

Isoperibolic calorimetry on modified Fleischmann–Pons cells

G. Preparata, M. Scorletti, M. VerPELLI

Dipartimento di Fisica, Università di Milano INFN, Sezione di Milano, Milan 20133, Italy

Received 29 September 1995; in revised form 2 February 1996

Abstract

We present a set of calorimetric data obtained with Fleischmann–Pons type cells, working in a novel electrostatic configuration aimed at achieving high deuterium loading. The analysis of such data, which includes an eight day run with a “blank” cell (Pt cathode), shows that: (a) the heat dissipation of the cells depends strongly on the physical processes occurring at the cathode; (b) the continuing calibration with periodic heat pulses yields accurate estimates of the excess enthalpies generated in the cells; (c) very high excess power densities are observed in the cells electrolyzing D_2O with Pd cathodes.

Keywords: Fleischmann–Pons cells; Calorimetry

1. Introduction

Six years after the announcement [1,2] on 23 March 1989 of the discovery of “anomalous” excess heat production in the electrolysis of heavy water with a Pd cathode, there are still doubts in the scientific community that the observations by Fleischmann and Pons (FP) might reflect some kind of artefact. For this reason, in spite of the large number of confirmations that the FP protocols do reproduce the original observations (see, for instance, the four volumes of the Proceedings of the first four International Conferences on Cold Fusion), cold fusion (CF) is still essentially ignored by the scientific community.

In this paper we develop methods of analysis for FP-type cells – cells electrolyzing heavy water with LiOD as electrolyte and a cathode of Pt (blank cells) or Pd (which we may call “black” cells) – with the aim of checking some subtle aspects of FP calorimetry [3], related to the peculiar behaviour that “black” cells exhibit when they are driven towards boiling point.

These methods are illustrated with some data from experiments described in detail elsewhere (to be published). As already implied in the title, the cells of our experiments (a schematic drawing of which is shown in Fig. 1) differ from the well-known FP cells in that they exploit an unusual electrostatic configuration which, as we shall see, provides an efficient source of excess enthalpy.

Before going into the necessary details, we will first briefly comment on the advantages for the detection of CF

of using the experimental strategy followed by FP. This version of isoperibolic calorimetry, using periodic low-power heat pulses and temperature readings *inside* the cells, in our opinion gives a calorimetric methodology that interferes very little with the CF phenomena, placing in particular no constraint upon the variation of the cell temperature. This latter aspect should not be underestimated for, as pointed out by FP since 1991, the process, whatever it is (and here we are being particularly non-committal for we want this paper to be essentially experimental; naturally we have some pretty good ideas (see Refs. [5,6]) as to what is causing CF) that causes the CF phenomena is sensitive to small temperature changes. Such “positive feedback” as Fleischmann likes to describe it may, if the calorimetric analysis is not designed to take this into account, completely obscure, indeed wipe out, a correct determination of the excess enthalpy evolved in the system. Furthermore, isoperibolic calorimetry allows us to work with a cell heat transfer coefficient that might change with time (provided its time variation over a heat pulse period is, within the experimental uncertainties, negligible). Such a possibility (within the strategy of “laissez-faire” that we adopt as far as the cells are concerned) is indeed a very likely one, for in the presence of high excess power densities localized in some regions of the Pd cathodes, such as one expects when CF phenomena occur, one must not be surprised if dissipation phenomena change, and with them the heat transfer coefficients that embody them thermodynamically.

One should bear in mind that by the generic term of “dissipation phenomena” we wish to indicate a set of physio-chemical processes that are related to the onset of CF phenomena, of which at present we have unfortunately no relevant information.

This paper is organized as follows: after a brief description of the geometry of the cells we recall the theoretical background which is the basis of the analysis that we carry out in the following section; finally a brief discussion of the results will conclude the paper.

2. The calorimetric equation

The physical system under analysis is an isoperibolic calorimeter, consisting of an open cylindrical cell, at a temperature $T_c(t)$, surrounded by a water bath maintained at a constant temperature T_b .

Since the calorimeter is at constant pressure, the relevant thermodynamic potential is the enthalpy H

$$dH = dU + P dV \quad (1)$$

Defining δQ as the heat flowing from the calorimeter to the bath and dW_{ext} as the external work done on the calorimeter, the first principle of thermodynamics reads

$$dH = dW_{\text{ext}} - \delta Q \quad (2)$$

The enthalpy sources inside the calorimeter are:

- the electric power producing electrolysis, whose rate is $w_{\text{el}}(t)$;
- the heat calibration pulse, with rate $h(t)$;
- any excess enthalpy production, whose rate we call $w_x(t)$.

