ANOMALOUS CALORIMETRIC RESULTS DURING LONG-TERM EVOLUTION OF DEUTERIUM ON PALLADIUM FROM ALKALINE DEUTEROXIDE ELECTROLYTE

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ABSTRACT

Convincing evidence of anomalous thermal fluxes from palladium cathodes in LiOD solutions is provided. When combined with other evidence for tritium formation, these argue for the existence of solid state nuclear processes in this system. Compared with previous work, effects are only seen at a relatively low level, and they appear to decrease with decreasing electrode surface/volume ratio. They are also observed in a sealed cell with internal gas recombination, which requires no thermodynamic corrections. The effect of lithium ion is seen to be specific, and the effect seems to involve only the palladium surface layers.

INTRODUCTION

In a recent publication, Fleischmann, Pons and Hawkins[1] have alluded to anomalous enthalpy production when deuterium is evolved on palladium from solutions of lithium deuteroxide in deuterium oxide after polarization over long periods of time. These experiments were conducted using a classical calorimetric technique, in which temperature changes were measured using Beckmann thermometers. The authors concluded that nuclear reactions of unknown type involving deuterons dissolved in palladium beyond the composition corresponding to that of the end of the (α+β) phase were taking place, since no significant neutrons or γ-radiation much above background were observed. The total excess thermal energy (4MJ), observed over a period of 120 hours, was much greater than the heat output from any possible chemical process. Such results have not been reported for cathode: that do not significantly absorb deuterium (e.g. platinum), or during hydrogen evolution or palladium from light water. In this paper, we report the results of work on anomalous heat production from palladium cathodes during deuterium evolution from lithium deuteroxide solutions in deuterium oxide. We also present results of control experiments with platinum cathodes evolving deuterium under identical conditions, and with palladium electrodes evolving hydrogen from lithium hydroxide-light water solutions.

EXPERIMENTAL

The investigations were conducted using an automatic precision microcalorimeter (Tronac Model 350, Orem, UT). This is a differential heat conduction instrument with a noise level of less than 0.3 µW and a precision better than 1 µW. The temperature fluctuations of the water bath in the microcalorimeter are controlled to ±0.0002°C. The instrument operates by electrically comparing the voltage signal ΔV across a thermoelectric junction assembly mounted around the working chamber with a similar signal from a reference chamber in the instrument, which avoids fluctuations in the baseline or in the instrument constant. The voltage determined is proportional to the temperature difference across the ends of the thermoelectric pile, and thus to the heat flux. The instrument includes a built-in calibration resistor (about 1000 Ω), with a maximum heat output of 25 mW. Since this level was much below the heat outputs measured, we constructed an extended calibration curve using a standard resistor of smaller value inside the electrochemical cell with and without electrolyte (Fig. 1). It includes any effects of temperature change inside the cell, and is linear over a wide heat flux range. The voltage signal ΔV is monitored using a high-impedance digital voltmeter and the instrument also provided a continuous chart-paper printout of these data, which is available for inspection. The heat flux from the calorimeter is given by $\Delta V.C$, where C is the slope from Figs. 1a and 1b, the calibration plots for the two chambers of the calorimeter. Since the bath temperature of the calorimeter can be adjusted in the range 2°-30° C, it was possible to verify the temperature-independence of the calibration. The value of C was 184.0 with a standard deviation of ±1.23.

Heat generation rates were measured in a closed stainless steel cell, which was used because of its high thermal conductivity. The cell fitted snugly in the working chamber of the microcalorimeter (1 cm × 5 cm × 5 cm) which was located in a large aluminum block in contact with a water bath maintained at 25°C. The latter temperature could be varied by means of a freon bath. Preliminary results established negligible corrections for the heat generated by oxidation of the stainless steel cell in the electrolyte.

Electrochemical cells were assembled with palladium wire cathodes (1 cm long, 0.05 cm diameter) surrounded by spirally wound platinum wire anodes (99.9995% pure, Alfa Products). All cathodes were cut from the same batch of palladium wire (99.997% pure, Alfa Products). Platinum wire leads (0.05 cm diameter) were spot welded to one end of the palladium cathodes and isolated from the solution by means of Teflon. In control cells, a similar electrode configuration was used with a platinum wire substituted for the palladium. All electrode specimens were cleaned using acetone followed by thorough rinsing with ultrapure water. The electrolytes initially used were 0.1 M lithium deuteroxide in 99.8% pure deuterium oxide (Aldrich Chemical Company), and 0.1 M lithium hydroxide in ultrapure light water. Both solutions were prepared by dissolving natural lithium metal ("^{n}Li" 99.9% Pure containing 93 wt % ^{7}Li, Aldrich Chemical Company) in light and heavy water. The cells with the palladium cathodes were examined in the heavy and light water electrolytes, and those with platinum cathodes in the deuterium oxide electrolyte only. In later experiments, 0.1 M NaOD, 1.0 M ^{n}LiOD, 0.1 M ^{7}LiOD and 0.17 M ^{6}LiOD electrolytes were used. They were prepared by dissolving "nuclear" grade sodium metal sealed under argon (Alfa Products), ^{7}Li (99.9% chemical purity, 99.8% isotopic purity, Eagle-Picher Industries) and ^{6}Li (99.97 %

chemical purity, 98.67% isotopic purity, Oak Ridge National Laboratory). The [7]Li isotope was supplier-sealed under argon, whereas the [6]Li was under oil, and was Soxhlet-extracted with hexane before use.

The electrical circuits were carefully checked for leakage currents to ground via the metal cell and it was verified that the working and counter electrodes connected to a constant-current power supply were indeed floating. Any AC component from the power line was verified to be less than 20 mV in 5 V. The cell voltage (V) was continuously monitored using a high-impedance digital voltmeter.

After allowing the stainless steel cell and its contents to thermally equilibrate in the microcalorimeter, palladium working electrodes were polarized cathodically in 0.1 M [n]LiOD at 0.06 A/cm^2 for 40 hours to allow saturation of the palladium with deuterium (or hydrogen) beyond the end of the ($\alpha+\beta$) phase composition. In preliminary work, this was immediately followed by the application of current densities of 0.6 A/cm^2, 1.0 A/cm^2, and 0.3 A/cm^2 for various times (see for example Fig. 2). In this example, the cell currents were 97.2 mA, 161 mA and 49.2 mA, respectively. The voltages were about 4.5V, 5.6V and 3.4V. Some voltage variation, discussed below, was seen as a function of time. While the cells were being polarized, the rates of heat generation were monitored. The heat input could be determined from instantaneous readings of the cell voltage, which could be read to within three (but not four) significant figures. The voltage at constant current showed a random noise in the range ± 2 to ± 10 mV due to variations in effective cell resistance resulting from gas evolution. The cell current, which showed small variations with time, could be determined to a precision of 0.1%. The calorimeter output was a low noise signal typically in the range 1500 to 2500 μV, which was read by a digital voltmeter to a precision of ± 10 μV.

