Research Article

Excess Power Measurements for Palladium–Boron Cathodes

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Abstract

Palladium–Boron (Pd–B) cathodes prepared at the US Naval Research Laboratory have produced electrochemical excess power effects using D_2O + LiOD electrolytes in nine of ten experiments conducted at three different laboratories and using three different types of calorimeters. The one failure was due to a structural defect in the Pd–B cathodes. An unusual result is the early appearance of the excess power effect for Pd–B cathodes. Three other research groups have also found excess power effects using these Navy Pd–B cathodes. Possible important factors for Pd–B electrodes are the removal of oxygen by the boron during processing, the increased mechanical strength versus pure palladium, less volumetric expansion of these electrodes during loading with deuterium, and the much slower escape of deuterium from this cathode.

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1. Introduction

One of the major goals of the US Navy program (Anomalous Effects in Deuterated Materials, 1992–1995) funded by the Office of Naval Research (ONR) was to produce our own palladium cathode materials at the Naval Research Laboratory (NRL). It was obvious at that time (1992) that the major problem in reproducing the Fleischmann–Pons (F–P) excess power effect in the Pd/D system resided within the palladium material. However, none of these Navy palladium metals and alloys were successful in producing significant excess power during the first two years (1992–1993) of this Navy program. This changed in 1994 with the NRL preparation of palladium–boron (Pa–B) alloy cathodes. Seven out of eight experiments using these Pd–B cathodes produced significant excess power in calorimetric experiments at the Navy laboratory at China Lake, California (Naval Air Warfare Center Weapons Division, NAWCWD). A different NRL Pd–B cathode produced excess power in 1997–1998 at the New Hydrogen Energy Laboratory (NHE) in Sapporo, Japan. An experiment in 2017 using this same Pd–B cathode again produced excess power at a Ridgecrest, California

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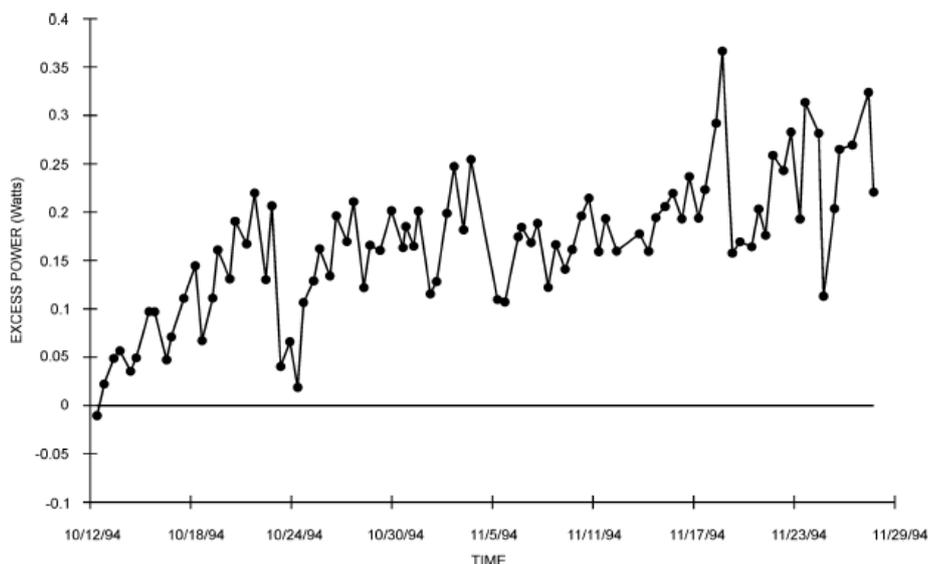
Figure 1. Excess power measurements for an NRL Pd–B rod (0.25 × 2.5 cm, 0.75 wt.% boron).

location. Two US Patents have been granted for this unique NRL Pd–B material [1]. These patents provide details on how these Pd–B materials were prepared.

2. China Lake Results, 1994–1995

These eight experiments at China Lake using the NRL Pd–B cathodes are documented in a Navy Report [2]. Figures for each experiment show the measured excess power for several different times each day. An example for one of the best experiments is shown in Figure 1.

A gradual increase in the excess power was observed over a 45-day time period and reached a maximum of about 350 mW. The total excess energy produced in this experiment was 636 kJ or 5.2 MJ per cubic centimeter of the Pd–B material.

Four isoperibolic calorimeters (A–D) of the same basic design as shown in Fig. 2 were used in these Pd–B experiments. Results for all eight experiments at China Lake are summarized in Table 1.

