Research Article

Modified Szpak Protocol for Excess Heat

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Abstract

In recent theoretical work, vacancies in PdD have been shown to be able to host molecular D_2, which is conjectured to be necessary for excess heat in Fleischmann–Pons experiments. Vacancies in the original Fleischmann–Pons experiment are proposed to be created through inadvertent codeposition at high loading. This suggests that a better approach should be to focus on experiments in which Pd codeposition is controlled, such as in the Szpak experiment. Unfortunately, the Szpak experiment has proven difficult to replicate, and we conjecture that this is due to low D/Pd loading. A modified protocol has been tested in which codeposition is carried out at higher current density with a lower $PdCl_2$ concentration. Positive results have been obtained in all of the tests done with this protocol so far.
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1. Introduction

Fleischmann, Pons, and coworkers first claimed to observe large amounts of excess energy in heavy water electrolysis experiments in early 1989 [1]. Controversy followed, as could have been expected due to the nature of the claims. Probably the biggest issue was that it was argued that the effect was nuclear, yet there were not energetic particles commensurate with the energy produced that would be expected if any known exothermic nuclear reaction were responsible. Also at issue was whether the experiment could be replicated, since in the months following the initial announcement a great many negative results were reported.

Over the many years that have ensued, enough positive results have been reported that those working in the field are sure that there is an excess heat effect associated with the Fleischmann–Pons experiment. There is not agreement on the physical mechanism responsible, but it is clear that the effect is new. One picture widely held by the researchers

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is that in the new physical process, two deuterons interact in some new way to make ^{4}He, with the reaction energy converted to condensed matter degrees of freedom prior to thermalization.

An effort was made by McKubre and coworkers to identify the necessary conditions required to see the effect, which allows a better understanding of why so many negative results were obtained early on [2]. In the SRI experiments it was found that cathodes that had not loaded to a peak D/Pd loading of about 0.95 were unlikely to produce an excess heat effect. As a separate requirement, the D/Pd loading needed to exceed about 0.85 during an excess heat event, since the excess power seemed to be roughly parabolic in loading above this threshold. Also, there was observed a requirement on the time during which the cathode was loaded prior to the observation of excess heat; typically a cathode would need to be loaded for 2–4 weeks before excess heat could be seen. These requirements generally were not met in essentially all of the early experiments where no excess heat was seen.

2. Vacancies

It seems reasonable to ask why such requirements on D/Pd loading and loading time are important in the Fleischmann–Pons experiment. In one line of argument, the issue has to do with arranging for two deuterons to come together to make D_2 inside the cathode. The basic problem is that the electron density is too high in PdD for D_2 to form. When the electron density is 0.06 electrons/Å^3 or higher, there is significant occupation of the antibonding orbitals, which results in a large separation between the deuterons. The lowest electron density in PdD due to the Pd occurs at the octahedral sites, where the electron density is near 0.08 electrons/Å^3. For a molecule to form, by analogy with sigma-bonded Pd:D_2, the electron density due to the Pd should be near 0.033 electrons/Å^3 [3]. It has been conjectured that such a low electron density can occur in the vicinity of a Pd vacancy, and recent density functional theory calculations suggest that sigma-bonded D_2 should be reasonably tightly bound near an O-site next to a vacancy where the other O-sites are occupied by deuterium atoms [4].

Given such an argument, we are motivated to consider the problem of vacancy formation in PdD. Vacancies are unstable in pure Pd, as it requires on the order of 1 eV to produce a Pd monovacancy in crystalline Pd. Adding H or D to Pd leads to a stabilization of the vacancies (see Figure 1), so that by the time the D/Pd loading reaches 0.95, the lattice near room temperature would be able to find a lower energy if it could rearrange into a different phase with on the order of 25% Pd vacancies. Fukai and coworkers took advantage of this effect to produce $Pd_{0.75}H$ in a superabundant vacancy phase where one out of every four Pd atomic sites was vacant [5].