Solvent was periodically added every 48 h to the cell to maintain constant volume due to loss of solution by electrolysis and any entrainment by evolved gas. The measured amount of solvent was 1.7 ml at a current density of 0.6 A/cm^2. This quantity corresponds to the theoretical amount for 100% dissociation of the electrolyte to hydrogen or deuterium and oxygen at a total cell current close to 0.1 A. In no case was the electrolyte level allowed to fall so that platinum or palladium wires were exposed above the electrolyte. After each addition, the cell and its contents were allowed to reequilibrate before further recordings were made.

RESULTS

Plots of the cell potential and of the excess rate of heat generation, recorded as a function of time for a palladium wire cathode in 0.1 M [n]LiOD, are presented in Figure 2. The rate of excess enthalpy generation, ΔQ, is given by:

$$\Delta Q = Q - \{E-(\Delta H/F)\}I \qquad (1)$$

where Q is the total rate of enthalpy generation, E is the cell potential, ΔH is the heat of formation of gaseous D_2 or H_2 and O_2 from liquid D_2O or H_2O, as appropriate, F is the numerical value of the Faraday in joules, and I is the current passing through the cell. The value of $\Delta H/F$ is 1.527 V for D_2O (rounded to 1.53 V) and 1.48 V for H_2O. The excess enthalpy flux for D_2O was therefore:

$$\Delta Q = \Delta V.C - (E - 1.53)I \qquad (2)$$

The correction for evaporation of solvent and the smaller effect of heat loss in the escaping gas was determined to be small (certainly less than -2 mW at a cell temperature maintained close to 25°C by the heat conduction calorimeter), compared with the order of magnitude of the heat flux changes sought.

Consideration of the precision of reading ΔV, E and I, along with the standard deviation of C, suggests the error in determining ΔQ using Equation 2 is ±3 mW. However, to verify that Equ. 2 can be used to accurately calculate the irreversible heat flux, it is necessary to show that recombination of the gases is small. Although it is possible to estimate the extent of recombination from the measured amount of solvent periodically added to the cell, for a more precise determination gas volumes from the operating cell were measured using a gas burette during electrolysis, both on the bench and in the calorimeter. Results obtained were always slightly less than, but within about 1% of, the theoretical value, indicating a small amount of recombination, presumably by diffusion of oxygen through the electrolyte to the cathode. If the fraction of gases recombining during the experiment is x, the heat flux input to the calorimeter will be (E - [1.53][1-x])I. If x is indeed 0.01, then the error in ΔQ will be positive and equal to about +1.5 mW, Thus, a small amount of recombination will tend to compensate the heat loss resulting from evaporation and other heat losses. Since these corrections are within the overall estimated error bars, the latter are shown as ± 3 mW on the plots of the experimental results. Breaks are shown in the plots corresponding to the re-equilibration times for the calorimeter after the cells were opened for verification or electrolyte addition. These corresponded to intervals of 1-2 hours.

The result in Fig. 2 shows an excess rate of heat generation (i.e. over and above the rate of heat generation due to irreversible losses in the electrochemical cell) several hours after the current density was increased to 0.6 A/cm^2 from 0.06 A/cm^2, the current density for charging of palladium with deuterium. It is interesting to note that at current densities of 0.6 and 1.0 A/cm^2, the excess rate of heat generation was 38 mW, whereas at 0.3 A/cm^2 it decreased to 29 mW. As a percentage of the irreversible heat flux input to the calorimeter, the excess heat was 6.1%, 13.2%, and 31.5% at 1.0, 0.6, and 0.3 A/cm^2 respectively. The fact that the rate of excess heat evolution increases as heat input (i.e., the reaction rate) to the calorimeter decreases is a strong argument against a spurious chemical explanation of this effect, particularly anomalous (and unobserved) recombination of deuterium and oxygen. The highest heat generation rate observed (at 0.6 A/cm^2) corresponded to 19.3 W/cm^3 of Pd, which is comparable to that reported by Fleischmann, Pons and Hawkins (26 W/cm^3).

A similar experiment to that shown in Figure 2 was carried out using a platinum cathode in 0.1 M ^{n}LiOD for a period of 80 hours. Since platinum does not form a hydrogen or deuterium bulk alloy, a current density of 0.6 A/cm^2 was applied from the beginning of the experiment. From the data in Figure 3, it is clear that there was no excess heat generation in this case. In a third experiment, electrolysis of H_2O from 0.1 M ^{n}LiOH using a palladium cathode, and the same current density sequence as in Fig. 2, did not reveal any excess heat generation, as shown in Figure 4. These results again demonstrate that recombination of evolved oxygen and deuterium gases within the electrochemical cell should not be a chemical source of the excess rate of heat generation

observed for deuterium evolution on a palladium cathode from the ^{n}LiOD electrolyte. The experiments in Figures 3 and 4 have been repeated three times with palladium cathodes in ^{n}LiOH electrolyte, and three times with platinum cathodes in ^{n}LiOD electrolyte, each giving identical results to the examples shown.

The sequence of current densities shown in Fig. 2 for palladium cathodes in ^{n}LiOD electrolyte was repeated for several different specimens of different dimensions, origins, and pre treatments. In all cases, some excess heat generation was observed, the quantity varying according to the nature of the specimen. All results are shown in Table 1. Following Fleischmann and Pons, anomalous heat flux results are expressed in W/cm^3. The highest value obtained (about 25 W/cm^3) was for an annealed wire, 0.05 cm diameter, from the same lot as that used for Fig. 2. These results are shown in Fig. 5-Relatively lower values (6-12 W/cm^3) were obtained on a spherical electrode, 0.2 cm diameter, prepared by melting another sample of the same wire. A further result was obtained on a 0.1 cm diameter wire of "investment" quality. Before stepping up the current density to 0.6 A/cm^2, charging was this time conducted at 0.06 A/cm^2 for two weeks. Results for this wire, expressed in terms of raw data (i.e., ΔV.C and [E - 1.53]I), are shown in Fig. 6. It can be seen that from the start of deuterium evolution at 0.6 A/cm^2, this electrode produced an excess heat flux at a low level. However, after about 12 hours, about 30-60 mW excess heat flux was produced, corresponding to 4-7 W/cm^3. In the case of the specimens shown in both Fig. 5 and Fig. 6, the anomalous heat production was associated with a falling cell potential as a function of time, although this was not consistently true of the other specimens studied. In contrast to the results shown in Figs. 2 and 5, some decay of anomalous heat occurs after 25 h in this case.