Table 1. Summary of China Lake Pd–B Experiments (1994-1995).

| Start date	Calorimeter	Pd–B dimensions (cm)	Weight % B	Maximum excess power (mW)
5/28/94	B	0.60 × 2.0	0.75	300
10/24/94	B	0.60 × 2.0	0.75	450
10/12/94	C	0.25 × 2.5	0.75	370
10/12/94	D	0.25 × 2.5	0.75	100/0
3/14/95	A	0.40 × 2.0	0.50	140
3/14/95	B	0.40 × 2.0	0.50	240
3/14/95	C	0.40 × 2.0	0.25	220
3/14/95	D	0.40 × 2.0	0.25	90
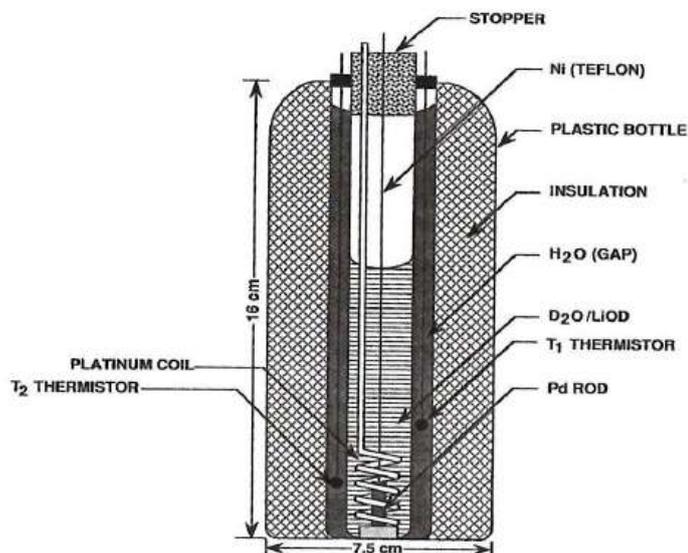
Figure 2. China Lake calorimetric design used for the Pd–B experiments (see [3,4]).

The structural defect for the Cell D (10/12/94) electrode (Table 1) was a folded metal region along almost the full length of the cathode similar to a crack which would be devoid of active electrochemistry. Even this cell showed a maximum of 100 mW in excess power, but most results were nearly evenly distributed between the normal three sigma calorimetric error range of ± 30 mW. Cell D (3/14/95) showed a brief 5-day initial period of excess power, but this promising start suddenly ended due to some unknown factor.

The small volume of this Pyrex glass calorimetric cell (18 mL of electrolyte) made it sensitive to temperature changes due to changes in the input power. Thermistors were used to measure the cell and bath temperatures to within 0.01 K [3,4].

