

Calorimetric Studies of Deuterated Pd Electrodes

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ABSTRACT

Calorimetric experiments were conducted to verify the caloric claims by Fleischmann and Pons. A twin-cell heat conduction calorimeter was used, rather than the quasi-adiabatic instrumentation of the original investigation. Under similar electrochemical conditions, the output of heat powers from experimental cells of Pd in 0.1M LiOD/D₂O and that from control cells of Pd in 0.1M LiOH/H₂O and Pt in 0.1M LiOD/D₂O were all in close agreement with input heat powers using simple theory. These results show no anomalous "excess" heat as claimed.

Fleischmann and Pons (1) reported that nuclear radiation and anomalous excess heat were observed when electrochemically incorporating deuterium atoms into a cathodically polarized palladium (Pd) electrode. If this is confirmed, it could have an important impact on the nation's power supply. We have been conducting experiments to attempt to verify the caloric claims under similar electrochemical conditions, but using a different calorimetric approach.

The calorimetric method used by the original investigators was "quasi-adiabatic" calorimetry. Conventional adiabatic calorimetry is suitable for short-term measurements where there is negligible leakage of heat from the experiment. Under those conditions, the quantity of released heat is determined from the corresponding linear temperature increase after experimental determination of the proportionality constant (i.e., the total heat capacity of cell and contents). If adiabatic instrumentation is used for long-term experiments, the resulting "quasi-adiabatic" steady-state temperature rise reflects a complex balance between heat generation and dissipation. While the method can be calibrated experimentally, it is in the general case very sensitive to such experimental conditions as the placement of the thermocouple, rate of stirring of electrolyte, temperature, and agitation of the external bath. In addition, in this particular case, there are potential sources of error corresponding to evolution of gases and evaporation of D₂O.

Recently, Appleby *et al.* (2) reported 10-15% excess heat from Pd with a diameter of 0.5 mm at a current density of 600 mA/cm² using a heat conduction calorimeter. They used a stainless steel cell container instead of the glass container used by Fleischmann and Pons (1).

In this paper, we will report the heat outputs from cells with both glass and stainless steel containers. We used a twin-cell heat conduction calorimeter as did Appleby *et al.* (2) since that instrumentation is more suitable for long-term measurements than is the quasi-adiabatic approach. The experimental cells comprised a deuterated Pd cathode and a Pt anode in a solution of lithium deuterioxide (LiOD) in deuterium oxide (D₂O). The control cells comprised either a Pd cathode in a solution of lithium hydroxide (LiOH) in water (H₂O) or a Pt cathode in a solution of LiOD in D₂O.

Experimental

Electrochemical cells.—Two types of cells were used in this work. The first type, shown in Fig. 1a, was made of a plain glass vial with a Teflon stopper which served as an electrode holder. A 1 mm diam hole in the stopper allowed the release of gases produced during electrolysis. The second type, shown in Fig. 1b, was made of a stainless steel can (316 liters) with a Teflon stopper but without a hole. The gases were able to exit through the fissure between the wall of the can and the Teflon holder and the fissure between the Pt leads and the Teflon holder.

Palladium (Pd) wires of 25 mm long × 1 mm in diam, (Englehard) were used in the glass cells. Pd wires 10 mm long × 0.5 mm in diam (99.997%, Johnson Matthey) were used in the stainless steel cells. In most measurements, the as-received wires were first rinsed in ethanol, distilled

water (H₂O), and then deuterium oxide (D₂O) before use. In some measurements, the Pd wires were heat-treated at 1140°C under vacuum for 4h before use. A platinum wire spot-welded on Pd was used as a lead from Pd to the outside of the cell. In the stainless steel cell, the Pt lead wire was wrapped with Teflon tape to prevent it from being exposed to the electrolyte. In the glass cell, a Pt gauze was used for anode, in the stainless steel cell, a helically wound Pt wire.