Results for two experiments for 0.5 mm diameter annealed Pd wires in 0.1 M ^{n}LiOD and ^{n}LiOH are shown in a more detailed form as a function of time in Table 2. In ^{n}LiOH solution, the cell voltage starts at 4.325 V and shows a slight initial rise as electrolysis proceeds, which we suggest may be due to the effect of impurities. This is followed by a fall as electrolysis proceeds and as the solution becomes more concentrated, hence more conductive. On adding 1.7 ml of solvent, the voltage increases to a value 200 mV greater than that initially observed, which again falls smoothly by 200 mV as the solvent is consumed. In all cases, the heat output from the calorimeter is slightly less than the heat input corrected assuming 100% Faradaic efficiency for electrolysis. In contrast, the cell voltage in ^{n}LiOD solution starts at a considerably higher voltage, reflecting its lower conductivity than that of ^{n}LiOH. This voltage initially falls as the solution concentrates over the first 24 h, then it shows a rise as the production of anomalous heat becomes more evident.

More results are shown in Fig. 7 for a 0.05 cm diameter "as-received" palladium wire initiated in ^{n}LiOD solution. An excess rate of heat generation can be seen starting about 3.5 h after the current density was increased to 0.6 A/cm^2 from 0.06 A/cm^2. After a rise time of a further 14 h, excess enthalpy generation had reached a maximum value of 36 mW, equivalent to 18.3 W/cm^3, compared with 19.3 W/cm^3 observed in Figure 2 for a specimen cut from the same wire sample. However, a rise time of 50 h was required to show the maximum effect in this case. After allowing the excess enthalpy generation to stabilize for 10 h, 0.1 M NaOD electrolyte was substituted, giving a rapid decay of the effect, most having disappeared after 4 h. The cell potential was about 340 mV lower in

the NaOD solution, whose specific conductivity is higher than that of 0.1 M ^{n}LiOD. After 24 h, the excess heat flux had fallen to 4 mW and the electrolyte was again changed to 0.1 M ^{n}LiOD. The excess heat flux then rapidly redeveloped, reaching a maximum similar to that observed earlier within 12 h. After a further 12 h, the electrolyte was changed for 1.0 M ^{n}LiOD. In this case build-up of the excess heat after recovery from switching off the current was slow, perhaps due to impurity accumulation by plating-out on the electrode surface from the more concentrated solution, in which the cell voltage was about 3.5 V, compared with about 5.2 V in 0.1 M ^{n}LiOD. The final rate of excess heat production was similar to that in the latter.

After 23 h the current was switched off and heat generation was allowed to decay. Fig. 8 shows the cell voltage and absolute heat decay rates on switch-off. The former is very rapid: After a change of scale, an open-circuit voltage of about 1 V is observed, corresponding to that for the oxidized platinum anode against the deuterium-charged palladium cathode. Within about 1 hour, the open circuit voltage decayed to about 350 mV, followed by a slow decay as deuterium was lost from the palladium and the platinum surface became reduced. The rate of heat decay is the same as that for a heated electrical resistance within the cell, hence it can also be described as instantaneous, corresponding in practice to the time constant of the microcalorimeter.

A similar set of results is shown in Fig. 9 for an annealed wire. In obtaining these, 0.1 M ^{7}LiOD electrolyte, rather than 0.1 M ^{n}LiOD, was substituted for 0.1 M NaOD. Results are broadly similar to those shown in Fig. 7, however, while the time interval from changing the current density tenfold to the appearance of excess enthalpy production on the palladium cathode was rapid (about 1 h), the rise time was slower (about 20 hours instead of 14 hours). It was also much slower than for the annealed wire studied in the same electrolyte in Fig. 5, where initiation of the phenomenon from switching the current density from 0.06 A/cm^2 to 0.6 A/cm^2 took only 2.2 h, reaching close to the maximum value after a further 3.5 h. The maximum excess enthalpy production was this time 34 mW, or 94% of that in Fig. 7. In the previous work reported, a similarly treated annealed wire produced 49 mW (25 W/cm^3). These differences may be due to the presence of trace impurities, since the palladium cathode surface blackens and roughens with use. Surface examination by the SEM shows mossy surface growths, and SIMS and Auger data (to be reported separately) show the presence of transition metals other than Pd, as well as a relatively large amount of Li, at the surface.

Fig. 10 shows similar data to those on Fig. 9, this time on an annealed wire immersed from the beginning in 0.17 M ^{6}LiOD electrolyte. Initiation time from the application of 0.6 A/cm^2 was almost instantaneous, and the slope of the rise was about the same as for ^{n}LiOD in Fig. 8. The final result obtained in this series of experiments is given in Fig. 11, which shows results for an untreated palladium electrode 2 mm in thickness cut from a 4 mm diameter rod (Johnson-Matthey) cut from the same rod stock used by the authors of Ref. 1. The disk-shaped electrode was immersed in 0.1 M ^{n}LiOD in a sealed cell containing a platinum black fuel cell electrode for gas recombination. In this case, no thermodynamic corrections at all are required in evaluating the results, which are shown in tabular form in Table 3. After precharging in 0.1 M ^{n}LiOD at 0.06 A/cm^2 for two weeks, the maximum excess enthalpy production was similar to that in other cells, about 30 mW, however it represented only about 3% of the maximum heat flux input of 900

mW. Because of limitations in the power supply used, the maximum current density was limited to 400 mA/cm^2. The most interesting effect noted is the abrupt fall in excess enthalpy production on reducing the current density from an initial value of 350 mA/cm^2 to 200 mA/cm^2, which is followed by a slow rise over 20 h. A further change to 400 mA/cm^2 results in a short horizontal characteristic, followed by a further slow rise. This may be interpreted as suggesting that 200 mA/cm^2 is perhaps close to a threshold current density for the anomalous heat phenomenon to occur, at least under the conditions used by us.