3. Japan Pd–B Results, 1997–1998

An appointment at the New Hydrogen Energy Laboratory (NHE) in Sapporo, Japan, for one of us (M.H. Miles) led to another study of a different NRL Pd–B electrode. This material contained 0.50% B by weight (Pd–0.5B) with rod dimensions of 0.47×2.01 cm. This new study was conducted in a Fleischmann–Pons Dewar calorimeter labelled ICARUS-1 with inner dimensions of 2.5×25.0 cm with the top 8.0 cm silvered. This glass Dewar cell contained 90 mL of 0.1 M LiOD. Calibrated thermistors gave the cell temperatures at two different cell locations to within 0.001 K. Calorimetric measurements were recorded every 300 s throughout this experiment. The analysis of the calorimetric data while in Japan [5] showed the same basic features for excess power versus time as later reported by Fleischmann in his independent and more compete analysis [6]. The peak excess power reached 460 mW (Ref. [6], Fig. A.19). Moreover, during the final cell boiling phase the excess power exceeded 9 W (Ref. [6], Fig. A.22). During the cell boiling, the Pd–0.5 B cathode was obviously the hot spot in the cell based upon the observation of the intense boiling and swirling action centered around this cathode over a three-hour period. This NHE experiment produced a total excess energy of 1.065 MJ over the 67-day period prior to cell boiling or 3.05 MJ per cubic centimeter of the Pd–B
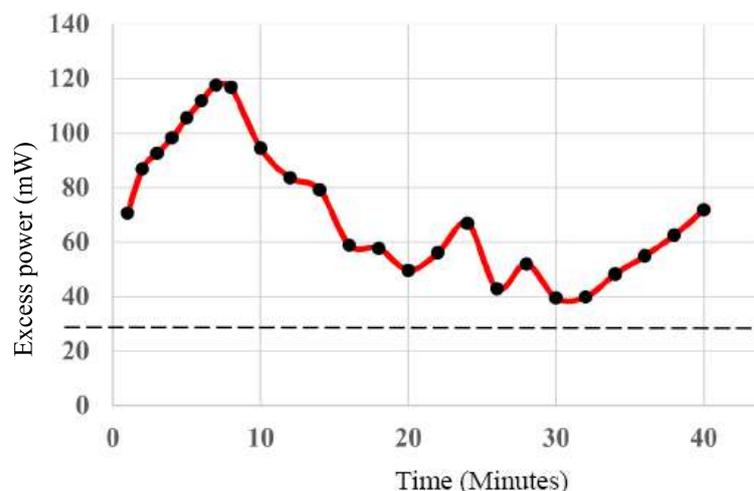
Figure 3. Early excess power for Pd–0.5 B with a peak of 118 mW at 7 min. The dashed line shows the maximum excess power possible due to deuterium loading at 0.150 A.
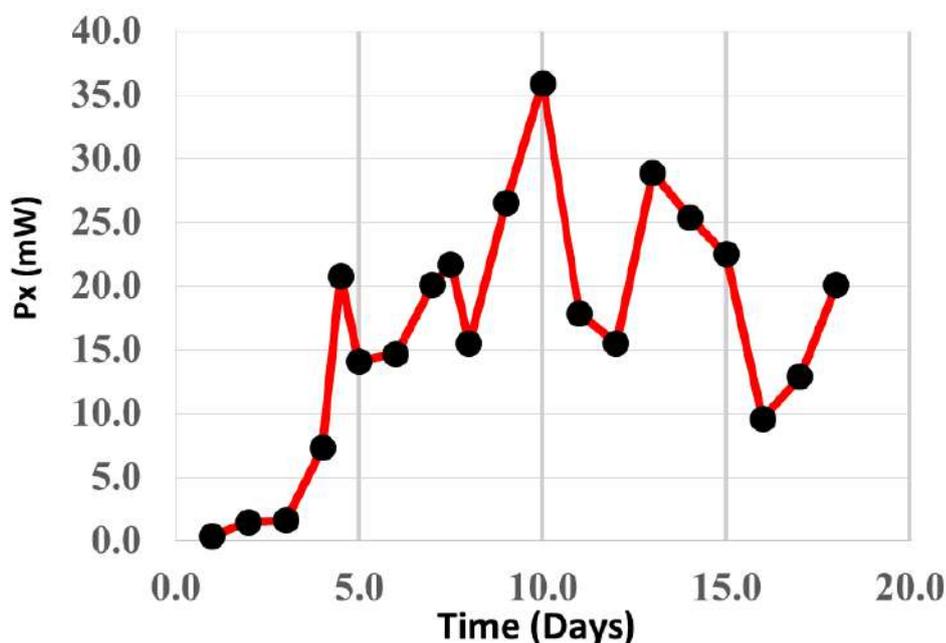
electrode [6].

An unusual feature of this Pd–0.5B experiment was the very early onset of the excess power effect. This early excess power was even measurable during the initial deuterium loading of the cathode (Ref. [6], Fig. A.21) and was well in excess of the maximum power possible (27 mW) for the exothermic loading of deuterium into palladium (–35.1 kJ/mol D_2) based on the applied current (0.150 A) and formation of $PdD_{0.6}$. This NHE Pd–0.5 B study gave an early mean excess power of 57 mW for the first 55 min and remained above 27 mW for the entire loading period of about four hours [6].

4. Ridgecrest Pd–B Results, 2017

The experiment conducted at Ridgecrest, California used the same Pd–0.5 B cathode as was used in Japan in 1997–1998. However, a different calorimeter was used consisting of two concentric copper tubes separated by insulation material as described elsewhere [7]. The most remarkable feature of this experiment was the very early appearance of excess power as shown in Figure 3. The dashed line in Fig. 3 shows the maximum excess power (27 mW) which could result from the exothermic loading of palladium with deuterium at the experimental cell current of 0.150 A assuming that the total cathodic current is used for the formation of $PdD_{0.6}$. The NHE and Ridgecrest experiments used the same Pd–0.5 B cathode but different calorimeters and gave similar results for the early excess enthalpy measurements. Both experiments gave more than double the excess enthalpy expected for the deuterium loading (–416 J). The measured values were –928 J for the Ridgecrest experiment and –1085 J for the NHE study assuming a loading period of 336 min for each. Any chemical reaction with boron would require about –260 kJ/mol B to explain this extra excess enthalpy. Additional measurements showed a decreasing excess power effect down to 18 mW at 336 min and near zero for the following day (Day 1 in Fig. 4).