The electrolyte solution of 0.1M LiOD in D₂O was prepared by dissolving the appropriate amount of Li in D₂O (D₂O, 99.8%, ICN Biomedicals, Incorporated, used as received). A 0.1M solution of LiOH in H₂O (deionized and distilled) was also prepared similarly.

Calorimetry.—A commercially available Hart Scientific Model 7709 heat conduction calorimeter was used to measure the heat output from the cells. This calorimeter is based on the Seebeck, or thermocouple effect, in which a voltage is produced proportional to the temperature difference across the thermoelectric devices (TED). The temperature difference and hence the voltage generated across the TED is directly proportional to the heat flow from the cell measured. Thus, by knowing the amount of voltage generated, the amount of heat can be calculated. Figure 2 is a schematic of the basic calorimeter design. The calorimeter consists of twin measuring cells mounted to TED, which are in turn mounted to a large aluminum block. This unit is then submerged in a constant temperature water bath. The aluminum block acts as a heat sink with a stable temperature. When a temperature change occurs in a measuring cell, heat either flows into or out of the heat sink through the TED. This generates a voltage which is then recorded. The twin-cell design has an advantage of canceling extraneous thermal effects. If the heat sink

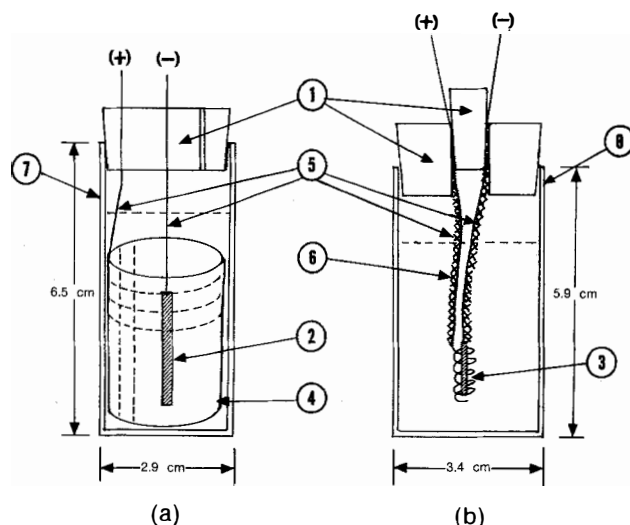


Fig. 1. Cell configurations. (a) Glass cell; (b) stainless steel cell. 1, Teflon holder; 2, Pd (diam, 1 mm; length: 25 mm); 3, Pd (diam 0.5 mm, length: 10 mm); 4, Pt gauze; 5, Pt wire; 6, Teflon tape wrap; 7, glass vial; 8, stainless steel can.

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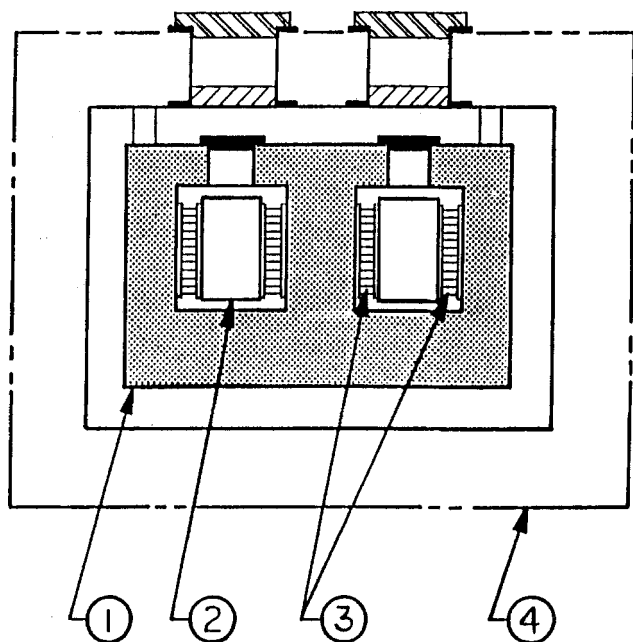