In this way, for the external work we may write

$$dW_{\text{ext}} = w_{\text{el}}(t) dt + h(t) dt + w_x(t) dt \quad (3)$$

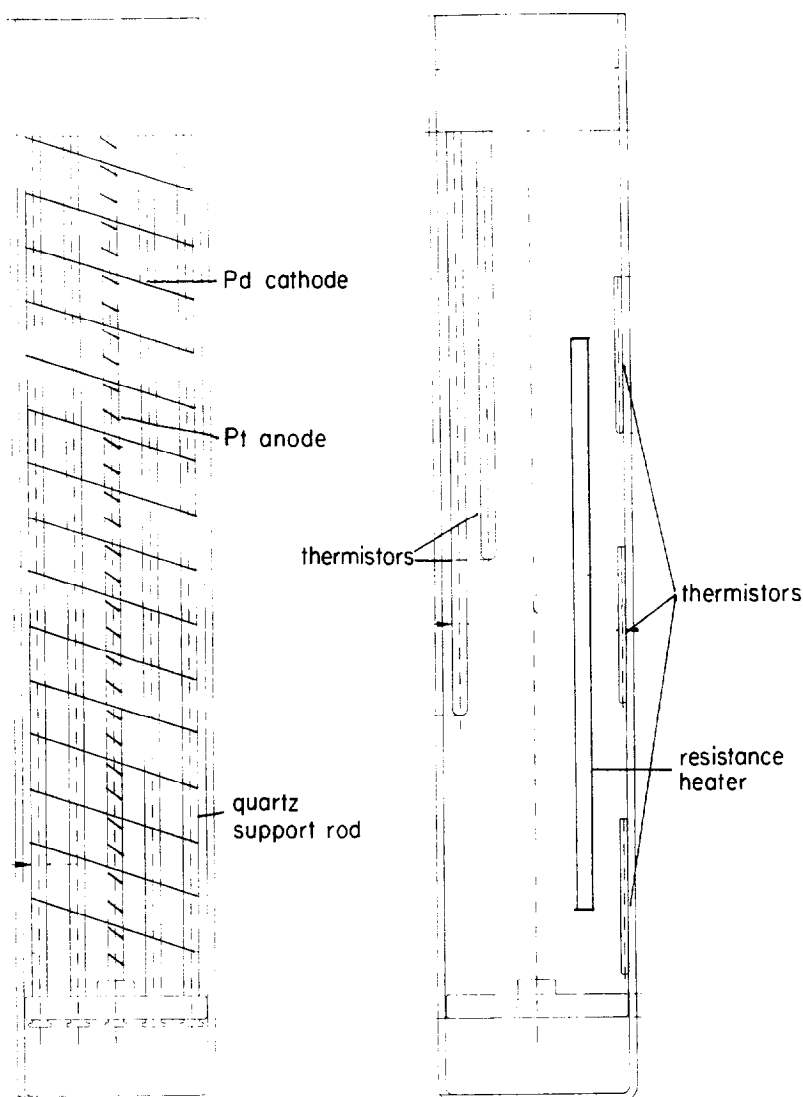


Fig. 1. A schematic drawing of the cell (diameter approximately 5 cm, height approximately 28 cm) used to collect the data analyzed in this paper. On the left the helicoidal Pd (Pt for the blank run) cathode (diameter 50 μm , $l \approx 250$ cm) and the Pt anode (diameter 250 μm) are shown, together with their quartz supports. On the right the spatial configuration of the PT100 thermistors array and the resistance heater used to calibrate the cell are shown.

As for δQ , we assume that all the heat leaving the cell flows to the bath, so that we may write the general expression

$$\delta Q = f(T_c, T_b, t) dt \quad (4)$$

Introducing the quantity $\Delta T(t) = T_c(t) - T_b$ we write, without loss of generality

$$f(T_c, T_b, t) = a_{ht}(\Delta T, T_b, t) \Delta T \quad (5)$$

which defines the “heat transfer coefficient” a_{ht} that contains all the non-trivial dependence of the heat transfer function on the temperatures as well as on time.

At the starting time t_s the calorimeter contains m_0 moles of electrolyte at a temperature T_b and with an enthalpy content H_0 . Any subsequent variation of the enthalpy content of the calorimeter is concomitant with the following processes:

- temperature variations, which are recorded by a thermistor inside the cell;
- variations in the content of the cell.

There are three processes that change the content of the calorimeter.

- (1) Decomposition of the electrolyte



This process is due to electrolysis and, perhaps, also to soft X-ray emission that may accompany the process of production of excess power. The gases leave the calorimeter and their enthalpy is lost.

- (2) Evaporation/boiling of the electrolyte. The gas stream leaves the calorimeter and its enthalpy is lost.
- (3) Addition of D_2O to the calorimeter to replace losses due to (1).

The molar rates for the three processes above are indicated by $\dot{m}_d(t)$, $\dot{m}_e(t)$ and $\dot{m}_a(t)$.