DISCUSSION

The detailed results reported above show that excess enthalpy production during electrolysis of D$_2$O solutions on Pd is a real effect, at least in certain electrolytes, and we thus confirm at least some aspects of the rather limited details given in the paper by Fleischmann, Pons and Hawkins[1]. By expressing their results in terms of the excess heat flux per unit volume of the electrode, these authors presumably assumed that they were observing a bulk phenomenon. However, their data scarcely suggest this, since in their reported work[1] at 0.008 A/cm^2, a change of electrode volume by a factor of 16 increased the excess heat flux by only 28%. The corresponding increase at 0.064 A/cm^2 was 38%, and at 0.512 A/cm^2, 257%. For a wire of diameter similar to that in Fig. 6, Fleischmann and Pons obtained 8.33 W/cm^3 excess enthalpy production at 0.512 A/cm^2. Hence, the high values for the 0.05 cm diameter wires used in this work, particularly the annealed specimen, may be atypical.

The results shown in Figs. 7, 9 and 10 show that excess enthalpy production required the presence of lithium in the electrolyte, indifferently ^{6}Li or ^{7}Li isotopes. Replacement of lithium-containing alkaline electrolyte by sodium causes a rapid fall in excess enthalpy production. The rate of this fall suggests that it is due to lithium leaching from the surface. This strongly suggests that a superficial chemical process underlies the effect, although it does not necessarily mean that the excess heat is of chemical origin. Furthermore, the results on the platinum cathodes, compared with those obtained with palladium, indicate that the effect is not exclusively at the metal surface, but appears to be only associated with dissolved (i.e., alloyed) deuterium (and not protonic hydrogen) present in the surface layers of palladium. When the current to the cell was switched off, rapid decay of the excess heat occurred, since ΔV decayed as a function of time in the same way as heat produced by an electric heater inside the cell. If we can discount continuously-occurring chemical explanations such as gas recombination for this phenomenon, other chemical events also seem unlikely. For example, 15 W/cm^3 for 80 h represents over 40,000 kJ/mole or 0.45 keV/Pd atom, which is far greater than either the bond strength of palladium (about 0.67 eV/Pd atom) or the latent heat of sublimation of the metal (4 eV/Pd atom). Even if all of the electrolyte had been involved in some chemical or physical change, this must involve about 17 kJ/mole, which should have been detected.

In the present work, the specific effect of lithium has been shown. This should be contrasted with the recent results of Iyengar[2], which show anomalous heat, with tritium formation, in 5 M NaOD at current densities in the 0.2-0.3 A/cm^2 range at Pd-Ag alloy electrodes. While lithium metal (with a deposition potential from pH 13 LiOH solution of

-2.310 V vs H_2 under the same conditions) is unlikely to plate out on the palladium cathode, LiD (deposition potential of LiH is -806 mV on the same scale) may well do so. We therefore suggest that the deposition of a lithium deuteride layer from a concentrated, i.e., almost D_2O-free electrolyte, at the cathode surface under high current density conditions for deuterium evolution may be responsible. Such a coating, once formed, may easily lose lithium ions into the palladium lattice, to form a superficial lithium alloy. Similarly, D$^-$ could lose its two electrons and also pass into the metal. Sodium deuteride, whose deposition potential is close to that of LiD, would also be expected to form on the electrode surface from NaOD solutions, but it may be less likely to alloy with the palladium lattice. With Pd-Ag electrodes and a 5M NaOD solution[2], the situation is evidently different. When electrodes exposed to LiOD solution are exposed to NaOD under the conditions used in this work, the superficial compounds formed may leach out, and anomalous enthalpy production stops. The NaOD data reported here are highly reproducible, and have been repeated a total of five times to date on different palladium cathode samples.

Whether nuclear events are responsible for anomalous heat production depends on the detection of nuclear products. In parallel work at this University, Wolf et al.[3] have examined neutron fluxes from cells containing the same 0.1 cm palladium wires reported in Figure 6, again operating in the 0.6 A/cm^2 range. Results have been inconsistent, neutrons occasionally being observed at a level of about five times background, i.e., many orders of magnitude less than that corresponding to the level of the excess heat flux observed, assuming the usual approximately equal branching ratios for $^2D + {}^2D \rightarrow {}^3He + {}^1n$ or $^3T + {}^1p$. Iyengar[2] has suggested a branching ratio of 10^8. Our collaborators at this University (Bockris et al.[4]) have observed high levels of tritium in the electrolyte ($> 10^6$ disintegrations/ml/min, compared with background values (200 disintegrations/ml/min) at the start of experiments. Their work showed that more tritium was formed in the gas phase than was present in the electrolyte. However, results have been sporadic, suggesting that tritium is formed within the electrode, at least initially. If the tritium formed corresponds to the anomalous heat, about 10^{16} atoms, (or 0.01% of the total palladium atoms present), should be formed over 80 h. High tritium levels in the electrolyte are only observed after charging for long times (2-6 weeks) at 0.06 A/cm^2. We have observed no significant amounts of tritium in the electrolyte during the course of the relatively short-term experiments reported above.

Samples of 0.05 cm and 0.1 cm diameter palladium wires in "as-received" form and after serving as cathodes in the above experiments were analyzed at Atomics International Division of Rocketdyne Corporation, Canoga Park, CA, and at Lawrence Livermore National Laboratory. Neither ^3He nor ^4He were observed above background (10^{12} and 2.5×10^{11} atoms per ml respectively). However, if no significant neutrons are observed, ^3He as a primary reaction product would not be expected. It is usually considered that ^4He is an improbable fusion product in a plasma phase, but perhaps it is not in a lattice, as noted in a recent paper by Walling and Simons[5]. If the process involves a skin effect, ^4He would probably escape in the solution. We should note that lack of ^3He in the bulk of the palladium indicates that no known deuterium fusion process involving the classical branching ratio between the $^3He + {}^1n$ and $^3T + {}^1p$ channels is occurring in the bulk at a enthalpy production level greater than a fraction of 1 μW. Similarly, the quantitative upper limit for tritium production in the bulk palladium in an electrode that

was assayed 5 days after a series of experiments was about 1.5×10^{15} atoms/ml, about 3000 times less than the amount expected from the enthalpy evolved. However, this electrode had degassed, and tritium and deuterium would have been lost both from the surface layers and the bulk. Further work is clearly needed to clarify the origin of the observed heat flux.