Fig. 2. Schematic view of Hart Scientific twin-cell heat conduction calorimeter. 1, Aluminum heat sink; 2, one of the twin cells; 3, thermoelectric sensors; 4, stable temperature environment.

drifts up in temperature a small amount, heat will flow into the cells through TED, causing an output voltage. However the cells are connected in a differential fashion; thus, the difference output voltage is reduced by an order of magnitude or more. This results in the long-term stability and the reproducibility of the base line. This method is capable of measuring heat rate of microwatts to watts with proper design, is heat capacity insensitive, and is suitable for long-term measurement.

Calibration was done as follows. A cell containing 10.37 Ω resistor dipped in Dow Corning silicone oil in a stainless steel can was used to provide a known heat power. The known heat power is the product of the voltage across the cell times the current. The calibration was done at heat powers of 10, 66, 264, and 670 mW. The corresponding voltages across TED were used to calculate the calibration constant, C W/volt. This constant is believed to be accurate to 2% based on the accuracy of the calibration constant. The results of a sample calibration run are shown in Table I.

Determination of excess heat power.—At the early stage of electrolysis, the formation of PdD_x alloy also produces heat. The diffusivity of H in the α phase of Pd is high at $4 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ (3). In the β phase, the diffusivity of H is somewhat lower, but is still high. The diffusivity of D in Pd is even higher than the diffusivity of H. Under our electrolysis condition, the 1 mm diam Pd sample was saturated by either H or D within a few hours. Since our cells were electrolyzed for at least two days before heat measurement, the heat power input [H_{in} (W)] to the cell is simply determined from the cell voltage (V_{cell}) and the current (I) applied to the cell using the relationship shown as follows: $H_{in} = (V_{cell} - V_{tn}) \times I$ where V_{tn} is the thermal neutral potential of water

Table I. Sample calibration run—Voltage reading of TED in mV.^a
Input power = 66.3 mW

9.899
9.912
9.907
9.930
9.897
9.924
9.894
9.900

Average 9.908 \pm 2.2%

^a Corrected to base line.

$$V_{tn} = 1.53\text{V for D}_2\text{O} \quad [1]$$

$$V_{tn} = 1.48\text{V for H}_2\text{O} \quad [2]$$

The heat power output [H_{out} (mW)] from the cell is simply the multiplication of calibration constant [C (W/volt)] and the voltage reading of TED [V_{TED} (volt)]. The excess heat power is H_{out} minus H_{in} . The percent of excess heat power is the percentage of excess heat power relative to H_{in} .

The current was applied using an ECO Battery Cycler. V_{TED} and the temperature of the Al block (T_{Al} °C) were monitored using Hart Scientific Model 1701 measuring system coupled with Keithley Model 197 Microvolt DVM. This data was recorded every 20 or 30 min using an IBM compatible PC.

Determination of D/Pd.—The amount of incorporated deuterium in the palladium was determined using a Perkin-Elmer TGS-2 thermogravimetric analyzer (TGA). This experiment was performed on selected samples after the calorimetric experiment was completed. The weight loss was assumed entirely due to deuterium.

Results and Discussion

Electrolyses were started outside of the calorimeter and continued for 2-12 weeks. Cells were occasionally transferred to the calorimeter in order to monitor heat production. For glass cells, the duration of monitoring varied from 1-3 days. For stainless steel cells, the duration of monitoring varied from 2-14 days due to smaller total current applied. During these periods, the level of electrolyte was maintained so the cathode was never exposed to the atmosphere. This eliminated the need to add water while the cell was in the calorimeter, so the temperature of the cell remained undisturbed.