The variation in enthalpy content is written as the following sum

$$dH = dH_c + dH_d + dH_e + dH_a \quad (7)$$

where (for an explanation of the symbols see Appendix B)

- (i) dH_c is the enthalpy variation of the calorimeter

$$dH_c = m(t)C_{p,D_2O} dT_c, \quad (8)$$

where $m(t)$ is the molar content of the calorimeter at the generic time t (including both the equivalent masses of the electrolyte and of the solid structure of the calorimeter);

- (ii) dH_d is the enthalpy variation caused by the decomposition of $\dot{m}_d(t)dt$ moles of D_2O into $\dot{m}_d(t)dt$ moles of D_2 and $\frac{1}{2}\dot{m}_d(t)dt$ moles of O_2 ; according to this we write

$$dH_d = \left\{ Q_d + \left[C_{p,D_2} + \frac{1}{2}C_{p,O_2} - C_{p,D_2O} \right] \Delta T(t) \right\} \times \dot{m}_d(t) dt \quad (9)$$

- (iii) dH_e is the enthalpy variation due to the evaporation/boiling

$$dH_e = \left\{ L_{D_2O} + \left[C_{p,D_2O,gas} - C_{p,D_2O} \right] \Delta T(t) \right\} \times \dot{m}_e(t) dt \quad (10)$$

- (iv) dH_a is the enthalpy variation due to the refill of the electrolyte; if the liquid flowing into the calorimeter has a constant temperature T_a (in our experiments, the refilling system is at the same temperature of the bath so that $T_a = T_b$) one can write

$$dH_a = C_{p,D_2O}(T_c - T_a)\dot{m}_a(t) dt = C_{p,D_2O}(\Delta T + T_b - T_a)\dot{m}_a(t) dt \quad (11)$$

The final equation that embodies all the above contributions is then

$$dH = m(t)C_{p,D_2O}d(\Delta T) + C_{p,D_2O} \left\{ \left[\dot{m}_a(t) - \dot{m}_d(t) - \dot{m}_e(t) \right] \Delta T + \dot{m}_a(t)(T_b - T_a) \right\} dt + \dot{m}_d(t) \left\{ Q_d + \left[C_{p,D_2} + \frac{1}{2}C_{p,O_2} \right] \Delta T(t) \right\} + \dot{m}_e(t) \left\{ L_{D_2O} + C_{p,D_2O,gas} \Delta T(t) \right\} dt \quad (12)$$

where all the terms following the first are to appear in the right-hand side of an energy balance equation describing the dissipated energy.

In order to evaluate the total enthalpy variation of the calorimeter one must determine the rates $\dot{m}_a(t)$, $\dot{m}_d(t)$ and $\dot{m}_e(t)$. Evidently the best way to do this would be to measure these three quantities. Actually, our calorimeter is equipped with a refilling system which maintains a constant level of electrolyte so we have

$$m(t) = m_0 \quad \forall t \quad (13)$$

while we measure the rate $\dot{m}_a(t)$ of the inflowing D_2O . As we have not yet set up an experimental apparatus to measure and analyze the gas stream leaving the cell, we must give some theoretical estimate of the quantities $\dot{m}_d(t)$ and $\dot{m}_e(t)$. For the decomposition process, we may write the general expression

$$\dot{m}_d(t) = \gamma \dot{m}_{el}(t) + \dot{m}_x(t) \quad (14)$$

where $\dot{m}_{el}(t)$ is the theoretical rate of electrolysis, γ its efficiency and $\dot{m}_x(t)$ accounts for any non-electrolytic process. For $\dot{m}_{el}(t)$ the Faraday law tells us that

$$\dot{m}_{el}(t) = \frac{1}{2} \frac{I_{el}(t)}{N} \frac{1}{e} = \frac{1}{2} \frac{I_{el}(t)}{2F} \quad (15)$$

and defining

$$V_{th} = \frac{Q_d}{2F} \quad (16)$$

the enthalpy variation for this process is

$$dH_{el} = V_{th} I_{el} dt \quad (17)$$

For the evaporation rate one has to consider two processes:

- surface evaporation/boiling;
- evaporation in the electrolysis bubbles.

Fleischmann and Pons [3,4] evaluated the evaporation rate in the bubbles under the assumption that inside the bubble the D_2O vapour is at the equilibrium pressure. If $p(T_c)$ is the equilibrium pressure for the vapour and p_o the pressure at which the bubble is created (assumed to be the atmospheric pressure), the pressure of D_2 is $\frac{2}{3}(p_o - p(T_c))$ and that of O_2 is $\frac{1}{3}(p_o - p(T_c))$. According to this, the D_2O content of a bubble is

$$n_{D_2O} = n_{D_2} \frac{p(T_c)}{\frac{2}{3}(p_o - p(T_c))} \quad (18)$$

and finally

$$\dot{m}_e(t) = \frac{3}{2} \dot{m}_d(t) \frac{\frac{p(T_c)}{p_o}}{1 - \frac{p(T_c)}{p_o}} \quad (19)$$

where, from the Clausius–Clapeyron equation, one has

$$\frac{p(T_c)}{p_o} = \exp \left\{ -\frac{L_{D_2O}}{R} \left[\frac{1}{T_c} - \frac{1}{T_{eb,D_2O}} \right] \right\} \quad (20)$$

