Anomalous effects in hydrogen-charged palladium — A review

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Abstract

There are more than 10 groups worldwide that have reported the measurement of excess heat in 1/3 of their experiments in open and/or closed electrochemical cells with a Pd solid metal cathode and deuterium containing electrolyte, or D₂ gas loading of Pd powders (see Table 1 of the main text). Most of these groups have occasionally experienced significant events lasting for time periods of hours to days with 50–200% excess heat measured as the ratio between electrical input energy and heat output energy. Moreover, these experimenters have improved their methods over time and it is to be noted that the reported excess heat effect has not diminished in frequency or magnitude. This paper cites selected data generated over the past 15 years to briefly summarize what has been reported about the production of excess heat in Pd cathodes charged with deuterium. A set of new materials experiments is suggested that, if performed, may help to reveal the underlying mechanism(s) responsible for the reported excess heat.

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1. Introduction

Fig. 1 is a schematic diagram of a modified, planar geometry Fleischmann and Pons cell presented here to review its main features [1]. A Pd cathode plate positioned between two parallel Pt-plate anodes are immersed in electrolyte (0.1 M LiOD in D₂O). Voltage applied between the electrodes causes hydrogen to enter the cathode. Hydrogen that evolves from the cathode and oxygen that evolves from the anodes are recombined by a catalyst residing above the liquid in closed cells, and allowed escape in open cells. A thermocouple measures the temperature of the electrolyte. The H/Pd ratio of the cathode is measured in situ by means of a four-point probe resistivity ratio R/R₀, where R₀ is the initial resistivity value, and the R/R₀ versus H/Pd is compared to literature values. This in-situ monitoring of the hydrogen concentration in Pd was not in use in the first year after the Fleischmann and Pons announcement [2]. Details of calorimetry will not be discussed in this short review.

Motivated by the report of excess heat by Fleischmann and Pons [1], a number of research groups from around the world have been conducting experiments on the Pd–D materials system more or less continuously since 1989. Considerable progress has been made on several fronts that include improved reproducibility of high loading (i.e., D/Pd > 0.90) of deuterium...
in Pd cathodes, improved reproducibility of measured excess heat in highly deuterium-loaded Pd cathodes, and improved in-situ measurement of the status of the Pd cathodes [2]. The materials science of hydrogen loading is now well enough understood that it may offer a reason why the many groups that tried to reproduce the heat effect in 1989–1990 were unsuccessful. Less encouraging are the facts that there is still no viable physical mechanism to explain the heat effect, and triggering the heat effect is still not empirically understood.


Many research groups attempted to reproduce the excess heat production and the neutron and gamma ray signals reported by Fleishmann and Pons in the year following their spectacular announcement. The nuclear data that Fleishmann and Pons presented proved to be in error and have never been reproduced. However, there remains the possibility that their excess heat production results may have been correct. One reason that most researchers were unsuccessful in achieving heat production may have been at least in part due to the lack of understanding of how to achieve H/Pd ratio of >0.90. Procedures required to achieve this loading [3] that were not generally known or followed include:

- Pd cracks under loading (~4% vol. change), especially for pure, annealed Pd, and the internal surface area of cracks are recombination sites for hydrogen and deloading in the cracks competes with electrolytic charging and the net loading is <0.9.
- Pd must be strengthened and toughened by alloying or mechanical treatment to avoid surface cracks.
- Pd must have an optimum grain size to load. H entry is primarily along grain boundaries.
- Pd must be loaded gently (gradually or cycled in current) or it will crack even after the above cathode preparation steps (loading time diffusion time).

Achievement of high loading with D is many times more difficult than for H.
- Catalytic surfaces are easily contaminated and often will not maintain water electrolysis efficiency over the time that is required for high H loading.

Unable to achieve high loading, and, therefore, excess heat, most researchers declared that heat production in Fleishmann and Pons cells is not a real effect and ceased working on the experiments.

3. Summary of past work

Table 1 is a partial list of groups that have measured excess heat in the palladium deuteride material system [4–13]. Previous work by many researchers has determined some necessary but not sufficient conditions to observe excess of heat [14]. These are:

<table>
<thead>
<tr>
<th>Research group</th>
<th>Institution</th>
<th>Cathode type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fleischmann</td>
<td>University of Utah</td>
<td>Rod</td>
<td>[1] (1990)</td>
</tr>
<tr>
<td>Oriani</td>
<td>University of Minnesota</td>
<td>Rod</td>
<td>[9] (1990)</td>
</tr>
<tr>
<td>Will</td>
<td>University of Utah</td>
<td>Rod</td>
<td>[12] (1990)</td>
</tr>
</tbody>
</table>

Abrupt changes in any of these parameters can stimulate the production of excess heat with greater frequency than a system maintained at steady state. It has been empirically found that a He–Ne laser (~10 mW CW) impinging on the Pd surface can stimulate the excess heat effect as well [15]. Two emerging trends are, that the incubation time for heat production decreases as the cathode volume decreases, and, that increased surface-to-volume ratio increases the specific energy/mass value of excess heat production.

