Research Article

Thermal Analysis of Explosions in an Open Palladium/Deuterium Electrolytic System

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Abstract

An explosion occurred in an open Pd/D electrolytic system at a low current density of 62 mA cm^{-2}. The average power was greater than 6.7 W (65 W cm^{-3} Pd or 430% of input power), and the incubation time was less than half an hour before the explosion. Thermal analysis indicates that the power of the explosion was 5.1–5.5 kW (or 50–53 kW cm^{-3} Pd), and the event developed in 2–17 s. It is concluded that this explosion was most probably caused by low energy nuclear reactions taking place in the Pd tube cathode rather than by chemical reactions.

Keywords: Cold fusion, CMNS, Explosion, Pd/D electrolytic system, Pd tube, LENR

1. Introduction

Since anomalous heat was announced by Fleischmann and Pons [1], there has been a great deal of research on Pd/D electrolytic systems [2]. Some explosions in various types of electrolytic cells have been reported [3–6]. The accident at SRI International was the most famous one; it was determined that this explosion was probably caused by deuterium and oxygen recombination [3]. However, data from explosions occurring in other labs indicate that some rapid exothermic reactions rather than chemical processes induced these phenomena [4–6]. In a previous paper, we summarized three explosions in our Pd/D electrolytic experiments which occurred in April 1991 [4]. After similar events take place

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again and again [5,6], it becomes incumbent upon a researcher to pay attention and analyze the results in detail. We did this and found some interesting features, which are presented here.

2. Electrolytic Cell and Explosions

The electrolytic system included a measuring cylinder with spout and foot ($\phi_{out}25.5 \times \phi_{in}23 \times 186$ mm^3, 77 m1, made of simple glass, not heat-resistant glass); ~ 0.4 M LiOD heavy water electrolyte (~ 39 m1 of D$_2$O with 0.3 wt.% of ^{6}LiD, ~ 9.4 cm of liquid height); a Pd tube[a] (ϕ_{out} 1.67 $\times \phi_{in}$ 1.07 $\times$ 80 mm^3, 0.103 cm^3, A_{out} = 4.20 cm^2, 1.3 g) cathode with the bottom end open, connected to a Ti wire lead inserted at the top end and mechanically clamped; a Pt mesh anode with a Pt wire lead, a round rubber plug platform holding the electrodes (ϕ_{top} 27 $\times \phi_{bottom}$ 21 $\times$ 22 mm^3, 15.5 g) being inserted about 12 mm into the measuring cylinder for sealing, except a blowhole ($\sim \phi$ 3 mm) to allow gas to escape freely, as shown in Fig. 1. Both the cathode and anode were immersed in the electrolyte before electrolysis. The cell was placed in a 1-liter glass beaker filled with 530 ml of light water, with the water level about 10 cm; the bath beaker was covered with a plastic annular lid. A thermometer was fixed at the lid; the sensor head of the thermometer was approximately halfway between the sidewalls of the electrolytic cell and bath beaker, and 2 cm above the beaker bottom, as shown in Fig. 1. The room temperature in the early morning of this season was 22°C; we will set this value as the bath temperature just before the explosion, because the record of the temperature was lost.
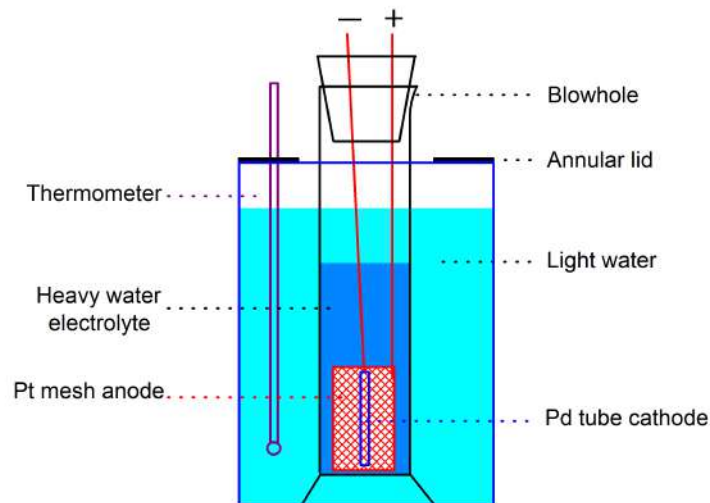

Figure 1.   Schematic of experimental set-up.