Consistent with this line of reasoning is to associate the requirement in the SRI experiments that the cathode reach a D/Pd loading of 0.95 with the loading required to stabilize vacancies in PdD. In essence, we need the vacancies so that we can form D_2 inside the cathode, and to do so we need for the cathode to reach a loading of 0.95 so that the vacancies can form. We might imagine that when the D/Pd loading reaches 0.95, that vacancies might be able to diffuse inward from the surface or from internal voids. Unfortunately, the atomic self-diffusion rate of Pd is very low; we would expect essentially no diffusion of Pd over the course of the experiment near room temperature.

So, at a D/Pd loading of 0.95, vacancy formation is favored thermodynamically, but the cathode seems to be restricted in its ability to make the needed vacancies. In the analysis of the elemental composition of cathodes used in Fleischmann–Pons experiments it has been noticed that a variety of elemental impurities appear in the outer 100-300 nm of the cathode, including Pt which is presumed to come from the Pt anode. This motivates us to consider the possibility that the Pt and other impurities were codeposited during electrolysis. Since considerable Pd is present in the outer layer, it follows that it too was most likely codeposited. This is significant since if this codeposition takes place at a loading of 0.95 or higher, then this codeposited layer should have superabundant vacancies. In this picture, the excess heat would result from reactions associated with D_2 formation in these vacancies. This is consistent with observations of ^{4}He in the gas phase associated with excess heat production, since had the helium been created in the bulk deeper than 1 micron it would have remained in the lattice since the diffusion coefficient is small.
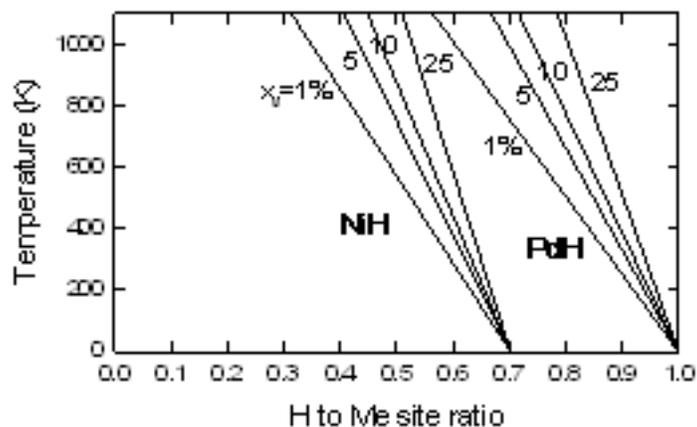
Figure 1. Estimated vacancy fraction in NiH and PdH as a function of loading and temperature. In PdH the maximum vacancy concentration at equilibrium is obtained at a loading near 0.95 at 300 K.
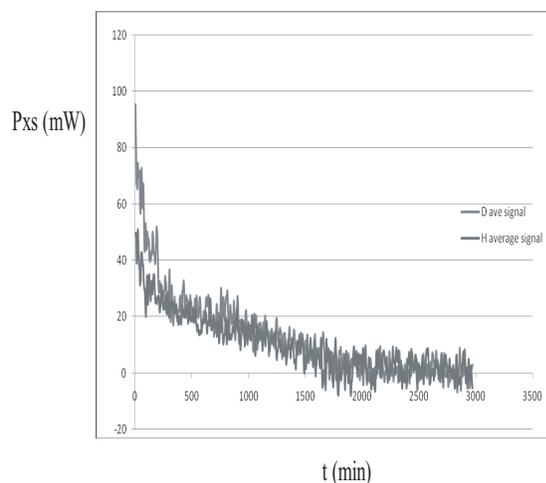
3. Codeposition and the Szpak Experiment

In view of the above arguments, we might consider the Fleischmann–Pons experiment to be a "bad" experiment in the sense that it works only because of a critical inadvertent and uncontrolled codeposition that takes a very long time (2–4 weeks) to occur. Since reasonably heroic electrochemical efforts are required to reach and sustain a loading near 0.95, we can begin to understand why the Fleischmann–Pons experiment has been so difficult to master over the years.

These arguments motivate us to consider the Szpak experiment, in which palladium is added to the electrolyte as $PdCl_2$, and codeposited on a copper substrate [6]. According to the ideas outlined above, this experiment has the potential to improve on the Fleischmann–Pons experiment since the Pd codeposition is now a key step in the experimental protocol, rather than occurring inadvertently. Rather than waiting for 2–4 weeks, we might expect excess power to be observed as soon as the Pd is codeposited in the Szpak experiment. This is consistent with observations in successful Szpak codeposition experiments.

