10^{-3}$ s. Smaller space and time steps slightly increase the peak temperature calculated due to the chemical reaction but considerably increase the computing time. For example, for a 10 mm diameter rod with $\Delta x = 5 \times 10^{-4}$ m and $\Delta t = 10^{-3}$ s the peak temperature is 879°C. When Δx is divided by 2 and Δt by 4 the peak reaches 912°C. The difference is not considered essential in the present study because even the set of physical data used is an approximation. In any case, the exact behavior must depend on many parameters that are out of reach in such a model, like effective activity of the metal surface. The surface characteristics can be very different from one sample to another one. Assuming that all hydrogen atoms are immediately oxidized is a strong hypothesis. It may approximately correspond to the rare events when self-heating was observed. However, in most cases there is no heating, probably because the surface does not readily catalyze the hydrogen oxidation. This model is a simplified one that can only shed some light on the major phenomena that may occur. It cannot exactly predict the temperature evolution.

4. Simulation Results

Figures 3 and 4 show the temperature of cylindrical rods for different parameters. The temperature rises slowly during the first minutes, then very rapidly until a peak is reached. The temperature progressively returns to the ambient. The calculation shows that the temperature at each moment is practically uniform between the axis and the surface. Figure 3
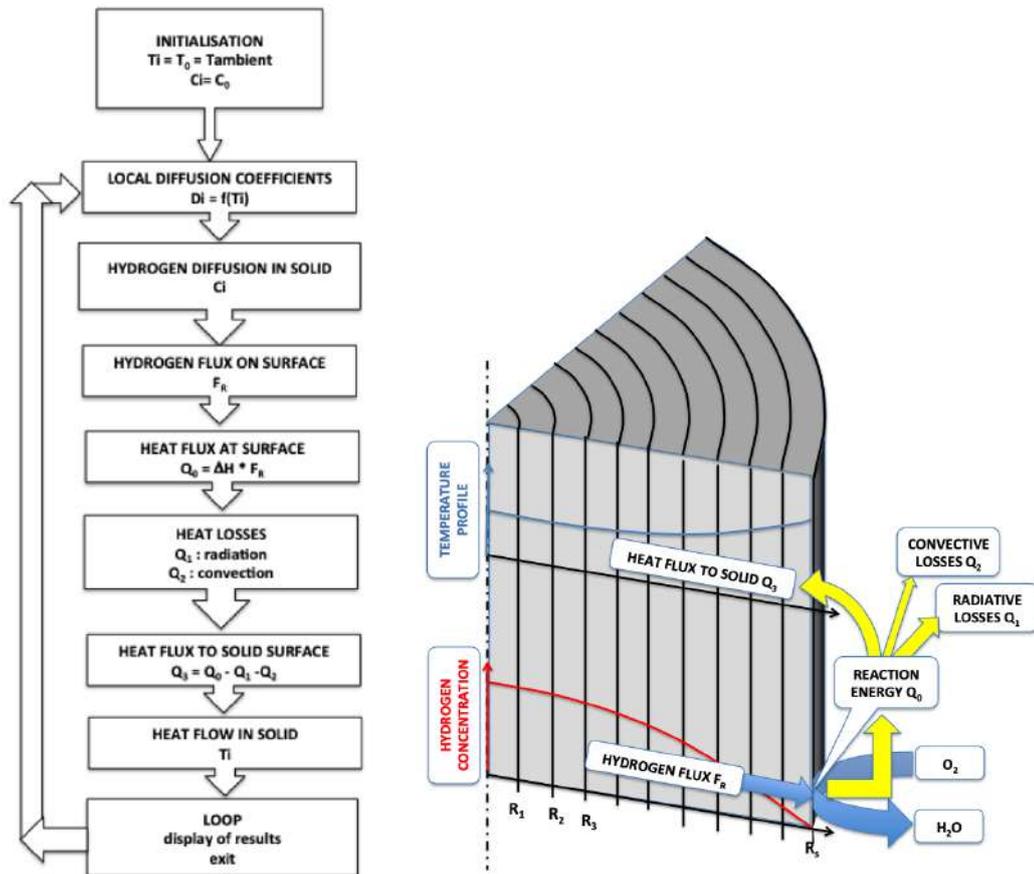
Figure 2.   Flow chart of the model and schematic representation (figure for a 2D configuration).

shows that the surface peak temperature is higher in the case of a 5 mm diameter rod than a 10 mm rod, but the heat burst lasts longer in the larger sample. Figure 4 shows that the process is faster and the peak temperature higher when the initial loading increases. This reflects the major influence of the temperature on the hydrogen diffusion coefficient.