The correct explanation for this early excess power using Pd–B cathodes is unknown. Possible explanations include chemical reactions involving boron or perhaps even a deuterium + boron-10 fusion reaction. Boron may somehow be an essential catalyst for the F–P excess heat effect. Normally, long electrolysis times may be required for boron in a Pyrex glass cell to be properly transferred to the palladium for cathodes not containing added boron. For Pd–B

Figure 4.   Daily averages for excess power (P_x) in the Pd–0.5 B Ridgecrest experiment of 2017.

electrodes, this catalyst would already be present at the beginning. The most likely explanation of the very early excess power shown in Fig. 3 is presented in the Appendix.

The measured excess power for other days of this Ridgecrest Pd–0.5 B experiment is shown in Fig. 4. The calorimetric results are accurate to within a few milliwatts of excess power ($\pm$ 3 mW), but the effect is much smaller than previously observed in Japan. This could be due to problems with the evolution of gas bubbles. Gas bubbles in this experiment tended to collect at the bottom of the cathode, which was sitting on a Teflon support. The growth and release of these bubbles also caused rather large uncertainties in the cell voltage. These lingering gas bubbles would block the electrochemistry at the bottom of the cathode and act similarly to a crack causing loss of the deuterium loading. This would likely result in smaller excess power effects. Problems with gas bubbles can also vary with the source of the D_2O [2].

5. Related Work

Two Pd–B experiments were also conducted at NRL in January 1995 using a new and accurate Hart Seebeck calorimeter. Both experiments used the NRL Pd–0.75 wt.% B cathodes with dimensions of 0.4×3.5 cm. These experiments were set up by one of us (M.H.M) during a two week visit at NRL. The exothermic deuterium loading for one experiment (Cell D) was measurable at about 7 mW for 20 h and gave -33 ± 3 kJ/mol D_2 for $PdD_{0.6}$ formation compared to the literature values of -35.1 kJ/mol D_2. However, the other Pd–0.75 B cathode (Cell C) gave evidence of an early excess power effect in addition to the exothermic deuterium loading. The initial excess power continued well beyond the expected loading time frame of about 20 hours for the cell current used. Notebook data recorded by one of us (M.H. Miles) for the first 64 h gave a maximum excess power of 12.8 mW for Cell C at 61.0 h. Even Cell D gave a small maximum excess power of 5.6 mW following the cell current increase to 24 mA/cm^2 (0.060 A). These accurate
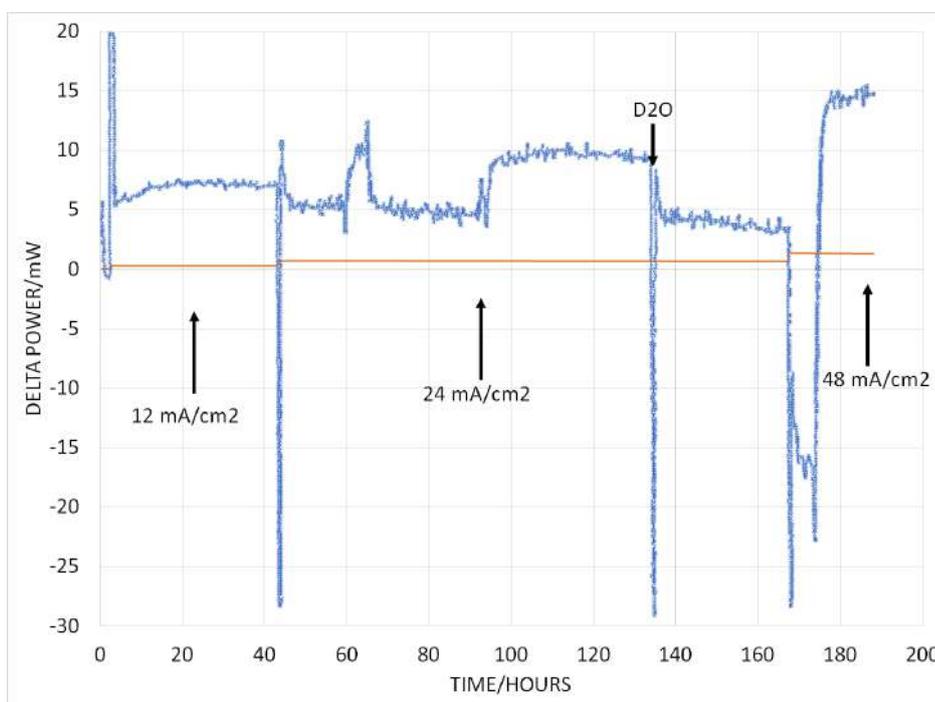
Figure 5. Early excess power for Pd–0.75 B at NRL using a Hart Seebeck calorimeter.