Three explosions happened in this Pd/D electrolytic system in April 1991. In these explosions, the rubber plug with the electrodes in it flew off about 1.5–3 m away, and electrical wires and alligator clips used to connect the DC

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[a]We measured the inner diameter of a Pd tube from the same batch as that used in this paper. It was 1.07 mm, and not 0.67 mm as listed in Ref. [4].
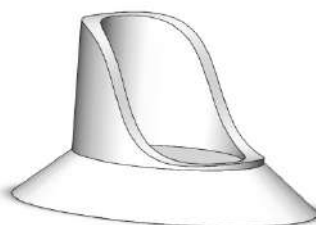
Figure 2. Artist's view of the fracture surface of the broken cell, based on memory.

power to the cell were left on the lab table. The ankle of cell broke as illustrated in Fig. 2. D_2O in the cell mixed with H_2O in the bath in the last case[b]. Because nobody was present at the scene of any of the explosions, there was no direct observation on any case except the last one having some records later as described below.

In the last event, the potentiostatic electrolysis with cell voltage of 7.5 V had continued for more than 50 h before the explosion. The applied current at the 50th hour of electrolysis was 0.26 A (or 62 mA cm^{-2}), which was slightly less than at the start. Voltage, current and bath temperature were manually recorded every hour and they were stable before the explosion. An experimenter (Da-Lun Wang) left the lab after the data recording at the 50th hour and came back half an hour later; the explosion took place during this period. It was found that the bath temperature had risen by 5°C. The rubber plug and the attached electrodes flew 2–3 m away and fell onto the floor. At the same time, one area in the middle-upper part of the Pd tube bulged out but the backside of this protruding section was not concave and the electrode was still as straight as before. This means this damage was not caused by any external force after the explosion but by an internal cause during the process. It was believed that the first two explosions were weaker than the last one because the cell remained intact and it only fell against the sidewall of the bath beaker in the first two. After these two cases, the plug was pressed firmly into the cell and this gave rise to a more violent explosion the third time. The last event will be discussed in detail.

3. Explosion Analysis

Firstly, we estimate the effect of electrolysis on thermal behaviors of this system. It is easy to determine that about 4.4 ml or 4.9 g of heavy water (a column of water in the cell $\sim$ 1.1 cm high) was consumed after 50 h of electrolysis; the height of electrolyte level in the cell was, therefore, 8.3 cm[c]. The heating power of electrolysis just before the explosion was: $P = I \times (U - 1.53 \text{ V}) = 1.55$ W, where 1.53 V is the thermoneutral potential for D_2O electrolysis. The temperature difference across the cell wall was:

$$\Delta T = \frac{Pt}{\kappa S} = 0.32°\text{C} \ll 5°\text{C}, \tag{1}$$

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[b]The statement that "the bottom of cell was blown out" in Ref. [4] is not accurate.
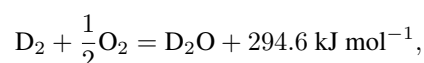[c]However, it is not sure if the cathode broke the meniscus of heavy water or not because all parts of cell were lost in home moving of lab afterwards.

where $t = 0.125$ cm, the thickness of glass sidewall; $\kappa = 9$ mW cm^{-1} K^{-1}, thermal conductivity of glass; $S = 66$ cm^2, the conduction area of the sidewall with the height of electrolyte level (8.3 cm). Therefore, the electrolysis power did not heat up the cell to a significant temperature rise before the explosion.

Based on the above conclusion and temperature measurement, the minimum excess energy released before the explosion would be the absorption heat of 530 ml of water and 34.6 ml of heavy water with a 5°C temperature rise: $\Delta Q = 12$ kJ. The heat dissipation after the explosion is omitted here.