Figure 5 illustrates the evolution in a 10 mm diameter rod of the local deuterium content for an initial loading of 0.5. The initial diffusion flow is largest near the surface because of the sharp concentration slope. The reaction progressively increases the temperature. The high temperature accelerates the diffusion rate, so that most of the hydrogen flows out within a few minutes. Once most of the hydrogen is gone, the temperature drops, and so does the diffusion rate. The end of the de-loading is slow.

Figure 6 shows the variations of the deuterium inventory in the metal with time. When the loading ratio is high the large peak temperature accelerates the diffusion. As a result, the final content after cooling down is lower when the initial loading increases. The same figure displays the gas content when the metal surface is supposed to remain cold. This can be the case if the surface is non-reactive so that the hydrogen does not react with air. The desorption is slow.
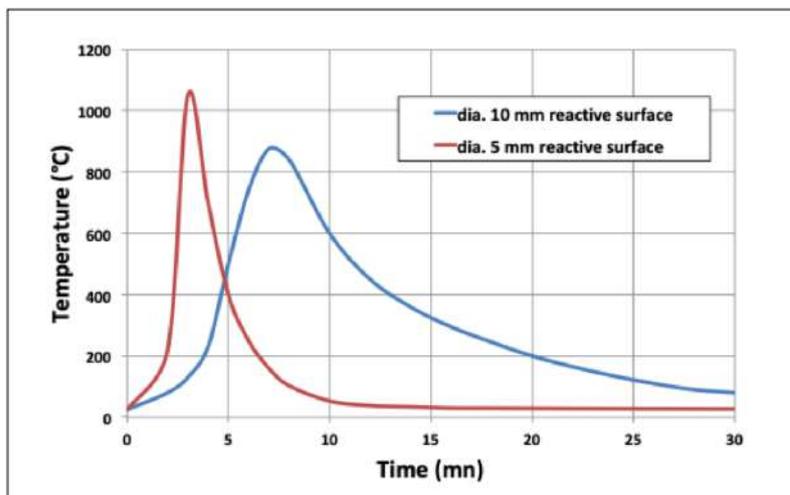
Figure 3.   Temperature evolution at the surface of different diameter rods – Initial deuterium loading ratio: $x = 0.9$.

The model was adapted for a 3D spherical configuration. In the case of a 10 mm diameter sphere with a deuterium loading ratio $x = 0.9$ the calculated peak temperature is 982°C instead of 875°C for a 10 mm diameter rod, and the peak is reached after 3 min instead of 7 min. Although the calculated values cannot be considered precise, the relative magnitude is probably meaningful.
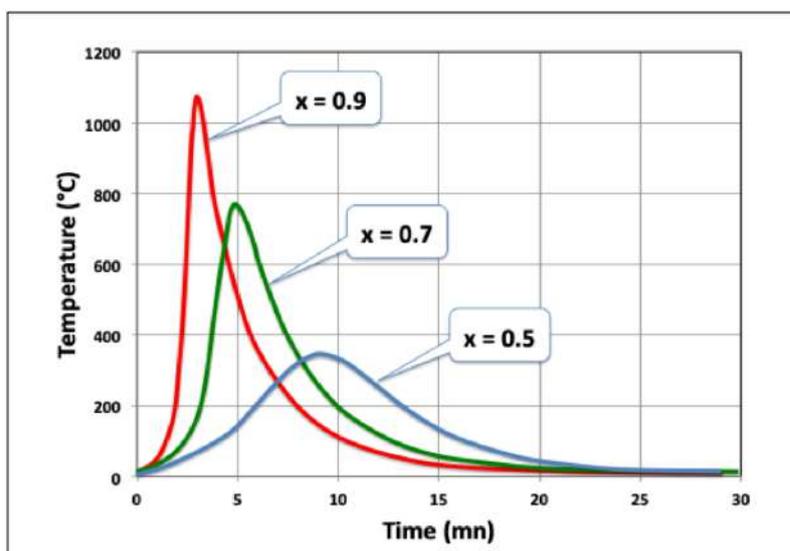