The ensemble of results, however, show that chemical enthalpy resulting from spurious gas-phase processes is a highly improbable explanation of the heat flux effects seen with LiOD isotopic species present. The results also persuasively show that the phenomena do not appear to be true bulk effects, but that they occur within the surface skin. The time-integrated results are much too large[1] to be explained by continuous chemical processes taking place in a thin superficial skin of palladium. It is also improbable that they can be cyclic chemical processes, for example lithium deposition taking place in surface cracks, followed by its dissolution to produce hydrogen, as one reviewer of this paper suggested. This would be akin to an a.c. impedance effect, and as such it should be detectable at the levels observed. The anomalous heat effects are however chemically initiated by Li ions, and they may well not be identical to those noted by Fleischmann, Pons and Hawkins[1]. Indeed, with larger electrodes, the excess enthalpy production observed here is relatively low grade compared with that reported by the latter authors. Our results on 0.1 cm diameter wires were about the same as those reported in Ref. 1, but as stated above, those with 0.05 cm diameter wires were significantly higher. We presently have no explanation of either this, or as to why the excess heat went through a maximum in the experiment shown in Fig. 2, or for the fall shown at 24 h in Fig. 6.

If the excess enthalpy production is due to nuclear fusion, lithium ions are most unlikely to be involved due to their s-electron screen and the apparent lack of an isotope effect. Further evidence is required to say whether they are due to some unusual form of $^2D + {}^2D$ fusion associated with the presence of the palladium lattice[5]. Finally, the fact that surface phenomena initiate the anomalous enthalpy production effects may explain the lack of success of many laboratories in reproducing the Fleischmann-Pons results, since such reactions are known to be very sensitive to surface pretreatment and to the effect of impurities that might be present.

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TABLE 1

Exp. #	Electrode Material		Electrolyte	Current Density	Rate of Excess Heat Generation
	Cathode	Anode		mA/cm^2	W/cm^3 of Pd
1	as-received Pd 0.5 mm dia. 10 mm long	Pt	0.1M LiOD	300	16.3
				600	19.3
				1000	18.5
2	as-received Pd 1.0 mm dia. 10 mm long	Pt	0.1M LiOD	600	4-7
3	annealed Pd 0.5 mm dia. 10 mm long	Pt	0.1M LiOD	600	22-25
4	arc-melted Pd 2.0mm dia. sphere	Pt	0.1M LiOD	600	6-12

Table 1: Excess Enthalpy Production from Various Pd Specimens in 0.1 M LiOD at 0.6 A/cm^2.

TABLE 2

Date	Time	Cell Current (mA)	Cell Voltage (V)	Power In (mW)	Power Out (mW)	Excess Heat (mW)
5/11	10:30	98.18	5.26	359.33	385.00	25.67
5/11	12:50	98.02	5.13	351.89	381.20	29.31
5/11	16:15	97.79	5.06	344.22	381.50	37.28
5/12	08:45	97.81	4.91	329.62	367.50	37.88
5/12	12:10	97.80	4.92	330.566	371.00	40.44
5/12	16:00	97.91	4.97	335.83	375.00	39.17
5/12	17:00	98.20	5.04	343.37	382.37	38.96
5/12	21:45	97.80	4.90	328.61	371.46	42.85
5/13	11:00	97.53	4.75	313.07	358.77	45.70
Calorimeter opened at 11:00 on 5/13 to measure electrolyte volume--1.7 ml/2 days consumed. 1.7 mls of D_2O was added.						
5/14	09:00	97.03	4.70	306.61	341.25	34.64
5/15	08:00	97.03	4.75	311.46	350.05	38.59

Date	Time	Cell Current (mA)	Cell Voltage (V)	Power In (mW)	Power Out (mW)	Excess Heat (mW)
5/27	11:30	96.40	4.325	274.46	271.80	-2.66
5/27	13:00	96.35	4.335	275.08	271.80	-3.28
5/27	18:00	96.40	4.330	274.74	271.80	-2.94
5/28	10:00	96.55	4.295	271.79	271.80	0.01
5/28	11:30	96.60	4.295	271.93	271.80	-0.13
5/28	20:00	96.61	4.280	270.51	268.18	-2.33
5/29	08:10	96.60	4.232	265.84	264.55	-1.29
Calorimeter opened at 08:15 on 5/29 to measure electrolyte volume—1.7 ml/2 days consumed. 1.7 mls of H_2O was added.						
5/29	12:00	96.58	4.532	29"4.47	293.54	-0.93
5/29	15:00	96.56	4.525	293.83	291.73	-2.10
5/29	17:00	96.45	4.520	293.20	291.73	-1.47
5/29	22:00	96.60	4.500	291.73	289.92	-1.81
5/30	08:10	96.61	4.450	286.90	286.30	-0.60
5/30	11:00	96.58	4.430	284.91	284.48	-0.43
5/30	15:30	96.55	4.410	282.89	282.67	-0.22
5/31	08:00	96.60	4.330	275.31	273.62	-1.69
5/31	15:30	96.58	4.320	274.29	273.62	-0.67

Table 2: Enthalpy data for Pd in 0.1 M LiOD and 0.1 M LiOH electrolytes. The cathodes consisted of a palladium wire (0.5 mm diameter, 1 cm in length, 0.159 cm^2, 1.96×10^{-3} cm^3, 99.997% pure) supplied by Johnson-Matthey. The electrodes were annealed at

950°C for 0.5 hr at 10^{-6} torr and afterwards allowed to cool in the furnace under vacuum. The electrodes were previously charged at 60 mA cm^{-2} for two days. The "closed" electrochemical cells initially contained 7.8 ml of electrolyte. The anodes were a spiral of platinum wire.

<div align="center">TABLE 3</div>

Date	Time	Cell Current (mA)	Cell Voltage (V)	Power In (mW)	Power Out (mW)	Excess Heat (mW)
7/4	08:00	100.75	4.440	447.33	465.85	18.52
7/4	10:30	175.60	6.175	1,084.33	1,122.18	37.85
7/4	12:50	175.25	6.090	1,067.27	1,110.70	43.43
7/4	15:10	175.25	6.030	1,059.77	1,095.70	36.00
7/4	16:25	175.70	6.010	1,055.96	1,089.14	33.18
7/4	22:55	175.70	6.050	1,062.99	1,099.50	36.51