4. Recent examples of excess heat

Two examples cells that are reported to produce excess heat are presented in the next 3 figures. In Figs. 2, 3 and 4, the cell was in a planer geometry (as in Fig. 1), closed system with 100 μm thick, ~4-cm²-area Pd foil, and run in current control mode. Fig. 2 shows time versus input power on the right ordinate and versus integrated energy on the left ordinate.
control cell in which the electrolyte is H₂O in 0.1 M LiOH [11]. Input power is determined by measurement of current and voltage and output power is measured by calorimetry. Note the time lag of response of the input and output power that is characteristic of the time constant of the calorimeter. The total integrated input energy is a well-behaved straight line, and the integrated output energy shows a curve that is below the input energy and is characteristic of small energy losses due to the 97% efficiency of the calorimeter.

Fig. 3 shows time versus excess power (output power–input power) on the right ordinate and integrated energy on the left ordinate, for a cell identical to that in Fig. 2 and in which the electrolyte is D₂O and 0.1 M LiOD [11]. At time 25,000 s, the cell begins to display excess power that behaves erratically until the cell is turned off. The integrated input energy monotonically increases and the integrated output energy initially displays a transient often seen as the cell heats up due to the initial turn on and is dependent on the initial cell temperature and input power history. The integrated output energy rises faster at the time the excess power is observed, and rises above the input energy by the end of the run. Taking into account the 3% energy loss of the calorimeter, this cell displayed a total of 8% excess power in the form of heat for the duration of this experiment.

Fig. 4 shows input and output power versus time for a cell in which the electrolyte is D₂O and 0.1 M LiOD. The input power was cycled between high and low values. At 220,000 s, the cell begins to display excess power that continues until the experiment is shut down. This cell produced 50% excess power, or 2.2 net W, averaged over a period of 12 days [6].

The primary criticisms of experiments that measure heat production during electrolysis of Pd in deuterium containing electrolytes are:

1. Energy is stored by some as yet unknown but straightforward mechanism during long incubation times and then released (battery).
2. Excess heat due to recombination of oxygen and hydrogen in cell (battery).
3. Calorimeter is not calibrated correctly (experimental error).
4. Energy inventory not measured correctly (experimental error).

Criticisms 1 and 2 are stored chemical energy explanations. Number 1 appears to be questionable since incubation times in some experiments that use small volume cathodes are as short as a few minutes and experiments that integrate the total energy do not detect endothermic processes that would signal energy storage prior to excess heat release. Number 2 appears to be questionable since excess heat has been measured in many closed-cell experiments where the energy from recombination of hydrogen and oxygen is continuously recovered. Individual experiments can always be criticized as having experimental errors and one might conclude that all researchers in Table 1 make similar subtle mistakes in order to refute their reports of excess heat. One might also conclude that there is ample evidence that excess heat is produced under certain conditions, and, that the results in Table 1 are consistent over time and collectively suggest that a closer look at this materials system is warranted.

5. Material properties of Pd at high hydrogen concentration

While there was a flurry of activity in the 1980s concerning superconductivity in Pd–H alloys, most of the research at that time involved hydrogen concentrations far less than Pd/H ratio of 0.90. The remainder of this paper discusses experiments that if done, could shed light on possible mechanism(s) that produce excess heat.

First, it is desirable to perform detailed tracking of the morphological and impurity changes to the cathodes and anodes ex situ before and after charging with hydrogen using a variety of methods such as SEM, XRD, XRF and ICP-OES, to name a few.

Second, in-situ experiments are necessary since electrochemical loading is one of the few methods to achieve high loading. Once the cell voltage is turned off, the hydrogen evolves from the cathode very rapidly, so ex-situ experiments on this material are impractical. In-situ experiments require propagation of signals into the liquid to the Pd foils and return. This restricts the signals that can be used to X-rays, gamma rays, neutrons and light waves in the transmission band of water, and to transducers at or near the foil.

Third, a reproducible materials system for such experiments is an absolute necessity. Fortunately, such a reproducible Pd cathode material has emerged from the work of group headed by V. Violante. His group has performed metallurgical studies of the effects of mechanical treatment and annealing on the ability to electrolytically load Pd foils with hydrogen [16,17]. Following Violante’s procedures, it is now possible to load Pd foils up to H/Pd > 0.90, with 100% reproducibility.

Armed with a reproducible Pd-H alloy materials system, what experiments can or should be performed? The following suggested experiments are by no means an exhaustive list, but do represent a cross-section of experiments that investigate different aspects of this material system.

1. Tensile stress — the first-order materials parameter of pressure and its related quantity tensile stress has never been investigated. Use of in-situ tensile apparatus on the cathode would assess the primary effect of stress on the loading, voltage, current, and temperature characteristics of the basic loading experiment and would characterize the stress behavior of this material system in any of the suggested experiments below.

2. High-energy X-ray scattering — this experiment monitors the Pd lattice as the hydrogen concentration increases. It will measure lattice expansion and any phase changes that might occur around Pd:H ratios of 1:1. This experiment has been performed only up H/Pd ratio of 0.76 [18,19].