Figure 4.   Influence of the initial deuterium loading ratio – Rod diameter: 5 mm.
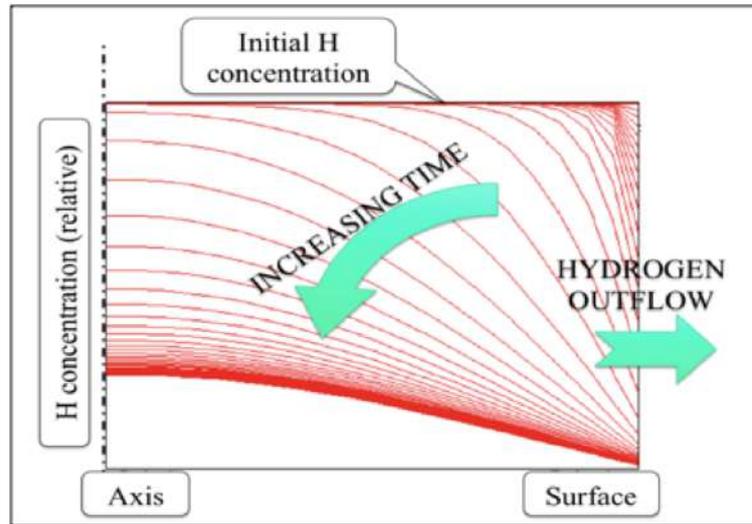
Figure 5. Example of evolution of the local deuterium content with time – Diameter: 10 mm. D distribution plotted every 30 s.

5. Conclusions of the Simulation

The model confirms what has been observed: A palladium sample loaded with hydrogen (or deuterium) can heat up when it is exposed to the air. The gas diffuses out of the metal and reacts at the surface with oxygen. The reaction increases the temperature of the metal. The higher temperature enhances diffusion, so that the process is
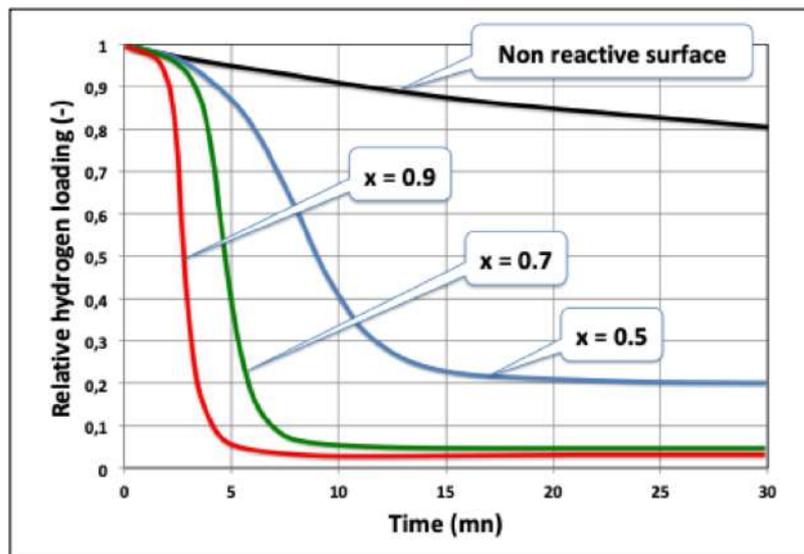

Figure 6. Ratio of the inventory of deuterium to the initial one. 10 mm diameter rod.

auto-accelerated. The reaction slows down once the hydrogen is depleted.

It remains to be clarified if the catalytic nature of the Pd is able to trigger the reaction of all the gas atoms coming to the surface or only a fraction of them, and if other conditions are necessary. Small samples heat up faster than large ones. The maximum temperature increases with the initial loading and the final hydrogen content left after cooling is lower. Cylinders and spheres react in a similar fashion, but the desorption is faster in 3D configuration (spheres) than in a 2D one (cylinders). Cubes being also a 3D configuration probably have the same behavior as spheres. The model is a simple one, so that the results presented here should only be considered as indicative.