Table 3: Excess enthalpy production in a sealed cell. The cathode consisted of a palladium disc (4 mm diameter, 2 mm thick, 0.501 cm^2, 2.51×10^{-2} cm^3, 99.997% pure) supplied by Johnson-Matthey. The electrode was previously charged at 60 mA cm^{-2} for two weeks. The sealed electrochemical cell initially contained 7.8 ml of 0.1 M D$_2$O. The anode was a spiral of platinum wire and the O$_2$-D$_2$ recombination catalyst was a segment of a fuel cell electrode.
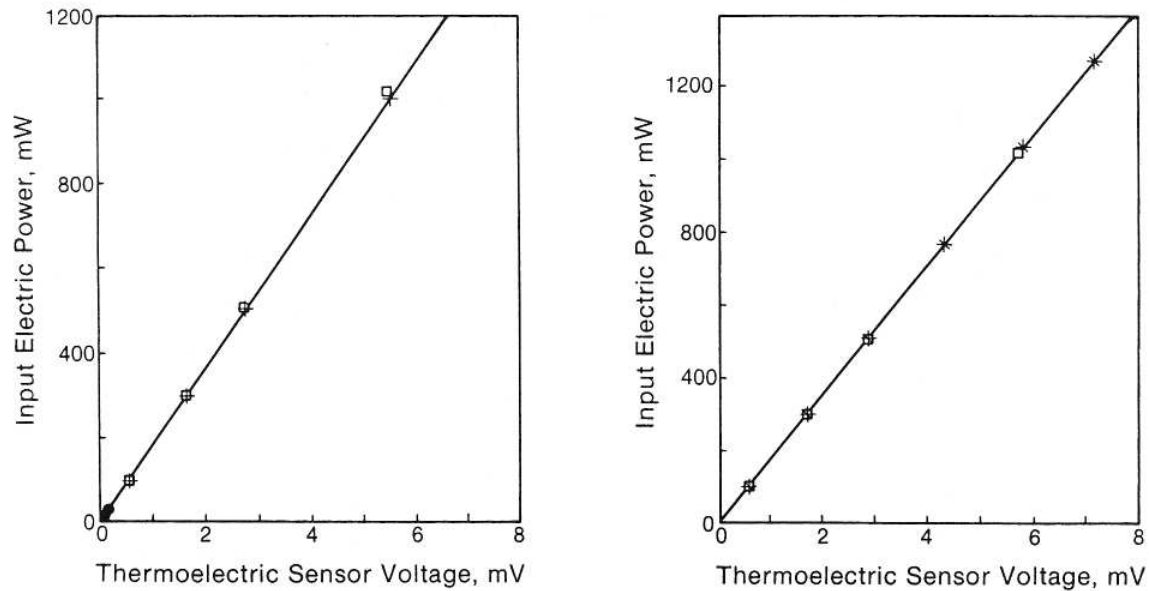
Figure 1: Calibration curve for microcalorimeter. ● : With built-in resistor (limited to 25 mW); + : With resistor in cell without electrolyte; □ : With resistor in cell containing electrolyte.
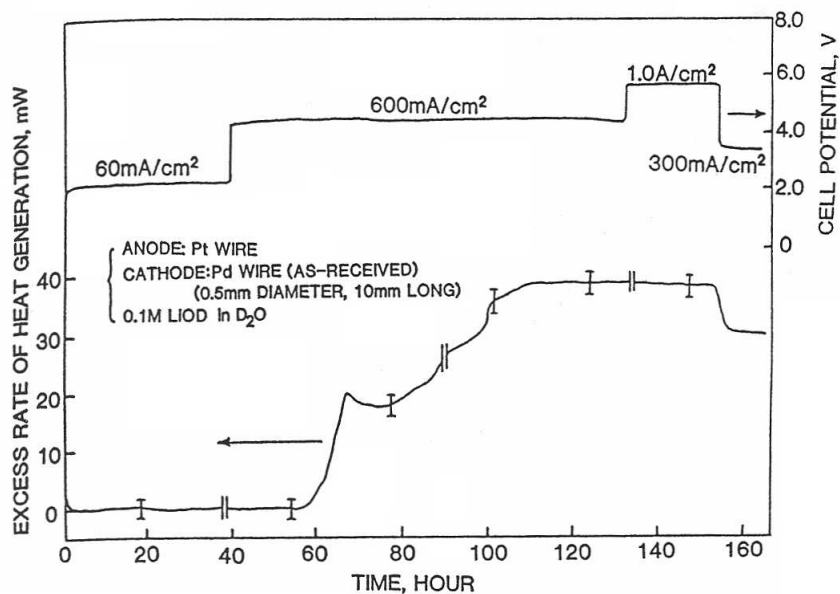
Figure 2: Cell potential and excess rate of heat generation on a 0.05 cm diameter as-received palladium cathode at various current densities as a function of time in 0.1MLiOD in D_2O.
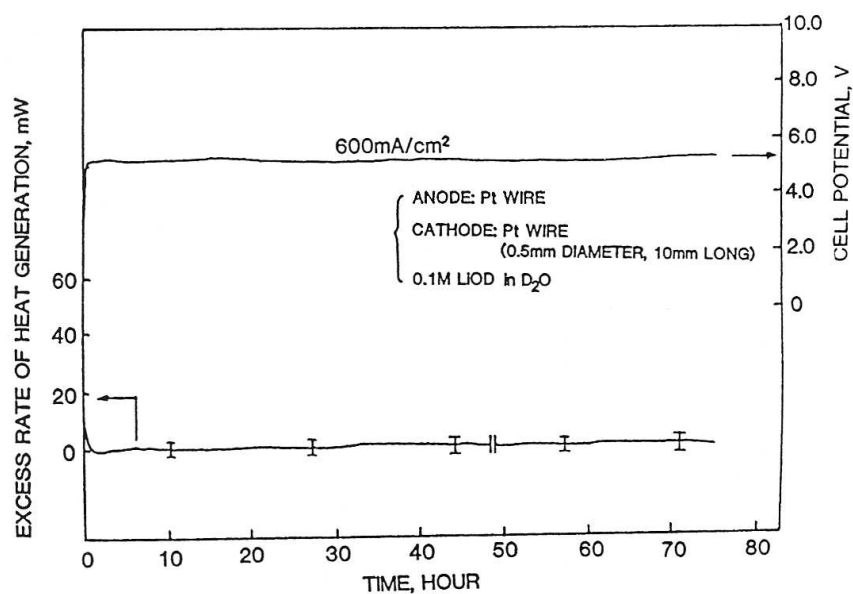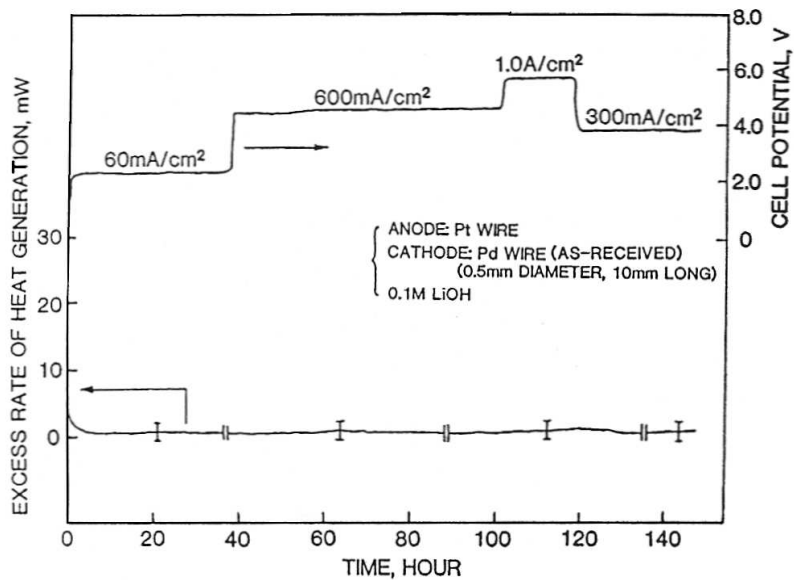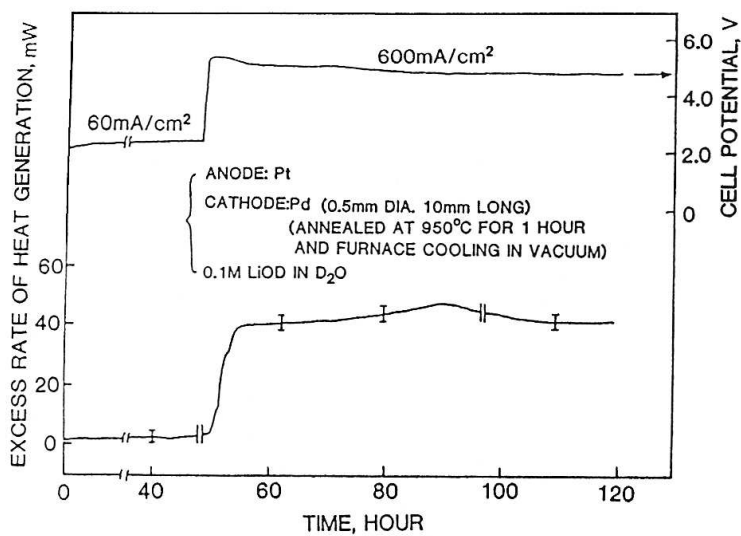