Note, however, that this calculation becomes inaccurate when $T_c \rightarrow T_{eb,D_2O}$. (It is for this reason that FP time the evaporation of the last half of the cell content [3].) Since we have no simple method for determining the rate $\dot{m}_e(t)$, we use the fact that due to the action of the refilling system

$$\dot{m}_a(t) - \dot{m}_d(t) - \dot{m}_e(t) = 0 \quad (21)$$

Then we assume that:

- the decomposition process is only due to electrolysis;
- the faradaic efficiency of electrolysis is effectively 100%.

In this way we have

$$\dot{m}_d(t) = \frac{1}{2} \frac{I_{el}(t)}{2F} \quad (22)$$

$$\dot{m}_e(t) = \dot{m}_a(t) - \dot{m}_d(t) \quad (23)$$

The calorimetric equation is then rewritten in the following form

$$dH/dt - dW_{ext}/dt + dQ/dt = 0 \quad (24)$$

According to our discussion¹ the explicit form of the calorimetric equation is then

$$m_0 C_{p,D_2O} \frac{d\Delta T}{dt}(t) + \dot{m}_a(t) C_{p,D_2O} (T_b - T_a) + \dot{m}_d(t) \left[C_{p,D_2} + \frac{1}{2} C_{p,O_2} \right] \Delta T(t)$$

$$+ \dot{m}_e(t) C_{p,D_2O} g \Delta T(t) + \dot{m}_d(t) Q_d + \dot{m}_e(t) L_{D_2O} + w_{el}(t) - h(t) - w_x(t) + a_{ht}(\Delta T, T_b, t) \Delta T(t) = 0 \quad (25)$$

which can be cast in the form

$$m_0 C_{p,D_2O} \frac{d\Delta T}{dt}(t) = w(t) + h(t) - a(t, T_b, \Delta T) \Delta T(t) \quad (26)$$

where

$$w(t) = w_{in}(t) - \dot{m}_a(t) C_{p,D_2O} (T_b - T_a) - \dot{m}_d(t) Q_d - \dot{m}_e(t) L_{D_2O} + w_x(t) \quad (27)$$

$$h(t) = \sum_i h_i [\theta(t - t_{s,i}) - \theta(t - t_{e,i})] \quad (28)$$

$$a(\Delta T, T_b, t) = a_{ht}(\Delta T, T_b, t) + \dot{m}_d(t) \left[C_{p,D_2} + \frac{1}{2} C_{p,O_2} \right] + \dot{m}_e(t) C_{p,D_2O,gas} \quad (29)$$

The “dissipation coefficient” a describes the whole energy dissipation of the cell to the surroundings (the bath and the atmosphere). As for the dependence of a on the various quantities, we observe that:

- (1) since the temperature T_b of the water bath is constant during any experiment, we can ignore the T_b dependence of a ;
- (2) the ΔT dependence of a is due to the fact that the heat transfer from the cell is dominated by conduction and radiative processes, the radiation process gives the well-known (quartic) temperature dependence to a ;
- (3) the explicit t dependence can be traced to the following facts:
 - electrolysis and evaporation contribute to the dissipation term, these processes not only depend on the temperature of the cell, but also have explicit time dependences (for instance due to the changes in the rate of electrolysis);
 - any (possible) dependence of the dissipation from the excess heat production, resulting from the appearance of new dissipative processes

¹ We have assumed that L_{D_2O} and Q_d and the various specific heats do not vary with temperature. If one wishes to consider the temperature dependence of these quantities, the enthalpy must be written as

$$H = \int_{T_r}^T C(T) dT$$

and in this case

- C_{p,D_2O} is evaluated at T_c .
- the other C_p s are evaluated as the mean of $C_p(T)$ in the temperature range $[T_b, T_c]$, and
- L_{D_2O} and Q_d are evaluated at T_c .

and from the extremely localized (in space) production of excess power, can affect the relative strengths of conduction and radiation.