calculations included small additional power terms related to the gas evolution, which were not considered in the NRL calculations [4,11].

This experiment for Cell C is shown in Fig. 5 for the first 200 h [8]. This is additional evidence for early excess power effects in the Pd–B system.

The gas exit lines were too long in this experiment and later became clogged with condensed D_2O vapor. Therefore, these two experiments were terminated, and these results were only reported in an internal NRL-ONR 1995 report [8].

Several other groups have tested this NRL Pd–B material and have found excess power effects, but none of this work has been published. Storms in New Mexico reported excess power for an alloy prepared by one of us (M.A.I) at NRL which contained 0.25 wt.% B with a cylindrical shape and dimensions of 0.47×1.75 cm [9]. This study used 0.008 M LiOD in 99.96% D_2O. The excess power measured by a Seebeck calorimeter reached 80 mW at a current density of 0.5 A/cm^2. Although a paper was prepared by Storms, this Pd–B study was never published. An NRL Pd–B cathode was also tested at SRI in a prismatic Seeback calorimeter by B. Bush and was observed to produce excess power at statistically significant levels [10].

6. Discussion

The major question is why do these NRL Pd–B cathodes produce the F–P excess heat effect while most other palladium materials do not? One possible answer is that the added boron removes oxygen from the palladium by forming B_2O_3 during the melting process. The less dense boron oxide then separates from the molten metal. Other clues for oxygen effects are the successful Johnson–Matthey materials specially produced under a blanket of cracked ammonia

(N_2+H_2). The hydrogen removes oxygen from the metal during the melting process in the form of H_2O vapor. These Johnson–Matthey cathodes also generally produced excess energy in F–P related electrochemical experiments [2,3,11]. A possible third clue is the electrochemical deposition of palladium and deuterium (co-deposition) from $D_2O + PdCl_2$ solutions which provides oxygen-free palladium and reproducible excess power effects (if done correctly) [12].

Another possible important factors for Pd–B cathodes is that the added boron produces a material of much greater mechanical strength than pure palladium [1,6]. There is very little volumetric expansion when Pd–B cathodes are loaded with deuterium. This suggests that Pd–B materials are less likely to crack during the loading process. Another feature is that these Pd–B materials load similarly to palladium cathodes, but the escape of deuterium (de-loading) when the current is removed is at least ten times slower than for pure palladium cathodes based on gravimetric studies. A possible explanation for such large differences in the rate of deuterium loading and de-loading for these Pd–B materials is that Pd–B may load electrochemically across the grains, but when the electrochemical current is removed, most of the deuterium escapes along grain boundaries which may be clogged with the boron atoms. With no applied current, there is no electrochemical potential to drive deuterium into other grains. When the cell current is first turned off for pure palladium cathodes, the escape of deuterium gas is much too rapid to be explained by the simple diffusion of deuterium from palladium grains at the electrode surface. It seems likely that the Pd–B materials are somehow much more restrictive than pure palladium cathodes in allowing deuterium to escape via the grain boundaries.

7. Summary

The NRL Pd–B cathodes have produced excess power in 9 out of 10 experiments conducted at three different laboratories and using three different types of calorimeters. The one exception was due to a structural defect, but even this electrode may have produced small excess power effects. Three other research groups using different calorimeters have also found excess power using NRL Pd–B cathodes in their experiments. There is often an unusual early excess power effect with the use of Pd–B cathodes. These Pd–B results indicate that the prolonged cold fusion controversy is likely related to the dependence of excess power effects on the palladium materials properties.