Secondly, a simulation test conducted after the explosion showed that it takes 2.1 kgf to blow out the plug. This corresponds to an excess pressure $\Delta p = 0.5$ bar. That is to say, the minimum pressure in the gas column of the cell was 1.5 bar just before the explosion. Four possible situations might lead to such high pressure and explosion; we consider the first three of them trivial:

(1) **Blowout of sealed cell.** Provided the system was completely closed due to a mistake in the assembly process before electrolysis, the cell would explode due to inner pressure increasing. However, it would only have needed 7 min to attain the pressure of 1.5 bar, not the 50 h it actually took. Furthermore, the blowhole of the cell was clean without any deposit of solute. There was no process which could seal the cell during electrolysis and heat up the bath water effectively; therefore, the possibility that the cell was sealed can be excluded.

(2) **Chemical explosion by $D_2 + O_2$ recombination.** The volume of the gas column above the electrolyte in the cell head space just before the explosion was 38 cm^3, the related heat production ΔQ_{chem} can be calculated using the optimal D_2/O_2 mixing ratio:

$$D_2 + \frac{1}{2}O_2 = D_2O + 294.6 \text{ kJ mol}^{-1},$$

$\Delta Q_{chem} = 0.31$ kJ, which is much less than the actual value 12 kJ and could not heat up the bath water too. The following discussion also rules out the explosive recombination because the steam flow purged the D_2+O_2 mix. Therefore the real explosion could not be caused by any chemical reaction.

(3) **Short-circuit of electrodes.** This possibility can be excluded for three reasons. Firstly, the electrode leads were hard wires and connections of lead-electrode were strong; a short-circuit could not happen during electrolysis. Secondly, unlike what happens with utility AC power, a short-circuit of DC power would change the constant-voltage mode to the constant-current mode, and the supplied power would be lower than before; therefore, the heating power in the cell could not rise. Thirdly, even if the DC power supplied the cell with the maximum output power (e.g. several tens of watts), it could not reach 5.1–5.5 kW of thermal power, which is the amount deduced below.

(4) **Heat burst in the Pd tube cathode.** Because these prosaic reasons cannot explain the explosion, the only likely explanation was that a heat burst of low energy nuclear reactions (cold fusion) took place in the tube cathode; the released energy heated the heavy water to the boiling point and high vapor pressure developed in a short time; the vapor could not escape the cell effectively and the explosion occurred.

We can estimate that the minimum temperature rise in the cell just before the explosion was 75°C using parameters of the excess energy $\Delta Q = 12$ kJ and the remaining electrolyte volume of 34.6 ml, provided the excess heat only transferred to the bath water of 530 ml (in other words, we assume it was adiabatic). Based on the initial temperature 22°C, the electrolyte would be greater than 97°C, very close to the boiling point of heavy water, 101°C. This also indicates that the electrolyte was boiling during the explosion.

The boiling point of heavy water is 113°C at a pressure of 1.5 bar [7][d]; the vapor density $\rho = 0.966$ mg cm^{-3} and

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[d]The boiling point of electrolyte shifted upward 0.45°C due to 0.4 M LiOD is neglected here to be conservative [8].

vaporization heat $\Delta H = 2012$ J g^{-1} correspondingly. Based on Bernoulli's law, the steam velocity escaping through the cell's blowhole in such conditions is

$$\nu_{\text{hole}} = \sqrt{\frac{2\Delta p}{\rho}} = 330 \text{ m s}^{-1}. \tag{2}$$

This value is close to the speed of sound in air. The explosive power can be estimated by two methods: one is the kinetic calculation described previously [4] and the other is a thermal transfer analysis here.

There are two limits, one is the adiabatic approximation, i.e. the excess heat was produced so fast that the heat loss was only carried by the steam across the blowhole; the corresponding power is

$$P_{\text{ad}} = \frac{\pi \phi_1^2 \rho \nu_{\text{hole}}}{4} \Delta H_{T_0 \to T} \tag{3}$$

with $\Delta H_{T_0 \to T} = 2264$ J g^{-1}, the enthalpy change of D$_2$O from liquid at 22°C (T_0), 1 bar to vapor at 113°C (T), 1.5 bar [7]. Using parameters $\phi_1 = 0.3$ cm, $\rho = 0.966$ mg cm^{-3} and $v_{\text{hole}} = 330$ m s^{-1}, we obtain the steam power through the blowhole is

$$P_{\text{ad}} = 5.1 \text{ kW}. \tag{4}$$

Another limit is the isothermal approximation, i.e., the assumption that the temperature rise of the cell was so slow that a stable temperature distribution was reached between the cell and its environment, and the temperature field in the cell was uniform. With this approximation the thermal power just before the explosion would be

$$P_{\text{iso}} = \frac{\pi \phi_1^2 \rho \nu_{\text{hole}}}{4} \Delta H + \alpha A(T - T_0). \tag{5}$$