Figure 3: Cell potential and excess rate of heat generation on a 0.05 cm diameter as-received platinum cathode at 0.6 A/cm^2 as a function of time in 0.1M LiOD in D_2O.

Figure 4: Cell potential and excess rate of heat generation on a 0.05 cm diameter as-received palladium cathode at various current densities as a function of time in 0.1 M LiOH.

Figure 5: Cell potential and excess rate of heat generation on a 0.05 cm diameter annealed palladium cathode at various current densities as a function of time in 0.1 M LiOD in D_2O.
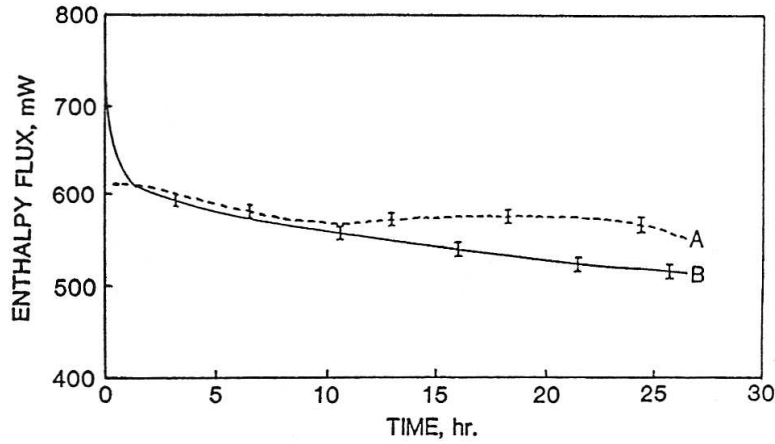
Figure 6: Heat flux: B - entering calorimeter and A - leaving calorimeter, for deuterium evolution at 0.6 A/cm^2 in 0.1M LiOD in D$_2$O on a 0.10 cm diameter as-received palladium cathode after charging for two weeks at 0.06 A/cm^2 as a function of time.
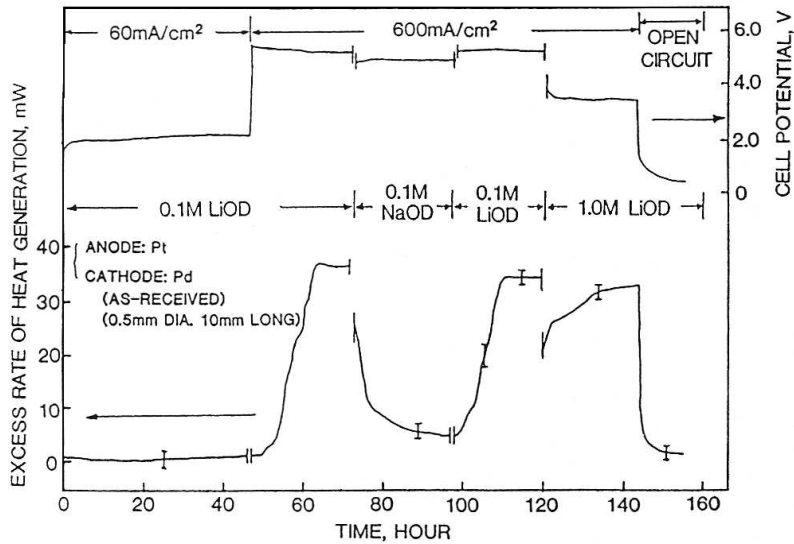
Figure 7: Excess enthalpy generation rates during electrolysis of D$_2$O on a Pd cathode in alkaline solutions showing the specific effect of lithium cation.
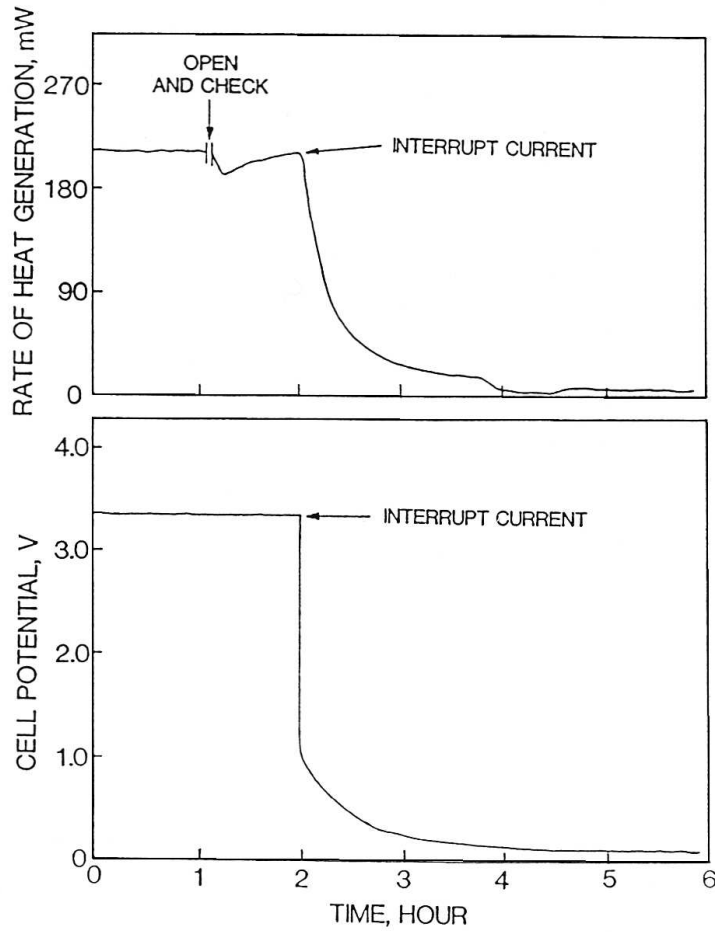
Figure 8: Chart recorder tracings showing the rapid decay of enthalpy generation rate on interruption of the electrolysis current. The decay of the open-circuit potential of the cell is apparent.
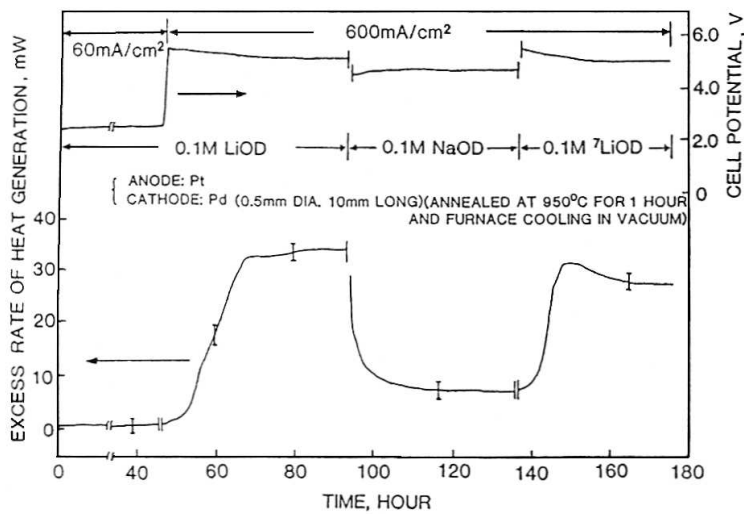