Appendix A. Notes Added in Revision

The immediate excess power for this Pd–B cathode (see Fig. 3) did not seem to be a real effect and some other explanation was needed. It now seems that a likely explanation is that the thermoneutral potential ($E_H = 1.527$ V) generally used in these studies does not apply at the beginning of an experiment when most of the electrogenerated deuterium gas is being loaded into the cathode rather than escaping into the gas phase and leaving the cell. During this period, the main electrochemical reaction would be

$$Pd + 0.3\,D_2O \rightarrow PdD_{0.6} + 0.15\,O_2 \qquad (A.1)$$

and not the normal $D_2O \rightarrow D_2 + 0.5\,O_2$ electrolysis reaction where $E_H = 1.527$ V.

The enthalpy change (ΔH°) for Reaction (A.1) is 53.3 kJ/mol, thus the thermoneutral potential is 0.921 V rather than 1.527 V assuming 100% of the deuterium is used for the deuterium loading. This assumption is likely a good approximation for the first 5–10 min of electrolysis but would become less accurate at longer time periods. If 50% of the deuterium was used for loading, then E_H would increase to 1.224 V. The use of 1.527 V for E_H is valid over most of the experiment except during the time period of deuterium loading.

The change in excess power (P_x) due to the use of $E_H = 1.527$ rather than $E_H = 0.921$ V at the beginning of an experiment is given by

$$\Delta P_x = (1.527 - 0.921)I = 0.606\,I. \tag{A.2}$$

Thus, the initial cell current of $I = 0.150$ A yields $\Delta P_x = 0.0909$ W or about 91 mW. This would account for most of the excess power in Fig. 3 for the first 10 min. If there were no cold fusion effects, then the initial excess power should be zero because the exothermic loading of PdD_x is included in Reaction (A.1). There is still a suggestion of a small excess power effect for Pd–0.5B in Fig. 3 after about 5 min where P_x exceeds 100 mW. The decreasing P_x in Fig. 3 after nine minutes is likely related to the decreasing percent of deuterium used for loading. It is not possible to accurately determine E_H during the intermediate loading periods. There were also excess power effects of about 20 mW measured after about 4 h of electrolysis when the loading process became insignificant. Fleischmann also noted a small excess power effect for Pd–0.5 B following the loading process [6]. The very early excess power in Fig. A.21 of [6] was also likely compromised by the use of $E_H = 1.527$ V during the initial loading period.

Verification of the effect of Reaction (A.1) was obtained from examination of early data from a previous experiment using a pure palladium cathode. Because of the smaller electrode size, the applied current was only 0.0365 A. Therefore, the expected effect from Eq. (A.2) was calculated as 22 mW. Experimentally, using $E_H = 1.527$ gave a similar early excess power effect of 20 mW within the first 10 min of electrolysis. Even the Pd–0.75 B studies at NRL shown in Fig. 5 shows a similar early excess power effect due to the use of $E_H = 1.527$ V. This explains the initial short spike of excess power exceeding 20 mW. From the cell current of 54 mA (12 mA/cm^2), the value of ΔP_x from Eq. (A.2) is 33 mW. Regarding Fig. 5, the sharp endothermic behavior when the cell current is increased or when D_2O is added results from the neglect of power that is used to heat the cell contents ($P_{CALOR} = C_p M\,dT/dt$). The delayed recovery of the excess power at 48 mA/cm^2 is likely related to the gas exit lines becoming clogged with condensed D_2O at the higher cell current [8]. Most researchers use short and vertical glass tubing for the exit of the gases and not long tubing lines that are prone for D_2O condensation.

There is still an early excess power effect for Pd–B cathodes, but it is not the immediate effect inferred by Fig. 3. However, this early excess power does appear near the end of the loading period as shown by Fig. 5 from the NRL Seebeck study as well as in the Japan and Ridgecrest results. Fleischmann commented on this in several places in the NRL Report [6]. An important comment by Fleischmann on p. 25 of [6] states: The major unexpected difference for this Pd–B electrode has been the observation of the development of "positive feedback" at a very early stage of the experiment (Day 3), at a low current density and at a low temperature. It is obviously very important to establish whether this early establishment of 'positive feedback' is a property of Pd–B alloys (the one used in this study) or whether some other factor is involved.

Fleischmann's use of "positive feedback" refers to the increase in excess power during the cell temperature increase with the first application of the in-cell heater. (See Fig. A.15, p. 75 of [6].) For Day 3, this observation of early excess power would not involve any change from the normal $E_H = 1.527$ V. Early excess power development late in the loading period or within a few days of electrolysis is an important property of Pd–B alloys.

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