6. Speculative Scenario to Explain the Meltdown that Occurred at Fleischmann and Pons Laboratory in 1985

In March 1985, Fleischmann and Pons were conducting an electrolysis experiment with a cathode made of a 1 cm cube piece of palladium. The cell exploded. There was no direct witness of the event that occurred at night during a weekend. This is acknowledged in the original Fleischmann and Pons paper [10]:

We have to report here that under the conditions of the last experiment, even using D_2O alone, a substantial portion of the cathode fused (melting point 1544°C), part of it vaporized, and the cell and contents and a part of the fume cupboard housing the experiment were destroyed.

Charles Beaudette describes the scene in his book [11]: *An early experiment consisted of a one-centimeter cube of palladium suspended in a flask of heavy water containing dissolved lithium metal*

Kevin Ashley was a graduate student of Pons in the chemistry department. He witnessed the scene the morning after the meltdown. This one morning I walk in, the door is open and Pons and Fleischmann are in the room with Joey. The lab is a mess and there is particulate dust in the air. On this lab bench are the remnants of an experiment. The bench was one of those black top benches that was made of very, very hard material. There were cabinets under one end of the bench, but the experiment was near the middle where there was nothing underneath. I was astonished that there was a hole through the thing. The hole was about a foot in diameter. Under the hole was a pretty good sized pit in the concrete floor. It may have been as much as four inches deep.

Because such damage requires a large amount of energy, it is often discussed within the CMNS community that this event was a strong evidence of nuclear reactions in this type of experiment. See for instance [12,13].

Another scenario is proposed here. This is admittedly a speculative one because there is no evidence left after so many years to prove it is correct. The experiment involved electrolysis "*in a flask of heavy water*" (see Fig. 7A). Electrolysis produces a stoichiometric mix of hydrogen and oxygen. This gas is highly explosive. In a previous paper, the author analyzed an explosion that occurred during a similar experiment [14]. The explosion can take the form of a rather benign deflagration. Under some circumstances, a phenomenon called Shock Wave Amplification by Coherent Energy Release (SWACER) transforms the explosion in a violent detonation able to develop shock wave pressures in excess of 40 bar. It is here supposed that the quantity of explosive gas contained in the cell was sufficient to detonate (Fig. 7B). The shock wave is stronger along its travelling path than on the other directions. If the shock wave was directed downwards it may have contributed significantly to the damage of the bench.

Once the cell was destroyed, the cathode fell on the bench, covered by debris from the explosion. It is further speculated that the palladium cube started to heat up, following the process explained above. The piece of metal kept hot for several minutes, sufficient to burn a hole in the bench, if it was not already broken by the explosion (Fig. 7C). All debris fell and accumulated on the floor, some covering the glowing piece of palladium. The concrete floor was subjected to a thermal shock during several minutes. In this scenario, the concrete may have exhibited some blistering (Fig. 7D). Further investigation could determine the relationship between the heat input and the extent of blistering. It is interesting to note that the large bas-relief at Stone Mountain near Atlanta was carved in granite via the use of oxy-fuel burners [15]. In this case the oxy-fuel burners produced sustained heating. It might be instructive to do some
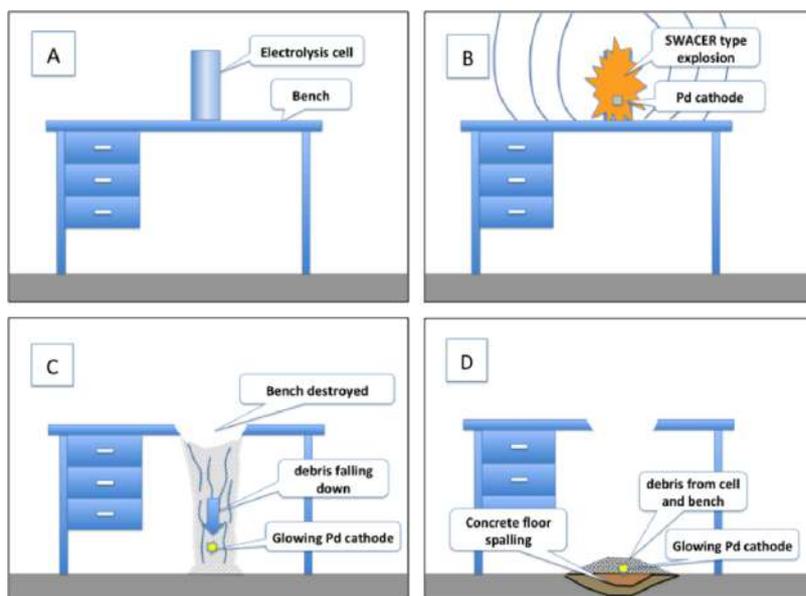
Figure 7. Potential scenario of the Fleischmann and Pons explosion event (A) Experimental setup, (B) SWACER type explosion in the gas phase of the cell, (C) debris on the floor and Pd self-heating and (D) spalling of the concrete floor.