So far we have implicitly assumed that the cell contents are at a uniform temperature. Actually, measurements with an array of thermistors placed in different cell positions have shown that this is not the case. This is due to the fact that the enthalpy rate production turns out to be concentrated in small regions (the cathode), producing strong temperature gradients inside the cell, thus we must consider a temperature field $T_c(t, \mathbf{x})$, rather than the cell temperature T_c . We are dealing in fact with an inhomogeneous calorimeter inside which we (usually) record the temperature at only one point, say \mathbf{x}_0 (note that we have used relatively large calorimeters with a substantial heat loss due to conduction, the thermal relaxation time of our system is about 2000 s. As FP have stressed, mixing in their long thin calorimeter is enhanced and their thermal relaxation time is increased to 5000 s; the regime in their calorimeter is therefore “well mixed”). What about the calorimetry of such a complicated system? The analysis carried out in Appendix A shows that such a calorimeter can be described by an equation like (26), with an “effective mass” and an “effective dissipation coefficient”. In other words, an inhomogeneous calorimeter behaves like a homogeneous one, but with an equivalent mass and dissipation coefficient. This means that such parameters depend critically on the distribution of the enthalpy sources inside the cell, on the history of the run and on the eventual excess enthalpy production; there is no way to “calibrate” the calorimeter with a previous (or parallel) blank experiment.

So, in order to have realistic energy balances, we must set up a calorimetric analysis that takes fully into account the inhomogeneity of our calorimeter. This analysis must of course, be carried out “in real time” and must provide us with the values of the dissipation coefficient and of the effective equivalent mass of the calorimeter for that particular run. This is accomplished by means of the heat calibration pulses $h(t)$ in a way that we describe in the following section.

3. Analysis

From what has just been said, the energy balance of the system, which might reveal the possible existence of excess power, presupposes a knowledge of the way in which, as a function of time, the calorimeter dissipates the energy. This fundamental piece of information is acquired through well-defined (and known) calibration pulses by which we interrogate the system in such a way as to:

- perturb the system as little as possible (thus leaving it in the (quasi-)stationary state at the time of the pulse);

- prolong the interrogation for a time longer than 5τ (where τ is the time constant of the calorimeter) and shorter than $|\dot{a}(t)/a(t)|^{-1}$, the inverse of the logarithmic time derivative of the dissipation coefficient.

Thus our starting point is Eq. (26)

$$mc_p \frac{d\Delta T}{dt}(t) + a(t)\Delta T(t) = w(t) + h(t) \quad (30)$$

where the left-hand side can be written

$$\begin{aligned} mc_p \frac{d\Delta T(t)}{dt} + a(t)\Delta T(t) \\ = mc_p \frac{d}{dt} \left[\Delta T(t) \exp \int dt' \frac{a(t')}{mc_p} \right] \exp - \int dt' \frac{a(t')}{mc_p} \end{aligned} \quad (31)$$

Assuming, according to the discussion above, that during the calibration pulse a can be considered constant, by introducing the quantity

$$\tau = \frac{mc_p}{a} \quad (32)$$

which has the dimension of time (and, indeed, is the local time constant of the system), the energy balance equation can be rewritten in the form

$$a\tau \frac{d}{dt} \left[\Delta T(t) \exp \frac{t}{\tau} \right] = [w_{in}(t) + h(t)] \exp \frac{t}{\tau} \quad (33)$$

Let us now consider the time interval $[t_0, t_0 + \Delta t]$, where Δt is chosen so as to satisfy, at least to a first approximation, the following hypotheses:

- (1) a (and thus τ) is constant;
- (2) the total enthalpy production (inflowing external power plus unknown excess power) can be described by the expression

$$w(t) = w_0 + \dot{w}(t - t_0) + \delta w(t) \quad (34)$$

where the fluctuations $\delta w(t)$ are small and vanish upon averaging over time intervals of the order of Δt .

Clearly, the validity of such hypotheses will have to be evaluated by an a posteriori check.

Let us suppose also that the system is perturbed by a constant heat pulse between the time t_s and t_e , so that we may write

$$h(t) = h[\theta(t - t_s) - \theta(t - t_e)] \quad (35)$$

where t_s and t_e may not both belong to the interval $[t_0, t_0 + \Delta t]$.

If the above hypotheses hold, for $t \in [t_0, t_0 + \Delta t]$, Eq. (26) becomes

$$\begin{aligned} a\tau \frac{d}{dt} \left[\Delta T(t) \exp \frac{t}{\tau} \right] \\ = \{w_0 + \dot{w}(t - t_0) + h[\theta(t - t_s) - \theta(t - t_e)]\} \exp \frac{t}{\tau} \end{aligned} \quad (36)$$

and can be easily integrated to give

$$\begin{aligned}
 a\Delta T(t) - a\Delta T(t_0) \exp - \frac{t-t_0}{\tau} \\
 = (w_0 - \dot{w}\tau) \left[1 - \exp - \frac{t-t_0}{\tau} \right] + \dot{w}(t-t_0) \\
 + h\theta(t-t_s)\theta(t_e-t) \left[1 - \exp - \frac{t-t_s}{\tau} \right] \\
 + h\theta(t-t_e) \left[\exp - \frac{t-t_e}{\tau} - \exp - \frac{t-t_s}{\tau} \right] \quad (37)
 \end{aligned}$$