3. Neutron scattering — this technique characterizes the deuterium sub-lattice positions and provides information on Pd and D phonons with inelastic scattering. This experiment cannot be performed with hydrogen due to the 9× shorter neutron scattering length in H2O compared to D2O.

4. Radioactive isotope spectroscopy — it has been suggested that a nuclear process is responsible for unusual effects in PdD [1]. This experiment turns this supposition on its head by purposely injecting isotopic material into experiments. One introduces a radioactive isotope or isomer into the Pd by thermal diffusion, and observes the effects of the PdD environment, if any, on gamma and X-ray radiation emitted from the decay of the excited nuclei. For example, one might observe a small energy shift, or change in the lifetime of the isomer at high loadings that would signal a chemical effect on the nuclei. Such influences have been observed [20], and this would be a survey experiment to determine if there are unusual excitations in this materials system that affects the nucleus directly. Candidate isomers are 270-day half-life 57Co electron capture decaying to 57Fe, and 2.7-day half-life 198Au Beta decaying to 198Hg. Both have relatively low energy gamma lines (14–412 keV), and Au also produces a 70 keV X-ray that probes the electron K-shell of Hg. Other candidates are 367-day half-life 106Ru Beta decaying to 106Pd emitting ~600 keV gammas, and 4-day half-life 100Pd electron capture decaying to 100Rh emitting high-energy gammas. All four isotopes are soluble in Pd. An alpha emitter might be monitored by Pd K X-ray excitation.

5. Mössbauer spectroscopy [21] — The isomer 57Co is commonly used to explore the hyperfine fields [22] acting at the 57Fe nucleus in solids. One can survey effects of H environment...
on magnetic and/or electric quadrupole hyperfine fields caused by distortion of the electron cloud in ns time resolution. In particular, the isomer shift, δ, indicates the degree of s-electron distortion that might be caused by the PdH lattice and excitations therein. It also can provide the magnitude of electric and/or magnetic field at the Fe nucleus. An external magnetic field is required for hyperfine magnetic studies.

6. Perturbed angular correlations (PAC) [21] — Internal hyperfine fields can be measured using gamma–gamma coincidence techniques on gamma emissions from radioactive isotopes diffused into Pd. A candidate is 367-day half-life \(^{106}\text{Ru}\) that Beta decays to excited \(^{106}\text{Pd}\) that emits gamma rays in a 624 and 512 keV cascade in time coincidence. The electric quadrupole moment of the excited state couples to the hyperfine electric field and processes. Measuring the time dependence of the anisotropic angular distribution of the emitted gamma rays captures this precession. One can obtain the lattice location of the Pd and the electric field acting at the Pd nucleus. This would assess possible disturbance of the s-electron orbitals around the nucleus that might be caused by the present of hydrogen in the lattice with time resolution of nanoseconds. Another candidate is 2.8-day half-life \(^{111}\text{Cd}\) that emits 419 and 247 keV gamma rays in time coincidence. Many others are possible.

7. Nuclear acoustic resonance (NAR) [23] — It has been suggested that acoustic excitation of PdD can trigger heat producing events. The NAR technique is usually used in conjunction with nuclear magnetic resonance (NMR). NMR is not well suited to metals and conducting liquids. However, NAR or just acoustic resonance can be used in conjunction with all of the experiments listed above, to assess the influence of natural acoustic resonance in the PdD determined by internal friction mechanisms and/or the geometry of the cathode. Natural resonances (up to hundreds of kHz) in the cathode excited using an in-situ or ex-situ acoustic transducer, can exchange energy with phonons and defects in the cathode that may influence the measurements 1–6 above.

6. Summary and conclusions

In this paper reports of anomalous heat in the materials system of highly hydrogen-loaded Pd were selected from the literature and highlighted. It was suggested that evidence for anomalous heat effects is now strong enough to warrant fundamental investigations of this system. Based upon the availability of new reproducible Pd–H foil materials with H/Pd ratio >0.90, a case was made that these foils could be a reliable platform for the exploration of the Pd–H system at high hydrogen fractions with a variety of sophisticated in-situ materials science techniques. A selected list of possible experiments was presented that if executed, may help to reveal the underlying mechanism(s) responsible for the excess heat data. The experiments would provide fundamental materials data on the primary phases and lattice position of the Pd and H, phonon modes of the H sub-lattice, stress-modified H-diffusion, influence of the H-rich chemical environment on nuclear decay, electron cloud distortion around the nucleus, electric and magnetic hyperfine fields at impurity nuclei and Pd, time dependence of these fields with nanosecond resolution, and the effect of acoustic waves on nuclear alignment in external and hyperfine fields. Individuals acting in isolation could not conduct these experiments. They require sophisticated experimental infrastructure, interested participants acting as a team, and sustained financial support.

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[13] Unpublished work. These laboratories are no longer working due to lack of institutional and funding support in the case of the government laboratory, and due to lack of funding in the case of the company. Their inclusion in this list is subjective and is based on my personal viewing of their data and operation of their experiments.
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