However, the D/Pd loading in the Szpak experiment is uncontrolled, which is of concern to us given the requirement that we need the D/Pd loading to be at or above 0.95 in order for the vacancies to be favored thermodynamically. That this is an issue in the Szpak experiment is reflected in the literature in the relative absence of replications showing excess heat.

From our perspective, this is perhaps simple to understand. The equilibrium loading in PdD depends on current density, and higher loading tends to occur at higher current density (certainly in the Volmer–Tafel regime). We would expect that the D/Pd loading relation will likely be different in a codeposition experiment than in a Pd rod or foil experiment, since the latter probably are dominated by internal Tafel losses that are probably absent in the codeposition experiment. Nevertheless, based on the arguments given above, we would ideally like to see codeposition run at a high current density to help ensure reaching a D/Pd loading of 0.95.

Unfortunately, codeposition at high current density is problematic in the Szpak experiment, primarily since an adhesion problem occurs when the Szpak experiment is run with too high of a current density [7]. If so, then there is a

Figure 2. Excess power as a function of time for the Szpak experiment (courtesy of D. Cravens); comparison between heavy water cell result (D_2O) and light water control (H_2O). Pd was codeposited on polished copper in 0.3M LiCl in D_2O with 0.03 M $PdCl_2$; the current density used for codeposition was 1 mA/cm^2 for 8 hours, then 3 mA/cm^2 for 8 hours, then 5 mA/cm^2 for 8 hours.

subtle difficulty built into the Szpak experiment. To get it to work, the D/Pd loading has to be very high at low current density; and if it happens not to be high enough, then large numbers of vacancies can't be created, and no excess heat will be seen. Although there have been many attempts to replicate the Szpak experiment, the number of confirmations is low, suggesting that this D/Pd loading issue may be important. Based on the discussion above, only those groups who are able to achieve very high loading at low current density have reported success in the Szpak experiment; the others have not obtained positive results (see the results in Fig. 2).

4. Modified Szpak Protocol at High Current Density

The original Szpak protocol uses LiCl at a concentration of 0.30 M and $PdCl_2$ at 0.05 M [6]. In [7], the current density is raised in steps to 1.3, 2.6, and 6.3 mA/cm^2. A low current protocol was used successfully by Miles, who used 6 mA of electrochemical current for 48 h, then 100 mA for another 48 h [8]. In our tests, this protocol did not produce excess power, which motivated us to explore modifications of the protocol. In an initial effort to produce more vacancies, we started our experiments at 6 V, 500 mA/cm^2, and it was observed (as others have found) that the adhesion of the codeposited Pd was poor; excessive palladium accumulation on the cathode caused bridging between the anode and cathode.