Several types of analysis are now possible [7]. One of the simplest, that we shall adopt in this paper, is the following:

- choose as t_0 the time of the switching on or off of the calibration pulse, and for Δt the period (usually 6 h) in which the calibration power is kept constant;
- in a time interval $[t_0 + 3\tau, t_0 + 4\tau]$ fit the data with a straight line

$$[\Delta T(t) - \Delta T(t_0)]_{fit} = c + d(t - t_0) \quad (38)$$

From Eq. (37), expanding the exponentials around the point $t_m = t_0 + \frac{7}{2}\tau$ (the midpoint of the interval used for the fit), we get

$$\begin{aligned}
 \Delta T(t) - \Delta T(t_0) \\
 = \left[\frac{h}{a} + \tau \Delta \dot{T}(t_0) - \frac{\dot{w}}{a} \tau \right] \left(1 - \frac{9}{2} \exp - \frac{7}{2} \right) \\
 + \left[\frac{\dot{w}}{a} + \left(\frac{h}{a\tau} + \Delta \dot{T}(t_0) - \frac{\dot{w}}{a} \right) \right] \exp - \frac{7}{2} \\
 + o \left(\frac{t-t_m}{\tau} \right) \quad (39)
 \end{aligned}$$

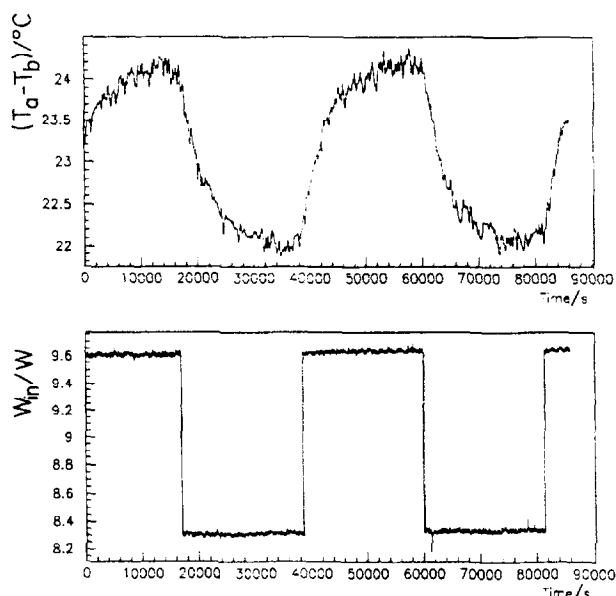


Fig. 2. Temperature above bath and input power vs. time for a typical one-day sample of the blank run. The calibration pulse has an intensity $h = 1.30$ W and a period of 12 h.

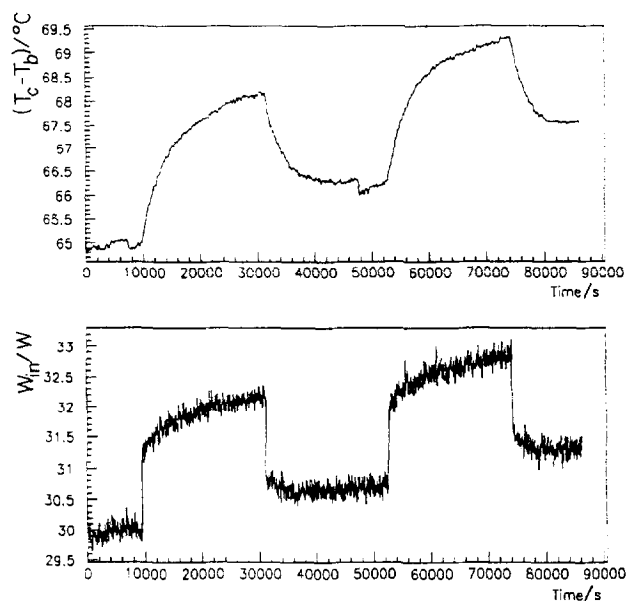


Fig. 3. Temperature above bath and input power vs. time for a typical one-day sample of run 2. The calibration pulse has an intensity $h = 1.23$ W and a period of 12 h.

(we have also checked that the first correction to this formula is completely negligible).

