

SPORADIC OBSERVATION OF THE FLEISCHMANN-PONS HEAT EFFECT

R. C. Kainthla, O. Velez, L. Kaba, G. H. Lin, N. J. C. Packham,
M. Szklarczyk, J. Wass and J. O'M. Bockris

Surface Electrochemistry Laboratory
Department of Chemistry
Texas A&M University
College Station, Texas 77843-3255, U.S.A.

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Abstract - An examination has been made of the heat production at ten palladium electrodes, each prepared in a different way. Seven of these produced heat during D_2 evolution in a D_2 - O_2 electrolysis cell (no recombination attempted) which coincided precisely with the prediction of classical electrochemical theory, and thus eliminated the suspicion of heat through unintended D_2 - O_2 recombination. Three electrodes clearly produced an excess heat of ~ 2.5 watts-cm⁻³. The heat was observed for periods of 10-33 hrs. In one electrode the excess heat production "shut off" (after 33 hrs) with no apparent cause: it did not return in five days of further electrolysis.

Fleischmann and Pons [1] reported the production of heat during the electrolysis of D_2O at a Pd cathode and Pt anode in excess of that predicted by the electrochemical theory for the heat production in cells. Some of the measurements even indicated that the total energy out of the cell as heat was greater than that going in as electricity. The paper attracted attention because it was suggested that the excess heat was due to D-D fusion occurring in Pd at high overpotential. A principal difficulty, since the announcement in March 1989, has been that many electrochemically inexperienced investigators have tried, but failed, to reproduce the alleged heat (however, cf. Huggins [2], Landau [3], MacKubre [4], Appleby and Srinivasan [5], Wadsworth [6]).

In this note, we report the observation of this excess heat effect in three electrodes out of ten prepared and examined.

The calorimeter used in the study was of the heat transfer type. The cell is a glass cylinder 10 cm. high and 5 cm in diameter. The cap is made of 1 cm thick Teflon with holes for the electrodes, the Joule heater and the temperature probe. The cell is placed inside another glass cylinder 12 cm. high and 7 cm. in diameter. For good heat transfer the space between the cylinders is filled with ethylene glycol. The assembly is immersed in a constant temperature bath (0.01° accuracy) and the temperature difference between the bath and the cell is monitored with thermistor thermometers (Omega 700 series thermistors with 0.01°C resolution).

The calorimeter was calibrated by passing different amount of direct current through the electric heater (resistance 275 Ω) in the solution of 0.1 M LiOD (made by dissolution of Li in D_2O) and noting the potential drop across it. For each value of the electrical power put in, steady state temperature difference (monitored on a y-t recorder) was noted and plotted to yield a calibration curve as shown in Fig. 1. This curve was repeatedly re-established by several of the authors of this paper and found to be stable to within ± 0.05 watts.

The 99.9% pure Pd rods, cast in a ZrO_2 crucible and drop hammered during production by Hoover and Strong, Richmond, VA, were obtained from Texas Coin Exchange. They were cut into 2.5 - 4.0 cm lengths. Nickel wire (0.38 mm diameter) was spot welded to the electrode to make connection to the power supply. The electrodes were charged in glass test-tubes for 18

- 30 days at current density $60 \text{ mA}\cdot\text{cm}^{-2}$. During charging Ni mesh was used as an anode while in the calorimeter Pt wire spiral was used. The electrodes had been pre-treated in various ways as shown in Table 1.

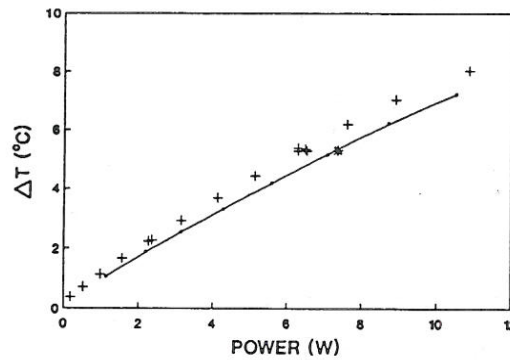


Fig. 1 Temperature difference between the cell and the constant temperature bath as a function of input power into the cell #2A with electrode B8. ■ - with electrical joule heater; + - charged Pd electrode in 0.1M LiOD solution, when excess heat was produced; * - charged Pd electrode in 0.1M LiOD solution, when excess heat ceased.