To address the adhesion and bridging problems, codeposition was attempted at high current density with a reduced concentration of Pd in the electrolyte. The resulting codeposited Pd layer had much improved adherence, and we observed excess power in all experiments with the modified protocol. In our modification of the Szpak protocol, we begin by plating a bare copper cathode with gold, typically for 5 min at 3 V and 200 mA/cm^2. The plating solution we used was obtained from GoldTouch Inc., TivaGlo 24 kt, stock number GLO1Q. The gold plating was applied to the copper substrate ($5 \times 10 \times 0.6$ mm) in a separate beaker before beginning the calorimetric part of the experiment. When plating was complete, the cathode was rinsed in tap water and dried. Our electrolyte was mixed using 100 g of 99.9% D_2O from Aldrich, 0.15M LiCl and 0.44 g palladium (II) chloride solution , 5 wt.% solution in 10 wt.% HCl. Our chemical concentration was nominally 50% less than the original Szpak protocol; however, the actual concentration of palladium was 0.00125 M , or 1/40-th of Szpak's original concentration of palladium. This drastic reduction of
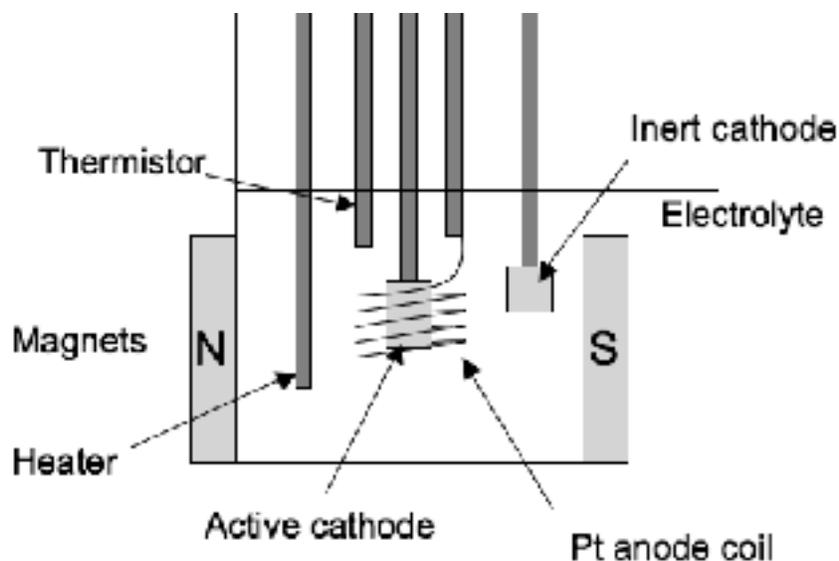
Figure 3.   Schematic of the cell used in our experiments.

concentration allowed us to reduce the rate at which palladium is deposited on the cathode, which we reasoned might allow improved Pd adhesion at higher current densities. Codeposition was done at about 500 mA/cm^2, and the solution clears in a couple of hours.

5. Experimental Set-up

The electrochemical cell contains the codeposition cathode (described above) surrounded by a spiral Pd anode, as depicted in Fig. 3. Also shown is a second "dead" (Ti) cathode which was used for calibration. Temperature sensors are indicated, and an immersion heater was used to set the cell temperature. External magnets were used in these experiments, as we have found in earlier work that they seem to help. A siphon (not shown) is located in the rear of the cell to allow replacement of the electrolyte during the experiment. All cells were closed and gases recombined using 1/8 inch alumina pellets coated with 0.5% platinum reduced (Alpha Aesar, #89106). The recombiner pellets were supported by a Teflon post attached to the cell lid as shown in Fig. 4. The recombiners worked well as long as cell temperature was maintained between 45 and 50°C. A bubbler containing spent electrolyte was used to monitor recombiner activity. In personal communications, Miles has reported that closed cells prevent the removal of H_2O impurity during electrolysis. The first author saw this confirmed using NMR analysis in 2004, so it is interesting that the presence of a small amount of H_2O does not seem to inhibit the heat producing effect during codeposition.

6. Calorimeter

Calorimetry at 1% level of precision using was done using a Seebeck calorimeter constructed using thermoelectric devices (TEC's) epoxied to a rectangular glass vessel with Duralco 128 thermal epoxy. The approach used in this study relies on air coupling to keep the cool side of the TEC's at a constant temperature. A schematic of the calorimeter is shown in Fig 5. A laser view port is visible, which provides access for cathode inspection and laser stimulation. The

Figure 4. The electrode holders and thermistor probes are 5 mm diameter sealed glass tubes. Hook up wire is 0.5 mm platinum wire spot welded to copper wire sealed inside the glass tubes. The platinum wire is sealed against the soft glass tubing making an airtight seal. Recombiner pellets are also shown.

area of the view port is $\sim 4\%$ of the total surface area of the calorimeter. A strong airflow up the axis of the heat sinks is provided by a 4 inch brushless DC fan. Two thermistors are secured in the aluminum trough to provide feedback for controlling air temperature to within $\pm 0.02°$C. Highly conductive thermal epoxy (Duralco 128) provides good thermal transfer, but is not electrically conductive.

The core of the calorimeter is a rectangular piece of borosilicate glass 15 cm long and 45 mm on each side (Friederich & Dimmock, #BST45-200, Fig. 5). The wall thickness is 2 mm. A square-to-round Teflon lid provides sealing for the electrochemical cell and support for up to six electrode holders/thermistor probes. The Teflon lid provides six pass through holes for one thermistor (Digi-Key, 2250 Ω, #615-1000-ND), an immersion heater, a gas vent tube, an anode, a main cathode, a calibration cathode or a siphon tube so that the electrolyte can be changed during operation without loss of precision. The lid also supports the recombiners as shown in Fig. 4.