By equating the coefficients of the straight line in Eq. (39) with the parameters of the fit (the value of $\Delta \dot{T}(t_0)$ can be extracted from the data), we easily obtain for the dissipation coefficient a [where $\overline{a(t)}$ denotes the average value of a at the time of the switching (on or off) of the heater]

$$\overline{a(t)} = \frac{h}{c \frac{1 - \exp - \frac{7}{2}}{1 - \frac{9}{2} \exp - \frac{7}{2}} + \tau [d - \Delta \dot{T}(t_0)]} \quad (40)$$

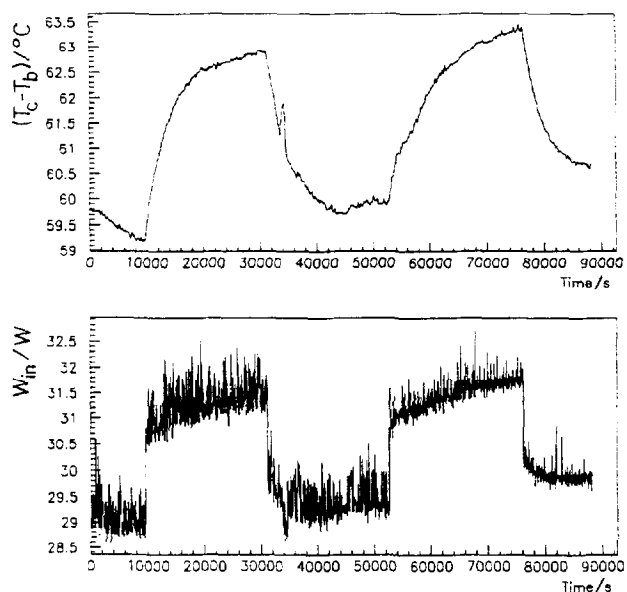


Fig. 4. Temperature above bath and input power vs. time for a typical one-day sample of run 3. The calibration pulse has an intensity $h = 1.59$ W and a period of 12 h.

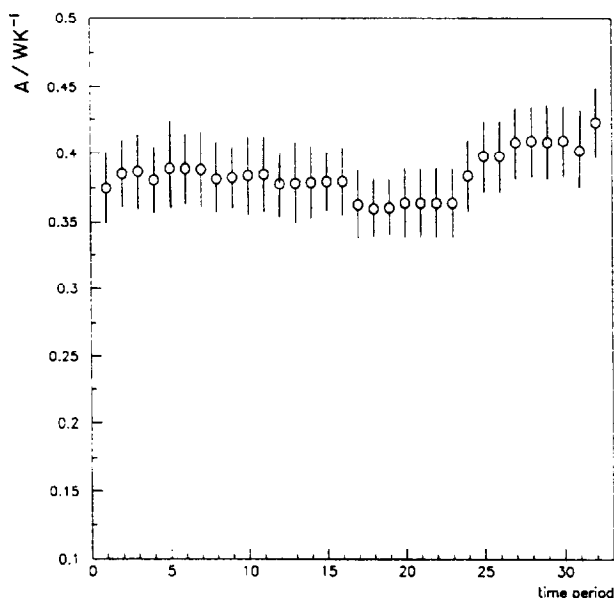


Fig. 5. The calculated dissipation coefficient $\overline{a(t)}$ for the blank cell. Every point corresponds to a period of 6 h and during this period a is assumed constant.

The standard procedures of the fitting will then also determine the experimental uncertainty that affects the evaluation of $\overline{a(t)}$. We also obtain the value of \dot{w}

$$\dot{w} = \overline{a(t)} \left[d - \frac{c}{\tau} \frac{\exp - \frac{t}{\tau}}{\left(1 - \frac{c}{2} \exp - \frac{t}{\tau}\right)} \right] \quad (41)$$

that we use as an internal consistency check of this procedure.

The numerical analysis starts with the value of τ (which is an input for the fit procedure) that corresponds to a dissipation coefficient which gives (approximately) no excess power. From this first set of values of $\overline{a(t)}$ we obtain

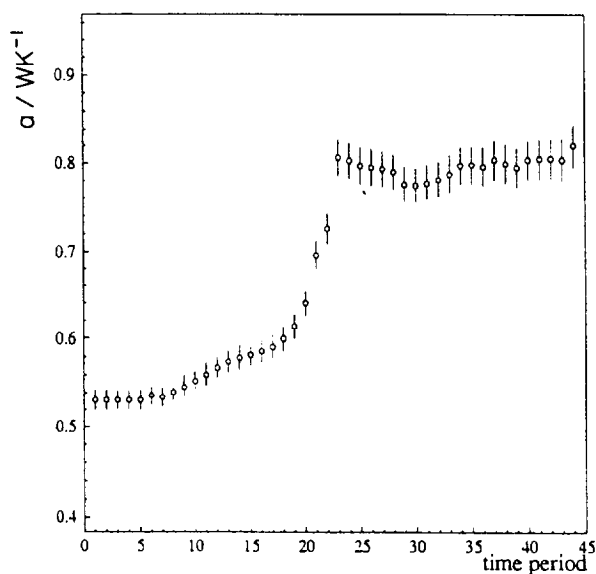


Fig. 6. As Fig. 5 for run 2.