Glass cells were used in early runs. Weight loss measurements indicated that the loss of deuterium oxide was purely due to electrolysis within 1% of accuracy. Therefore, we believe there is no significant recombination of oxygen and deuterium in the electrolysis cell. Figure 3 shows a typical one-day plot of percent excess heat power as a function of time for a Pd cathode in a 0.1M solution of LiOD in D₂O at current densities of 60 and 240 mA/cm². The corresponding heat powers were approximately 80 and 650 mW, respectively. The excess heat power observed was within 2% of the input heat. The annealed Pd showed similar results as the nontreated Pd.

The excess heat power from the control cells, Pt/0.1M LiOD in D₂O and Pd/0.1M LiOH in H₂O, is shown in Fig. 4. The time axis shown is the actual time since electrolysis started. The excess heat power is again within 2% of the input heat. These results do not support Fleischmann and Pons' claims (1) of about 20% excess heat from Pd of 1 mm in diam and 10 cm in length.

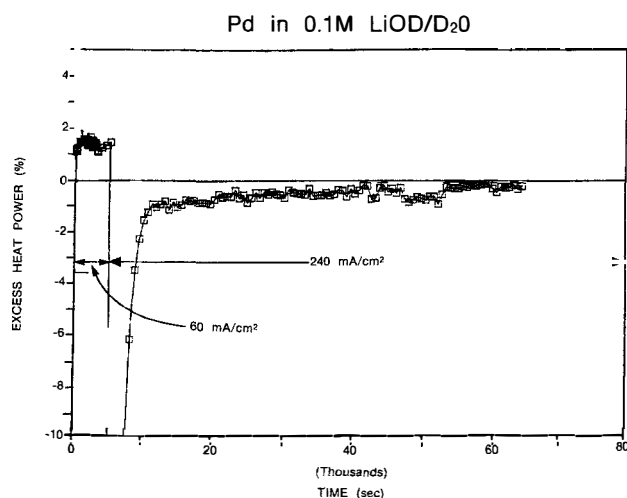


Fig. 3. Percent of excess heat power (%) as a function of time in a day for Pd in 0.1M LiOD/D₂O at current densities of 60 and 240 mA/cm² in glass cell.

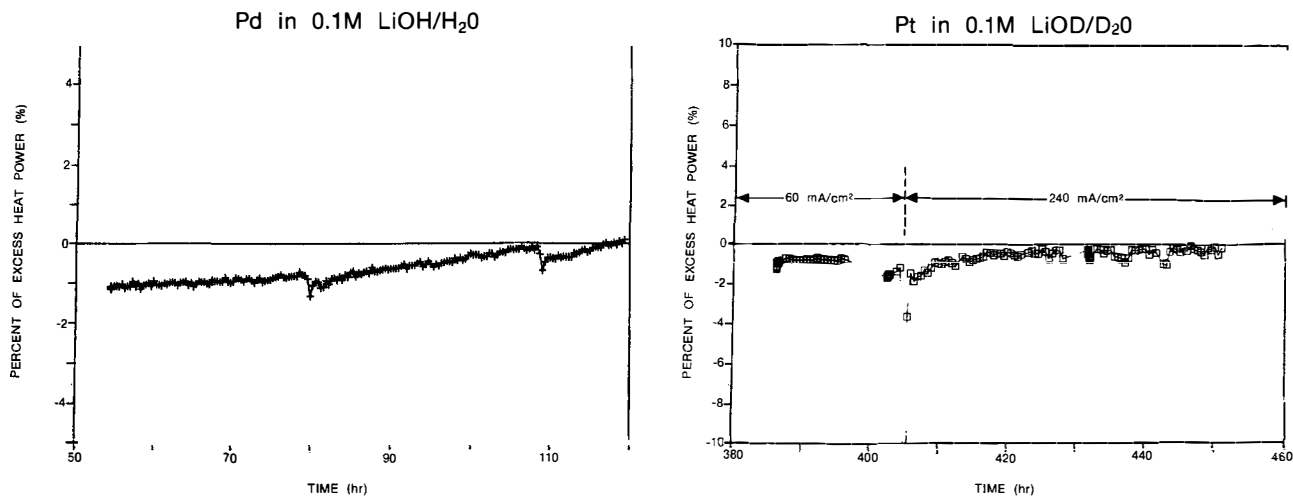


Fig. 4. Percent of excess heat power (%) as a function of time in glass cells. (a, left) Pd in 0.1M LiOH/H₂O at 60 mA/cm²; (b, right) Pt in 0.1M LiOD/D₂O at 60 and 240 mA/cm².

