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Calorimetric measurements during long-term electrolysis of some LiOD solutions

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Abstract

Long-term calorimetric measurements of energy production during the electrolysis of LiOD solutions with palladium or titanium electrodes were carried out using an automated diathermal calorimeter. No excess energy attributable to "cold fusion" was detected.

INTRODUCTION

In the context of recent claims [1,2] of excess energy production during electrolysis of LiOD solutions with palladium cathodes, we decided to carry out calorimetric studies to supplement our efforts to detect ^{4}He or T production by a mass spectroscopic technique [3]. The magnitude of the excess enthalpy expected from cold fusion (i.e. the enthalpy change over and above that established for normal electrochemical processes), and previously claimed by Fleischmann and co-workers [1,2] is so large that it should be easily detected, even with very simple calorimetry. Because "cold fusion", if it occurs at all, is expected only at odd intervals, or after long induction periods, we employed a calorimeter designed to operate unattended over long periods. For that purpose we constructed a simple diathermal calorimeter monitored with a computer controlled data system.

CALORIMETRIC TECHNIQUE

In a calorimeter designed to measure a constant heat flux, thermal power is exchanged with the surroundings (or "bath") at a constant rate

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$(dq/dt)_{\mathrm{calorimeter}} = -(dq/dt)_{\mathrm{bath}}$. If the bath is held at constant temperature the cell will come to a different (and higher) temperature after sufficient time. If the temperature difference is not too large, the process is first order and $(dq/dt) = -k(T_{\mathrm{cell}} - \mathrm{T}_{\mathrm{bath}})$. The proportionality constant k may be deduced by making a series of steady state measurements at different heat fluxes. It is also useful to examine the kinetics of the first order decay of $(T_{\mathrm{cell}} - T_{\mathrm{bath}})$ when the power input to the cell is switched off. In that case the heat flux, cell to bath, decays as the cell temperature drops, $d(dq/dt) = -c\ dT$. The cell temperature reaches bath temperature after a suitably long time, where $T_{\mathrm{cell},\infty} = T_\infty = T_{\mathrm{bath}}$. Appropriate substitution leads to

$$\ln[(T - T_\infty)/(T_0 - T_\infty)] = -(k/c)(t - t_0) \tag{1}$$

where T_0 is the cell temperature at time t_0 when the decay process is started. For the present experiments the total temperature change is small, amounting at most to a few degrees, and the temperature difference $T_{\mathrm{cell}} - T_{\mathrm{bath}}$ is accurately proportional to the change in resistance of the platinum RTD temperature sensors,` $\Delta T = a\ \Delta R$, so

$$(t - t_0) = -(c/k)\ \ln[(\Delta R - \Delta R_\infty)/(\Delta R_0 - \Delta R_\infty)] \tag{2}$$

We determined c/k and k by appropriate measurements of decay rates and steady state measurements of resistance differences as a function of heat flux into the electrochemical cell. Least squares analysis of the individual runs showing ΔR versus t allowed definition of the fitting parameters $-(c/k)$, ΔR_∞ and t_0. The assumption of first order decay was nicely borne out by the measurements.

In long-time electrolysis runs the amount of material in the calorimeter slowly decreased as D_2 (or H_2) and O_2 gassed off, and the assumption of constant mass, which is intrinsic to the development above, was not met. The result was a slow drift in $(T_{\mathrm{cell}} - \mathrm{T}_{\mathrm{bath}})$ which continued until make-up water was added. (Typically about 25% of the starting material was electrolyzed; make-up water was added every few days, and the amount of fluid in the cell was never allowed to drop below 95% of the initial value.) In any event the slow drift from this cause can in no sense disturb the detection of periodic or occasional energy bursts of the kind claimed by Fleischmann and Pons. Those bursts should appear as large peaks on time–temperature plots of the calorimeter data. Indeed, Fleischmann et al. [2] showed figures of several time–temperature plots displaying large transient peaks of this nature.

CALORIMETRIC EXPERIMENT

The calorimeter resulting from the considerations above is shown diagrammatically in Fig. 1. The electrolysis cell and its surrounding air jacket

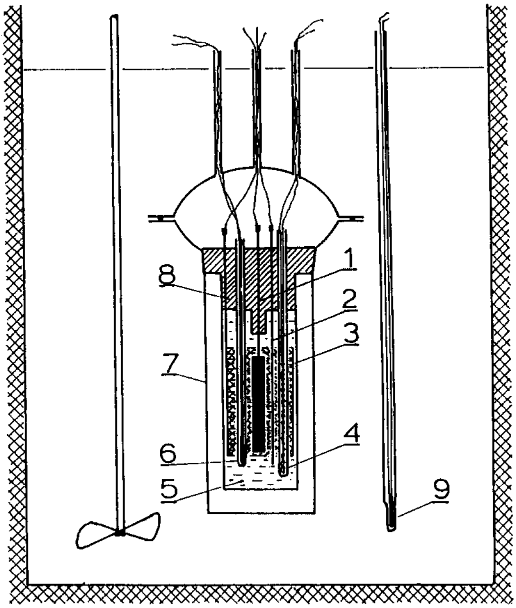

Fig. 1. Electrolysis cell used for diathermal calorimetric measurements. Key: 1, Pd or Ti cathode; 2, reference electrode; 3, Pt anode concentric to cathode; 4, calibration electrical resistance heater; 5, electrolyte solution; 6, platinum resistance thermometer (cell); 7, external glass jacket separated from electrolysis cell by 0.5 cm air gap; 8, Teflon cap; 9, platinum resitance thermometer (bath).