Two Cu plates are epoxied to the outside of the cell wall; magnets are epoxied to the Cu plates; and TEC's are epoxied to the magnets. The Cu plates provide an optional high voltage electric field; the two magnets provide a 500 G magnetic field at the cathode (United Nuclear, two 2" $\times$ $^1/_4$" plate magnets). The copper plates are electrically insulated by the Duralco 128 epoxy. A 25 $\times$ 50 mm viewport provides visual and laser access to the cathode during operation without loss of calorimetric precision (Fig. 5). The 50 $\times$ 50 mm TEC's (Thermal Enterprises, eBay store, # TEC310117657888) are epoxied directly to the electrochemical cell except the area containing the copper plates and magnets, providing for rapid heat transfer and thermal equilibration. The thermal epoxy used was Duralco 128 with 10% flexibilizer (Cotronics Corp., # 105RF-1) to avoid thermal expansion damage.

7. Calorimeter Performance

The Seebeck calorimeter was typically run in a controlled temperature enclosure capable of holding the ambient temperature at a set point ranging from 15 to 35°C; 25 $\pm$ 0.02°C was the preferred temperature set point. Calibration checks were run before each experiment using a titanium cathode which is known to be inert in LiCl, PdCl2, and D$_2$O
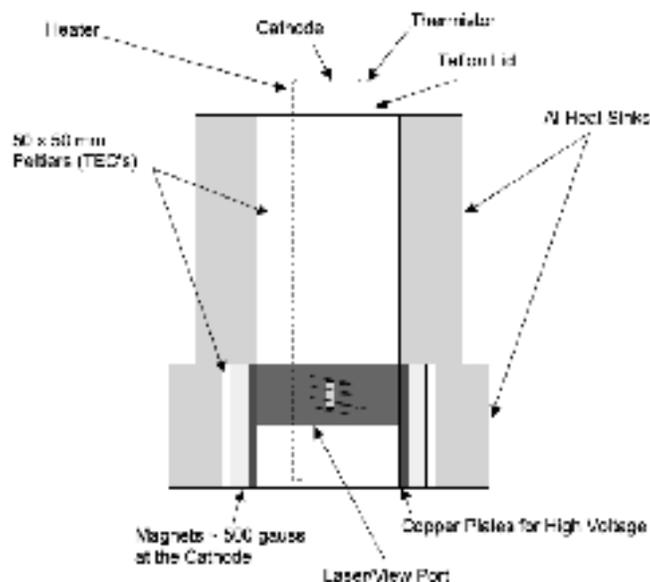
Figure 5.   Schematic of the Seebeck calorimeter.

electrolyte. The anode was a coil of platinum wire with an inside diameter of 12 mm and 5 turns over the cathode length. An immersion heater was in the cell and provided constant DC power at 11 W to keep the cell temperature about 45°C so the recombiners would work properly in the chloride environment. A calibration was typically performed before each experiment over the power range to be tested (11–14 W). The immersion heater provided a constant 11 W and the electrolysis power was varied over 0.5–3.5 W The cell was closed and recombination of the gases was provided by alumina pellets coated with 0.5% platinum. The cell was not mechanically stirred, although the external magnetic field provided some degree of stirring.

The fitting coefficients of the calorimeter vary slightly depending on how the lid pass-throughs are configured for the experiment, which is the motivation to perform a calibration check before each experiment. However, once calibrated for a particular experiment, the Seebeck calorimeter retains the calibration coefficients even if the calorimeter is opened for maintenance. The Seebeck produces a good calibration plot over a wide range of power. As long as 0.5 W of electrolysis is provided for stirring, heater power can be substituted for electrolysis power for on-the-fly calibration checks (Fig. 6).