tests to check if a piece of glowing metal can have similar effects.

7. General Conclusions

Palladium cathodes loaded with hydrogen or deuterium can heat up once exposed to air. Such events are rare but have been observed by several researchers. The simplified numerical model shows that temperature levels in accordance with the experiences can be attained. The process requires that the hydrogen present at the metal surface react readily with the oxygen from the air. The metal catalytic activity is the key that triggers the reaction (or fails to trigger it).

The combination of a detonation in the gas phase of the cell and of the self-heating of the palladium piece of metal may offer an alternative explanation of the event that occurred at Utah University in 1985 when Fleischmann and Pons were conducting an electrolysis experiment with a 1 cm cube palladium cathode.

Post-scriptum

The authors acknowledge they were tempted by David French to do this study. Unfortunately, David passed away on December 2, 2018. His co-authors want to dedicate this work to his memory.

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Comment by a Reviewer

This paper, like others from Ruer, is a valuable contribution to the literature on LENR. However, there is one aspect of the current paper that deserves additional consideration.

In Section 7, the author wrote "In March 1985, Fleischmann and Pons were conducting an electrolyze experiment with a cathode made of a 1 cm cube piece of palladium. The cell exploded." He also stated "Another scenario is proposed here. This is admittedly a speculative one because there is no evidence left after so many years to prove it is correct." It is unclear to this reviewer why the author speculates on the existence of an explosion, given the reports on damage caused by the event by eye witnesses and others, who have talked to eye witnesses of the damage. The damage to the bench under the experiment would require a tightly directed explosion. While explosions can be directed by confinement, as in a gun, or by using shaped charges, there were neither of those conditions in the Fleischmann–Pons experiment. An explosion in the head space above the electrolyte in the glass cell would most likely produce more or less isotropic damage. In the unlikely case that a propagating shock front did develop, what the author calls a Shock Wave Amplification by Coherent Energy Release (SWACER), it could have been directed either upward or downward, as he assumes. If directed downward toward the bench, the shock wave would have encountered the electrolyte, cubic cathode, anode and glass cell, which would have deflected some of the shock energy into a larger solid angle. That would have resulted in a lesser shock over a larger area on the surface of the bench. Hence, even if there was a downward directed explosion, its interaction with the experimental cell and its contents would have caused it to be much less focused. A broad hole in the bench was reported. But, that is at odds with what Fleischmann told Forsley, namely that the hole in the bench was about the diameter of a thumb.

The damage to the floor is better documented. It is noted in the autobiography by Chase Peterson, the President of the University of Utah at the time of the incident. This reviewer talked to Kevin Ashely about the event. He was a student in that building, who saw the damage to the Fleischmann–Pons experiment on the morning it was discovered.

He validated the reported diameter of about eight inches (20 cm) for the damage in the floor. That damage implies either of two scenarios. The first is a narrowly directed blast that made it through the bench, and still had enough energy to produce the reported damage in the floor in a very short time. The second possibility is much more likely. It is a hot piece of Pd burning a small hole through the bench, and then sitting on the concrete while continuing to produce nuclear energy. This second scenario is remarkable, but much more plausible than an explosion that, most likely, would have gone out in all directions.

In summary, this reviewer believes that it is wrong to invoke an explosion to explain the damage to the experiment, bench top and concrete floor. A runaway nuclear event in the cubic palladium cathode could have destroyed the cell, burned through the bench and damaged the concrete, if it continued to produce substantial heat for a significant time.