(introduced to give convenient values for k and k/c) are completely submerged in a reservoir (bath) containing about 70 dm^3 of water. The bath is not thermostatted but is large enough appreciably to damp room temperature fluctuations. Over long times the bath thermally averages room temperature, but a slow thermal wave with an amplitude of 0.01 to 0.02 K for $(T_{\text{cell}} - T_{\text{bath}})$ and one-day periodicity is observed. That slow change is the equivalent, peak to peak, of 1–2% or so of the thermal flux, and sets the limit on sensitivity for the detection of slow changes in heat flux. More rapid changes, say ones with characteristic rise times of 1 h or less, can be detected with somewhat better sensitivity, about 0.5%. The electrodes and calibrating heater are powered from a potentiostat to assure a constant current for electrolysis or calibration. The electrolysis or heater currents are measured by determining the voltage drop across a standard resistor. Cell and bath temperatures were measured with four-terminal 100 Ω platinum wound RTD elements. The electrolysis or heater calibration currents were recorded with an Apple II computer using a DAISI AI-13 interface. The RTD resistances were also read by the computer, which queried a high precision Guildine 9576 datastore digital voltmeter in its remote mode.

During electrolysis, RTD resistances and electrolysis current and voltage were periodically sampled by the computer and the data were stored. The frequency of measurement was adjustable, but we normally made a complete reading once every 5 or 10 min, usually reading data every minute (or less), testing for large excursions from a running average, but printing or storing data points less frequently, say every 10 min. In any event we were always careful to record with a frequency much higher than the equivalent of the thermal relaxation time of the calorimeter. This insured that no significant excursion of the heat flux from its characteristic average value would be missed by the data collection routine. The scheme considerably eases the data analysis problem.

Power input to the electrochemical cell is divided into an electrochemical part (used to generate gaseous oxygen and hydrogen from the electrolyte) and a thermal part. The latter is calculated from

$$P_{\mathrm{cell,thermal}} = (\mathrm{d}q/\mathrm{d}t)_{\mathrm{cell}} = (U_{\mathrm{sr}}/R_{\mathrm{sr}})(U_{\mathrm{cell}} - E_{\mathrm{th}}) \qquad (3)$$

where U_{sr} is the voltage drop across the standard resistor, $R_{\mathrm{sr}} = 4.919\ \Omega$, U_{cell} is the measured voltage difference between the anode and the cathode of the electrolysis cell, and E_{th} is the thermochemical voltage as calculated from the free energy of formation of D_2O (or H_2O for control experiments) from the elements, $E_{\mathrm{th}} = -\Delta G_{\mathrm{f}}/2F$. The free energy is not the standard state value but should be corrected for the fact that neither product nor reactants are in their standard states, nor are the experiments at precisely the standard temperature of 298 K. However, the differences are small and may be neglected at the level of precision appropriate to the present experiments.

ELECTROLYSES

We used several sets of electrodes in the calorimetric experiments. In the first, a Pd rod cathode (6.35 mm diam. × 25 mm) with an active surface of 5.30 cm^2 running against a concentric platinum cylinder anode was employed. A second series of measurements was made with a titanium cathode (6.35 mm diam. × 60 mm) running against the Pt anode. Yet another group used a tubular Pd/Ag cathode of the type described in a previous paper [3]. The electrolysis cell was filled with about 75 cm^3 of 0.25 M LiOD dissolved in D_2O (or approximately the same volume of 0.25 M LiOH dissolved in H_2O in control experiments). Many runs were performed over a reasonable range of current densitites. Typically the electrochemical parameters and RTD resistances were sampled every minute. Ten point averages were calculated and stored for the duration of the run, which lasted normally between 2 days and 2 weeks. The thermal relaxation time of the calorimeter (see discussion above) is long compared with the rate of accumulation of data, so that it would be impossible to miss thermal excursions of the kind described by Fleischmann and co-workers [1,2]. All time–temperature plots for many experiments made during the 18 month