The typical percent excess heat power from cells using a stainless steel container is shown in Fig. 5. The heat power levels were about 9 and 310 mW at current densities of 60 and 600 mA/cm², respectively. The observed excess heat power at 60 mA/cm² was sometimes slightly higher than the 2% accuracy of the calorimeter. However, the excess heat at 600 mA/cm² was within the accuracy of the calorimeter in all cases.

Under conditions similar to ours, Appleby *et al.* (2) found that there was no excess heat for Pd in 0.1M LiOD/D₂O at a current density of 60 mA/cm², but 10-15% excess heat at 600 mA/cm². We cannot explain the discrepancies between our results and theirs. It is also interesting to note

that Fleischmann *et al.* (1) found excess heats of 23, 19, and 5% from Pd of a diameter of 1 mm at current densities of 8, 64, and 512 mA/cm², respectively. The excess heats at current densities of 8 and 64 mA/cm² observed by them do not agree with the results of Appleby *et al.* (2), if we do not consider the difference in containers used.

The excess heat power observed from experimental cells of Pd in 0.1M LiOD/D₂O and from control cells, both Pd in 0.1M LiOH/H₂O and Pt in 0.1M LiOD/D₂O, are all less than 2-3%. Since these values are similar and below the estimated accuracy level of the calorimeter, we must conclude that the present experiments provide no evidence for the production of anomalous heat under the Fleischmann-