8. Experiment 684d

Experiment 684d was designed to permit changing or repositioning of the electrodes and removal/replacement of the electrolyte while the experiment is running. This can be done without changing calorimeter performance or calibration. The cathode used for 684d was a $4 \times 10 \times 0.6$ mm Cu substrate plated with Au for 5 min at 3 V, 200 mA. The anode coil was 0.999 Pt wire with an ID of 12 mm. The electrolyte was 0.15 M LiCl and nominally 0.025 M palladium (II) chloride solution , 5 wt.% in 10 wt.% HCl, in 100 mL of 99.9% D_2O. The actual concentration of palladium was 0.00125 M as mentioned above, which was 1/40-th of the original Szpak concentration. A 5 mm glass tube 16 cm long was located in the rear of the cell to remove/replace electrolyte during the experiment. The cathode width was
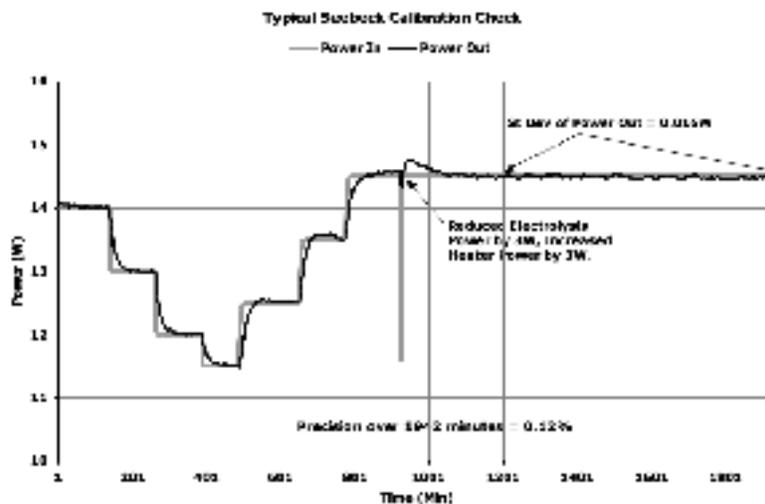
Figure 6. Results from calibration test which shows that calibration provides for a good input/output power balance over the tested range of 11.5–14.5 W (Pout - Pin) /Pin at ∼ 0.12% over the entire range tested.

reduced from previous experiments so the cathode could be withdrawn through the 5 mm lid pass-through during the experiment.

Results from this experiment are shown in Fig. 7. Up to point 800, the "dead" Ti cathode was electrolyzed at 3 W outside of the anode coil (see Fig. 3); the cell during this time was in power balance to within 1%. At point 800, electrolysis was diverted to the gold plated copper cathode inside the Pt anode coil. An excess power signal of 250 mW appeared very quickly and cell temperature increased at the same time by 4–5°C. The excess power signal and cell temperature remained elevated, producing ∼ 7 kJ of excess energy. At point 1100, a pump was activated to remove the deuterium-based electrolyte and replace it with hydrogen-based electrolyte of identical volume and concentration as that used at the start of the experiment. As seen in Fig. 7, the excess power signal declined over a nine-hour period after replacing D_2O with H_2O.

9. Experiment 685

Experiment 685 was similar to 684d: the cathode was gold plated copper, $5 \times 10 \times 0.6$ mm, plated with gold for 5 min at the same current. The electrolyte was fresh for 685, while 684d ran with electrolyte that had been used once previously (the freshness of the electrolyte may be a factor). The "dead" Ti cathode was electrolyzed over points 0 - 1100 and appeared to produce about 100 mW of excess power (no excess power was expected since Ti seemed to be inactive in previous work we have done). At point 1100 of Fig. 8 , electrolysis power was switched to the active gold-plated copper cathode and a very robust excess power signal appeared immediately, recovering 110 kJ of excess energy. The signal showed no signs of diminishing over 60 h.