The first term on the right-hand side of Eq. (5) is similar to Eq. (3) except $\Delta H_{T_0 \to T}(2.246$ J g$^{-1})$ being replaced with the vaporization heat ΔH (2 012 J g^{-1}) at 113°C and 1.5 bar, it is 4.5 kW. The second term on the right-hand side of Eq. (5) is the cell's convection heat loss on the outer surface of sidewall immersed in water with area $A = 80$ cm^2, $T = 113$°C and $T_0 = 22$°C. α is the heat transfer factor:

$$\alpha = cRa^n \frac{\alpha}{h}, \tag{6}$$

where the constants c and n depend on the magnitude of Rayleigh number Ra [9]:

$$Ra = \frac{g\beta(T - T_0)h^3}{\nu\alpha} \tag{7}$$

with the gravitational acceleration $g = 979.75$ cm s^{-2}, the height $h = 10$ cm and water's parameters at temperature of $(T + T_0)/2$ [10,11]: the thermal expansion coefficient $\beta = 5.61 \times 10^{-4}$ K^{-1}, the kinematic viscosity $\nu = 4.32 \times 10^{-3}$ cm^2 s^{-1}, the thermal conductivity $\lambda = 6.65$ mW cm^{-1} K^{-1} and the thermal diffusivity $\alpha = 1.62 \times 10^{-3}$ cm^2 s^{-1}. We obtain the Rayleigh number $Ra = 7.3 \times 10^9$. The corresponding constant are $c = 0.1$ and $n = 1/3$ for $10^9 < Ra < 10^{13}$ [9]. The heat transfer factor is $\alpha = 0.129$ W cm^{-2} K^{-1} and the convection power in water is 960 W. On the other hand, the convection power in air is only 0.3 W and radiation power is only 11 W, we neglect them consequently. Therefore the thermal power just before the explosion under the isothermal approximation is

$$P_{\text{iso}} = 4.5 + 0.96 \approx 5.5 \text{ kW}. \tag{8}$$

These two different estimations give close amplitudes of explosion intensity; the actual power should be a value between these two approximations

$$P = 5.1 \text{ to } 5.5 \text{ kW}. \tag{9}$$

The explosion power density is

$$\frac{P}{V_d} = 50 \text{ to } 53 \text{ kW cm}^{-3} \text{ Pd}, \tag{10}$$

where $V_{\text{Pd}} = 0.103$ cm^3, the volume of Pd tube. Of course, this is only the minimum amplitude provided that the rate of anomalous reaction was uniform in the whole sample. Because of the localization characteristic of excess heat production as observed that one area of the Pd tube being strongly distorted after the explosion (see Section 2), the actual power density should be much greater than the value in Eq. (10). Considering the reaction region was confined in a length equal to the diameter of the Pd tube, the corresponding volume is 2.2×10^{-3} cm^3, then the local explosive power density is

$$\frac{P}{V_{\text{Pd . local}}} = 2.3 \text{ to } 2.5 \text{ MW cm}^{-3} \text{ Pd}. \tag{11}$$

Of course, the above values only characterize the explosive phase. It needs time to warm the cell from the bath temperature to the boiling point; we can estimate the lower limit of time for excess heat accumulation from total heat and the explosion power with the adiabatic approximation

$$t > \frac{\Delta Q}{P_{\text{ad}}} = 2.4 \text{ s}. \tag{12}$$

However, the electrolyte would boil away under this high power in a short time; we can estimate the time to boil dry is

$$t_{\text{dryout}} = \frac{m \Delta H_{T_0 \to T}}{P_{\text{ad}}} = 17 \text{ s} \tag{13}$$

with $m = 38$ g, the mass of electrolyte at 50 h of electrolysis. This means that a high power in the order of kilowatts could not continue for tens of seconds; otherwise, the cell would dry out and explosion would not occur. The time of thermal run-away should be

$$2.4 \text{ s} < t_{\text{run-away}} < 17 \text{ s}. \tag{14}$$

Referring to Mizuno's explosion [5], the developing time of cell's temperature increase from the ambient value to the boiling point was only ~ 17 s. It seems the corresponding time in our cases also is in the same order of magnitude.