TABLE 1

Pre-treatments and charging solution composition for different Pd electrodes (Sample B 0.3 cm diameter: Sample A 0.1 cm diameter)

Sample	Pre-treatment	Charging Solution	Excess Heat
B1	No treatment	0.1M LiOD	No
B2	No treatment	0.1M LiOD + 0.001M NaCN	No
B3	Annealed at 800°C for 6 hrs	0.1M LiOD	No
B4	Annealed at 800°C for 6 hrs	0.1M LiOD + 0.001M NaCN	No
B5	Acid etch	0.1M LiOD	No
B6	Acid etch	0.1M LiOD + 0.001M NaCN	No
B7	Electrochemical oxide removal	0.1M LiOD	No
B8	Electrochemical oxide removal	0.1M LiOD + 0.001M NaCN	Yes
B9	No treatment, charged in U tube	0.1M LiOD	Yes
A9	No treatment, charged in U tube	0.1M LiOD	Yes

The electrodes were moved from the charging cells to the calorimeter in a minimum amount of time and the current density increased to $>300 \text{ mA}\cdot\text{cm}^{-2}$. After attainment of steady state, the temperature difference was noted and the current density was varied from 100-500 $\text{mA}\cdot\text{cm}^{-2}$. The temperature difference was plotted as a function of the rate of heat dissipation in the cell, calculated according to the equation:

$$W_{\text{est}} = (E - 1.54) \cdot I \quad (1)$$

where: E - cell voltage, [V], I - current, [A], 1.54 - the thermoneutral potential for heavy water. This formula is valid when no recombination reaction takes place in the cell and the only chemical transformation is the splitting of D_2O . In a separate experiment the total volume of the gases evolved was measured at several current densities and observed to correspond to 100% (within $\pm 1\%$) current efficiency for gas evolution i.e., no recombination of D_2 and O_2 . During the calorimetric measurements the experiments were watched continuously. D_2O was added to the cell to maintain the solution level constant and no part of the Pd electrode was allowed to be outside the solution. The Pt wire from the counterelectrode was encased in teflon sleeve.

In most of the cases, including Pt in LiOD solution, the points corresponding to W_{est} and ΔT were exactly on the calibration graph. However, for samples B9 and B8 the points

used as an anode while were decisively (upto 1.1 watts) above heat production values indicated by the calibration curve showing that the rate of heat production was above that estimated from equation (1). The results are given in Fig. 1 for sample B8, for different amount of input power. Figure shows the excess heat as a function of the current density. Table 2 gives the summary of the results obtained.

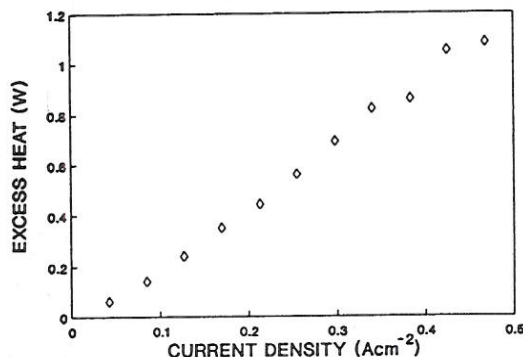


Fig. 2 Excess heat as a function of current density for electrode B8.

TABLE 2

Heat output from sample B8

i [mA/cm ²]	W_{est} (watts)	W_{exp} (watts)	$W_{exp}-W_{est}$ (watts)	$\Delta W/W_{est}$ [%]	
468	8.91	9.99	1.08	12	
425	7.61	8.66	1.05	14	
NaCN No	383	6.40	7.35	0.86	13
NaCN No	340	5.14	5.96	0.82	16
NaCN No	298	4.13	4.82	0.69	18
NaCN No	255	3.15	3.71	0.56	18
NaCN No	213	2.28	2.72	0.44	19
NaCN No	170	1.57	1.92	0.35	22
NaCN Yes	128	0.98	1.22	0.24	25
Yes	85	0.52	0.66	0.14	27
Yes	42	0.18	0.24	0.06	33

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nt Pd electrodes

ion	Excess Heat
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NaCN	No
NaCN	No
NaCN	No
NaCN	No
NaCN	No
NaCN	Yes
	Yes
	Yes

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The cell produced excess heat for a time period of -33 hrs at which time the current through the cell was stopped for -5 min. When the current was switched on again no excess heat was observed ($W_{est}-\Delta T$ points were again exactly on the calibration line). The cell was kept running for five days, but the excess heat could not be re-obtained.