10. Experiments 690a and 691d

These experiments were performed as a matched pair with one using a heavy water electrolyte, and one using a light water electrolyte as a control. During the first four hours of these two experiments, the cells were electrolyzed using
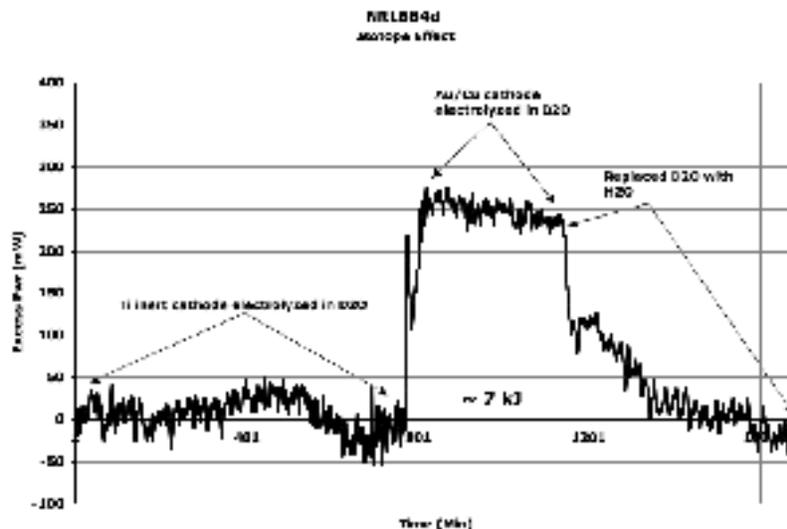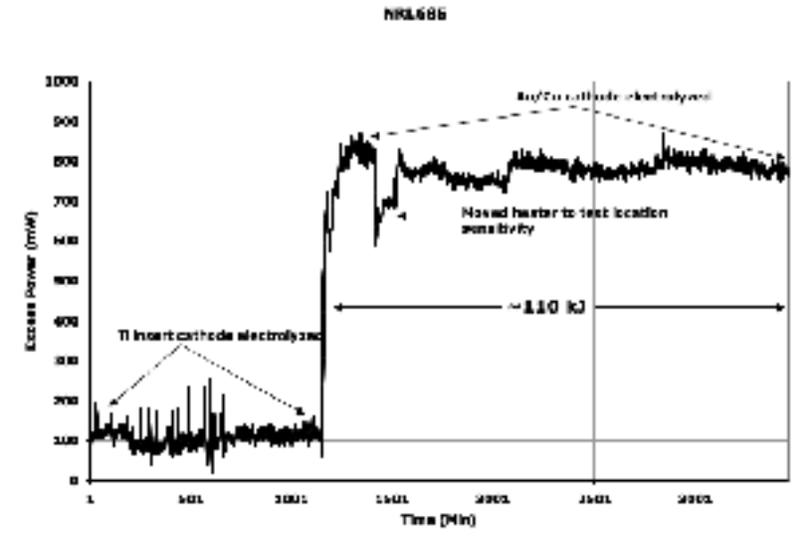
Figure 7. Excess power as a function of time for 684d. From minute 0 to minute 800 the cell was run using the "dead" Ti cathode; between 800 and 1100 the Pd/Au/Cu cathode was used and excess heat was seen; after 1100 the D_2O electrolyte was replaced by H_2O and the system returned to power balance.

LiCl as a salt. After the cells were in thermal equilibrium at minute marker 240, palladium chloride was added to the cells. As can be seen from the data shown in Fig. 9, the two cells responded very differently. Experiment 690a (D_2O) produced a robust exothermic response, recovering almost 4 kJ of excess energy over 4 hours. In contrast, 691d (H_2O) produced a slightly endothermic response from H_2O based electrolyte, absorbing approximately 529 J of energy. In both experiments, 0.44 g of palladium (II) chloride solution, 5 wt.% solution in 10 wt.% HCl was added to the electrolysis cell. The endothermic response observed in this experiment could have been due to calorimeter error, high loading of the palladium, or chemical reactions producing a net absorption of energy. We discounted calorimeter error because the instrument was well calibrated before experiment 691d and a post-experiment test was made of the calorimeter, which showed the instrument remained in good calibration. We also discounted the possibility of endothermic high loading because the amount of palladium on the cathode was too small to produce the observed 529 J endotherm. In a personal communication, Dr. Melvin Miles suggested that the reaction $HCl + H_2O \rightarrow HClO + H_2$ forming hypochlorous acid would be a good candidate. Dr. Miles estimated the net enthalpy change to be $+332.1$ kJ/mol. We estimated that the amount of chlorine available for this reaction was 0.0016 mol from adding 0.44 g of $PdCl_2$ solution and from the existing LiCl in the cell at the time of the addition. The palladium chloride solution was weighed on an inexpensive lab scale with an accuracy estimated at 5%. So, the calculated net enthalpy change was in the range of 503–555 J and agreed with the observed value of $+529$ J within experimental accuracy.