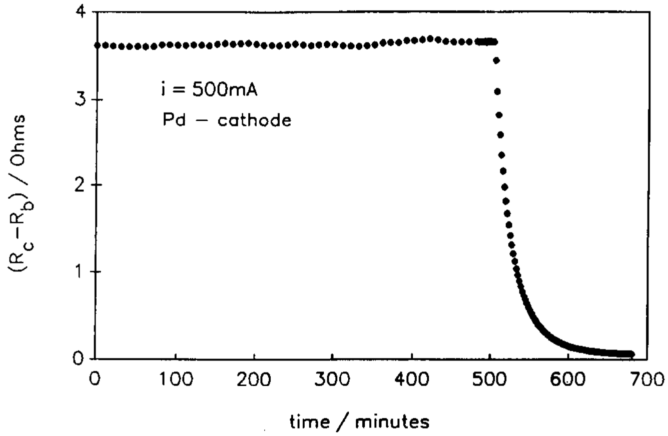

Fig. 2. RTD resistance–time curves in the region of the ending portion of an electrolysis run. The cooling curve which results from turning off the electrolysis is clearly shown. The zero time marker is arbitrarily inserted; this particular run lasted 37 days with very slow temperature drifts centered around $(R_c - R_b) \approx 3.7\ \Omega$. The slow resistance changes shown in the approximately level portion are typical of the slow drift in the equilibration point of the calorimeter as room temperature shifts. They set the limit on the sensitivity for the detection of thermal events with long time constants.

period between June 1989 and December 1990 show no deviation from smooth steady state behavior and no excess power production which we can attribute to "cold fusion". Those few anomalies which we did observe early in the development of our experimental procedures disappeared as we refined apparatus and techniques.

In addition to the steady state electrolyses described above and reported in more detail below, we made a number of runs where the voltage applied to the cathode was pulsed periodically (with a frequency on the order of tens of seconds) between zero and 1.6–1.7 V, reasoning that this technique would pulse the D atom activity in the Pd lattice. No anomalous heating was observed under these conditions.

The ending part of a typical electrolysis run is shown in Fig. 2, and results of a typical set of runs are reported in Tables 1 and 2. Numerical

TABLE 1

Calorimeter calibrations with a Pd cathode cell (see eqns. (1)–(3))

I (A)	P_{heater} (W)	ΔR_0 (Ω)	ΔR_∞ (Ω)	δR (Ω)	K (W Ω^{-1})
0.0500	0.0432	0.2296	0.0498	0.1864	0.2317
0.0749	0.0962	0.3806	0.0457	0.3349	0.2873
0.0998	0.1713	0.5445	0.0478	0.4967	0.3449
0.1497	0.3855	0.9521	0.0492	0.9029	0.4270
0.1996	0.6843	1.4809	0.0506	1.4303	0.4784

TABLE 2

Results of one series of calorimetric measurements of heat balances during electrolysis of LiOD solutions with a Pd cathode

I (A)	0.0980	0.1990	0.2498
U_{cell} (V)	3.1378	3.5316	3.7322
P_{in} (W)	0.1595	0.3963	0.5456
ΔR_0 (Ω)	0.5428	0.9796	1.2597
ΔR_∞ (Ω)	0.0512	0.0496	0.0518
δR (Ω)	0.4916	0.9300	1.2079
K (W Ω^{-1})	0.3444	0.4296	0.4567
P_{loss} (W)	0.1693	0.3996	0.5517
$(P_{\mathrm{in}} - P_{\mathrm{loss}})$ (W)	−0.0098	−0.0033	−0.0061

P_{in} is calculated from eqn. (3), K is interpolated from calibration data like that in Table 1, and used to obtain $P_{\mathrm{loss}} = K(\Delta R_0 - \Delta R_\infty)$.

analysis of the cooling at the end of a run yields $\delta R = \Delta R_0 - \Delta R_\infty$, and the heat loss from the cell at steady state $(\mathrm{d}q/\mathrm{d}t) = K\delta R$ is obtained by picking the appropriate value of K from a calibration plot of data such as those found in the last column of Table 1. The heat balances are within 1% except for the low-current run where the relative errors are larger.

A complete report of our calorimetric effort extending over many months is available [4]. These data, which are not presented here in any detail, can be summarized with the statement that we were unable to detect any thermal inconsistencies which can be attributed to untoward effects such as "cold fusion" (i.e. thermal excursions with time constants between 1 min and several hours yielding heat balances deviating by more than a few percent from the electrochemically calculated values).

CONCLUSION

The present calorimeter was designed to detect power bursts during electrolysis of LiOD–D_2O solutions using a palladium (or titanium) cathode. Our interest was frankly focused on large excursions from those heating rates expected from normal electrochemical processes. The calorimeter is of sufficient sensitivity to detect an excess power pulse of as little as several minutes duration in runs lasting between several days and several weeks. Our experience with this apparatus during a period of development and use in excess of one year reveal no excess heat production. We have also recently reported experiments designed to detect the production of trace amounts of helium and/or tritium in the interior of a palladium–silver electrode during electrolysis of LiOD solutions. Electrolysis products that diffused through the evacuated tubular electrode were concentrated by reaction of H_2, HD and D_2 with CuO, then analyzed by mass spectroscopy and radiometry. The limit of detection for ^{4}He was

1×10^{11} atoms. No evidence for production of helium or tritium by "cold fusion" was detected [3]. This result disagrees with that of Bush et al. [5].

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