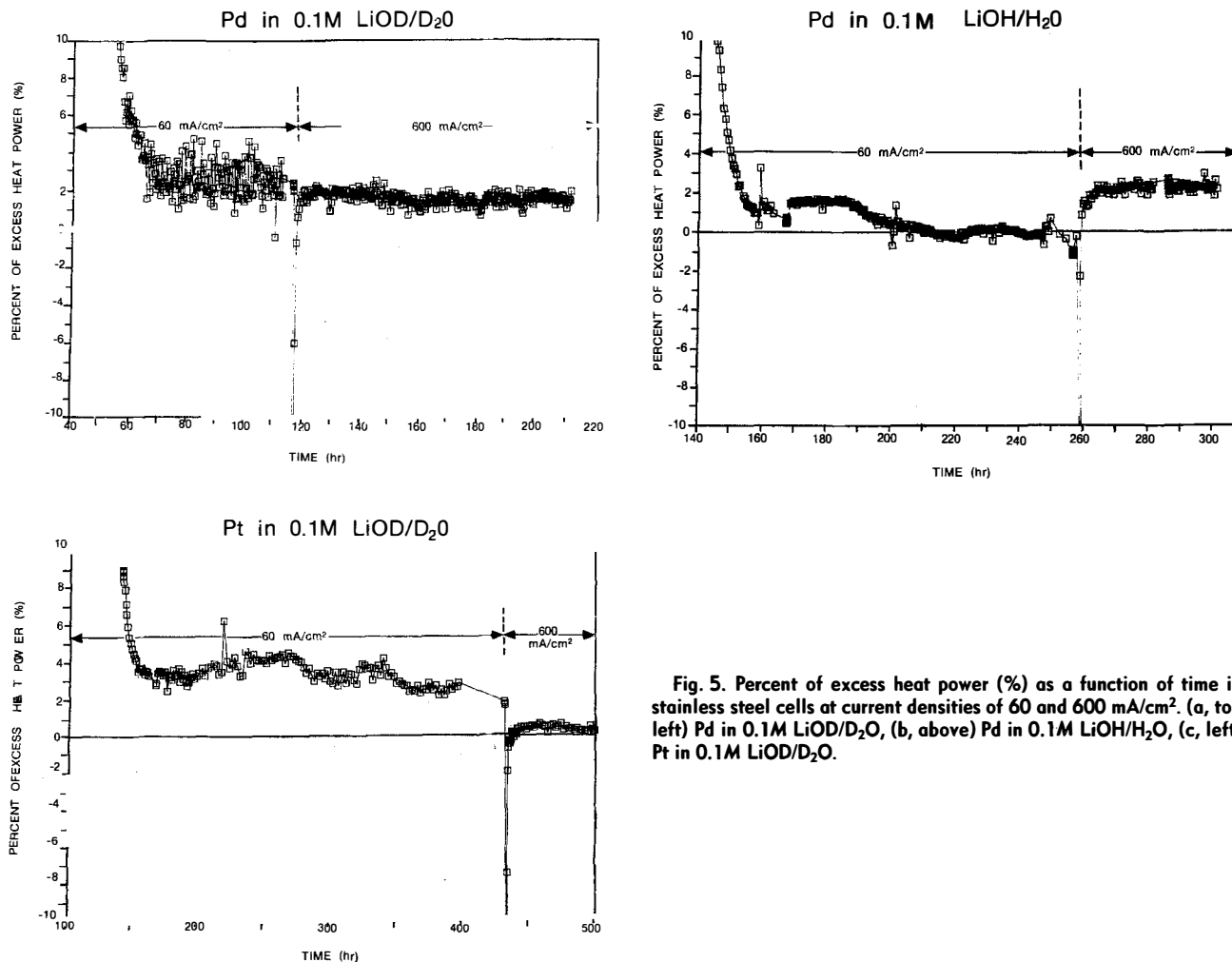


Fig. 5. Percent of excess heat power (%) as a function of time in stainless steel cells at current densities of 60 and 600 mA/cm². (a, top left) Pd in 0.1M LiOD/D₂O, (b, above) Pd in 0.1M LiOH/H₂O, (c, left) Pt in 0.1M LiOD/D₂O.

Table II. Average percent excess heat power of experimental and control cells

Cell type	Cathode electrode type	Electrolyte	Current density (mA/cm ²)	Average percent excess heat power (%)
Glass	Pd, as received 1.0 mm diam 25 mm long	0.1M LiOD/D ₂ O	60	1.0
			240	-0.5
Glass	Pd, vacuum annealed 1.0 mm diam 25 mm long	0.1M LiOD/D ₂ O	60	1
			240	-0.5
Glass (control)	Pd, as received 1.0 mm diam 25 mm long	0.1M LiOH/H ₂ O	60	-0.5
Glass (control)	Pt, as received 1.0 mm diam 25 mm long	0.1M LiOD/D ₂ O	60	-0.7
			240	-0.5
SS can	Pd, as received 0.5 mm diam 10 mm long	0.1M LiOD/D ₂ O	60	2
			600	2
SS can (control)	Pd, as received 0.5 mm diam 10 mm long	0.1M LiOH/H ₂ O	60	1
			600	2
SS can (control)	Pt, as received 0.5 mm diam 10 mm long	0.1M LiOD/D ₂ O	60	3
			600	0.5

Pons experimental conditions. Recently, Fleming *et al.* (4) reported results similar to ours from both the open and the closed cells using a twin-cell isothermal calorimeter.

The amount of deuterium in palladium was measured after the calorimetric experiment was completed. The value was typically $0.65 \leq x \leq 0.70$ in PdD_x.

Summary

It may be noted that the present results do not eliminate the possibility of anomalous heat production below the 2% level of confidence of our experiments. Table II summarizes the results from both the glass cells and the stainless steel cells using the twin-cell heat conduction calorimeter. We conclude that under our experimental conditions no anomalous heat of the magnitude reported by either Fleischmann and Pons (1) or Appleby *et al.* (2) could be detected.

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