11. Discussion

The experiments reported here began as part of a program focused on the Szpak experiment as a possible cold fusion "lab rat" experiment. One motivation for this has been the difficulties over the years in obtaining Pd cathodes which are capable of attaining a high D/Pd loading and giving high levels of excess power. Recent advances at ENEA Frascati have improved the situation, but issues remain. However, if it is the case that the important thing that is going on in the

Figure 8. Excess power as a function of time for experiment 685. Between minute 1 and minute 1100 the "dead" Ti cathode was electrolyzed; after 1100 electrolysis was switched to the Pd/Au/Cu cathode with an associated increase in the excess power. A variation in the excess power is noted at a time when the immersion heater location was changed.

Fleischmann–Pons experiment is the creation of vancancies in the outer 100–300 nm of the surface through inadvertent codeposition, then we should be able to do better pursuing codeposition experiments.
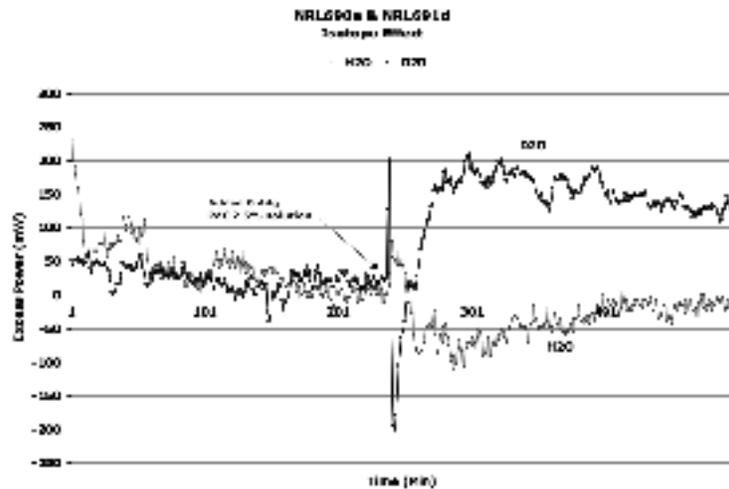
Figure 9. Excess power as a function of time for the heavy water cell (690a) and a matched light water cell (691d). The cells were run to near power balance up to 240 min, where $PdCl_2$ was added.

The best known codeposition experiment is the Szpak experiment, which has so far given positive excess heat results in the hands of only a few groups. In light of the ideas discussed above, codeposition experiments should probably play a much bigger role in the field. So, the obvious question is: what makes the Szpak experiment so difficult to replicate? If it is vacancy production, then the clear answer is that the loading needs to be higher during Pd codeposition, which suggests that the weak link in the Szpak protocol is the relatively low current density. Low current density is needed so that the Pd adheres; at higher current densities the Pd does not adhere well at a $PdCl_2$ concentration of 0.05 M.

We encountered this problem, and in response, we explored a modification of the Szpak protocol where the $PdCl_2$ concentration is reduced, which allows the Pd to stick even when the codeposition is done at much higher current density. Positive excess heat results were obtained in all experiments we have done using this protocol so far.

In the recent SPAWAR codeposition experiments that focus on energetic particles, the current density is low during codeposition, which in our view results in fewer vacancies. In codeposition excess heat experiments carried out in 1990, the cell was run in a potentiostatic mode with a stepped protocol: 30 min at -0.5 V (-5.5 mA), then 2 h at -2.0 V (-25 mA to -40 mA); then 16 h at -2.5 V (-78 mA at the end); excess heat was sought after the Pd plated out with -190 mA [9]. The copper substrate in this case started out roughly 1 inch square, and sufficient Pd codeposited so that the cathode was approximately spherical with a 1 inch diameter (100 mL electrolyte was used) at the end of codeposition. Note that we used a higher current density than was used in this older experiment.

Acknowledgment

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