The upper limit of incubation time should be half an hour as described in Section 2. Using this time scale, we obtain the lower limit of excess power is 6.7 W or 430% of input power, the corresponding power density is

$$\frac{\bar{P}}{V_d} = 65 \text{ W cm}^{-3} \text{ Pd}. \tag{15}$$

4. Discussion

We can reconstruct the explosion process based on the above analysis. We can infer that the explosive process was probably caused by low energy nuclear reactions. At first, one local region of Pd tube electrode met some unknown criteria to produce intense cold fusion. The exothermic reaction released energy and heated up the cathode and the surrounding electrolyte. The positive feedback between temperature and reaction rate promoted the excess power to increase exponentially with time. After about ten seconds, the excess power was so great that the temperature at the nuclear reaction region (< 1 mm^3) of Pd tube rose to more than one thousand Celsius degrees and the metal lattice distorted strongly as observed afterwards due to thermo-stresses; the surrounding heavy water vaporized, and the electrolyte boiled. When the excess power was so high that the cell produced steam which could not escape through the cell's blowhole efficiently, the inner pressure rose rapidly and exceeded the threshold value, 1.5 bar. At that moment, the excess power reached 5.1–5.5 kW. The explosion followed: The plug was ejected, the D$_2$O temperature dropped instantly from 113 to 101°C, the ankle of cell was broken due to thermo-stresses in the wall of cell as illustrated in Fig. 2. All three of these processes happened at almost the same time, so we will not deal with them separately. The remaining electrolyte in the cracked cell mixed with the water in the bath and the mixture's temperature rose by 5°C. It must be pointed out that because some hot heavy water escaped in the form of vapor as shown in Eqs. (3) and (5), the value of 12 kJ is an underestimate of the actual energy release. On the other hand, although the D$_2$O bubbles probably ejected liquid out of the cell, which might fall back in the water bath; however, this effect only slightly modified the overall heat of 12 kJ, but it did not qualitatively changed the conclusion.

When we review this explosion 24 years later, it reveals more details that were omitted at that time.

Firstly, the system was operated at a current density of 62 mA cm^{-2}, which was lower than the well known threshold value of 100–150 mA cm^{-2} for excess heat production [2]. Excess heat at low current densities of 44–53 mA cm^{-2} were also reported by one of the authors 9 years after this explosion [12]. These facts indicate the requirement of current density for excess heat production may be lower than previously thought.

Secondly, although the loading ratio of deuterium in the cathode was not measured in this experiment, the D/Pd was probably not high for two reasons: (i) The current density applied here was less than in most cold fusion experiments that produce excess heat; (ii) The tube cathode had only the outer surface polarized during electrolysis. The inner surface had much low current density due to deuterium gas formation and high resistance of electrolyte in the tube. This means that deuterium absorbed on the outer surface would be desorbed on the inner surface. Therefore, the loading ratio of deuterium in the tube electrode was probably less than that of a solid electrode with the same area of outer surface. These facts may indicate that the threshold value of the loading ratio for excess heat production is not a necessary condition as reported later [12].

After these explosions, a video recorder was installed to monitor the electrolytic cell and obtain more information on explosions. However, no explosion ever occurred after that.

Obviously, the explosion here is similar to that in a W–H$_2$O electrolytic system observed by Mizuno [5]. The same features are the prominent excess heat and probably the rapid development time.

There was also an explosion in a Pd/D electrolytic system at SRI International [3]. Because it was a closed system and parameters are complex, we cannot reach a clear conclusion as here. Biberian reported the explosion in a similar open Pd tube/D electrolytic cell at low current [6]; we tend to conclude this was the same event as we experienced.

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