Figure 9: Excess enthalpy generation rates during electrolysis of D_2O on a Pd cathode in alkaline solutions showing 0.1 M electrolyte changes in the sequence $^nLiOD \rightarrow NaOD \rightarrow {}^7LiOD$.
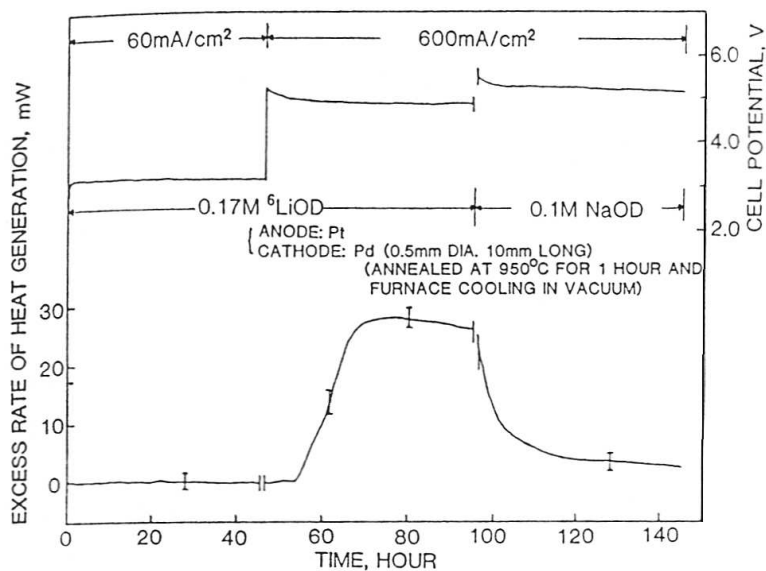
Figure 10: Excess enthalpy generation rates during electrolysis of D_2O on a Pd cathode in 0.17 M ^{6}LiOD as a function of time, showing the decay of excess heat flux to negligible values when the electrolyte was changed to 0.1 M NaOD.
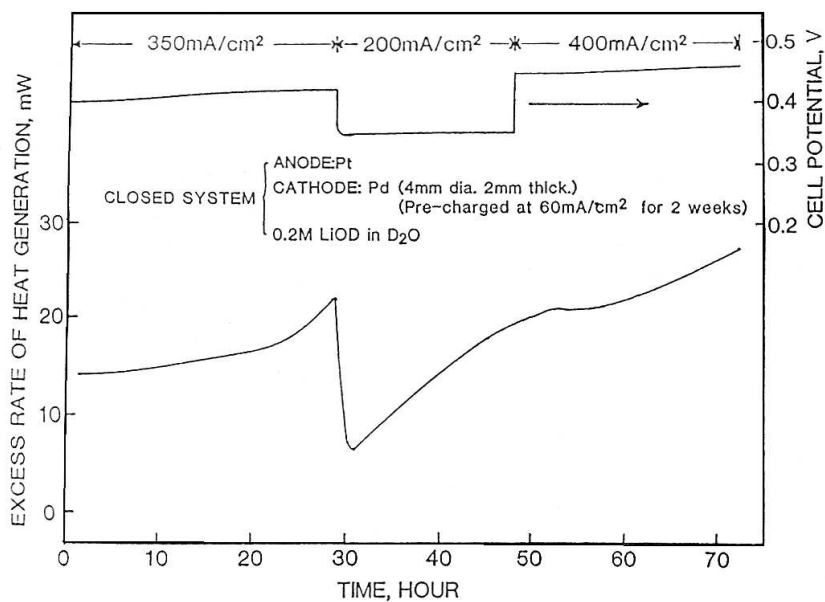

Figure 11: Excess enthalpy generation rates on a palladium disc electrode on electrolyzing a 0.1M LiOD solution in a sealed cell.