Figure 3 shows the calorimetric results for sample B9. There are some distinct differences between the sample B8 and B9. Thus, in the case of B8, the excess heat was observed as soon as the current was switched on. However, in the case of B9, as the current was increased from 0.05 A to 1 A and then back to 0.05 A, the points were very close to the calibration curve. But, in the third cycle, the points moved distinctly above the line and stayed above it. The absolute value of the excess heat for this sample was about half the value obtained for sample B8.

In addition to the above two samples, another Pd electrode of 0.1 cm diameter was tested in a micro-calorimeter (in Center for Electrochemical Systems and Hydrogen Research) and observed to produce excess heat (Fig. 4).

Thus, out of ten electrodes examined for at least 10 days for possible excess heat production, we have observed heat production in excess of that expected from electrochemical theory in three cases, i.e., for electrodes B8, B9 and A9.

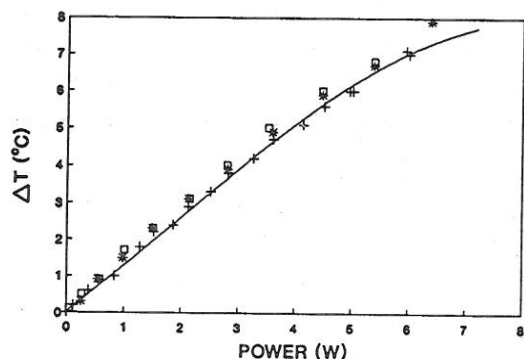


Fig. 3 Temperature difference between the cell and the constant temperature bath as a function of input power into the cell #1 with electrode B9. — - with electrical joule heater; + - charged Pd electrode in 0.1M LiOD solution immediately after transfer from the charging cell to the calorimeter; * and □ - after cycling the electrode from 0.1 A to 1.0 A and back to 0.15 A.

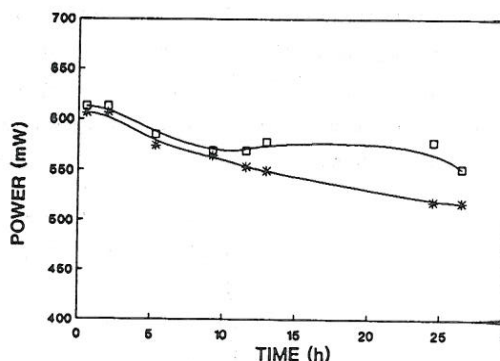


Fig. 4 Power output from the microcalorimeter with 0.1 cm diameter and 1 cm long Pd electrode in 0.1M LiOD solution. ■ - power input according to eq 1; + - measured output power.

The following tentative conclusions can be made:

1) The excess heat observed is around 5 watts cm^{-3} at 400 mA-cm^{-2} . Evidence for the absence of untoward heat production (e.g., from recombination) was given strongly by the persistent falling of points, from many electrodes, precisely on the calibration curve of Fig. 1 (zero excess heat). This agreement also served to verify the eq. $(E-1.54) \times I$ for the normal production of heat from D_2O electrolysis cell.

2) The absolute excess heat produced with electrodes as small as 1 cm in length and 1mm. in diameter at 100 mA-cm^{-2} may therefore be as small as 0.04 watts - many calorimeters at present being used would not have sufficient sensitivity.

3) The effect lasts for times of more than 30 hrs. However, it can suddenly ceases and does not recover.

There is insufficient evidence to know if there is a connection between the excess heat observed here and the emission of neutrons and tritium observed at this University on other (mostly 0.1 cm. diameter) electrodes [7].

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SOME ASPECTS

* To whom correspondence should be addressed.
Chemistry.

ABSTRACT

A constant temperature bath was used to measure the thermal energy output of a sheet electrode during electrolysis. The results are expected from the theory of the electrode.

INTRODUCTION

Recently it has been suggested that the excess enthalpy observed in the electrolysis of water is due to the production of a highly energetic form of the Pd cathode. This form is believed to be a helium atom, which is repulsion between the highly improbable to occur it might be of the same energy output as the electrical energy input (impossible) than the fusion reaction. Whilst there is no evidence whether there