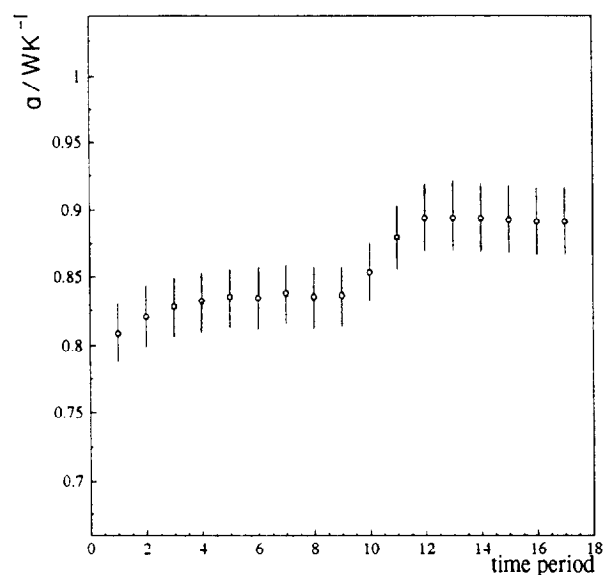


Fig. 7. As Fig. 5 for run 3.

a new value of τ ; we then iterate this procedure until consistency is reached, i.e. until the values of $\overline{a(t)}$ and τ satisfy Eq. (32). By inserting the function $a(t)$ – which is a slowly varying function of time – in Eq. (26), we evaluate the energy balance of the cell and obtain the function $w_x(t)$.

In this paper we show the results obtained by applying the method just described to three different runs, with two different calorimeters (that we call “cell A” and “cell B”):

- (1) a “blank” run (Pt cathode polarized in D_2O) in cell A, eight days long;
- (2) a “black” run (Pd cathode polarized in D_2O) in cell A, eleven days long;

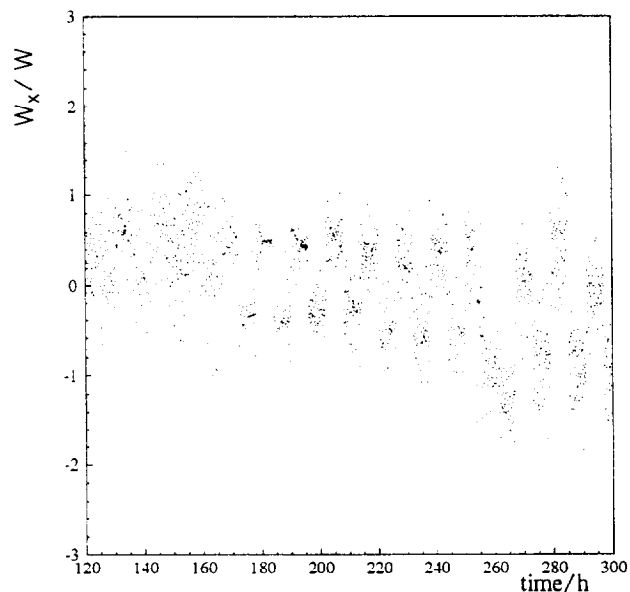


Fig. 8. Excess power vs. time for the blank cell. The typical error for this run is about 0.7 W.

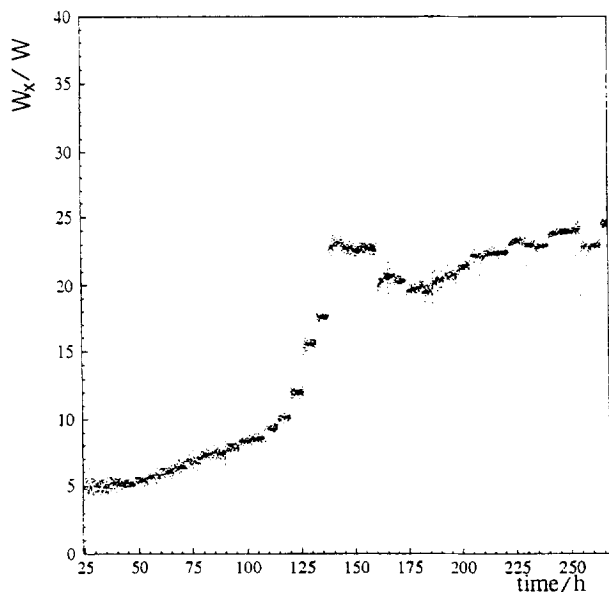


Fig. 9. Excess power vs. time for run 2. The typical error for this run is about 2.0 W.

(3) a “black” run (Pd cathode polarized in D_2O) in cell B, four days long.

Figs. 2, 3 and 4 show some typical experimental data (temperature and input power vs. time) for the three experiments, while Figs. 5, 6 and 7 show the values of the dissipation coefficient $\overline{a(t)}$ obtained with the method described above. We observe that the values of $\overline{a(t)}$ for the first two runs are noticeably different, though the cell and the bath are the same. We believe that there are two possible origins of such an unexpected fact:

the appearance of new dissipation processes associated with the physical mechanisms responsible for the production of excess heat;

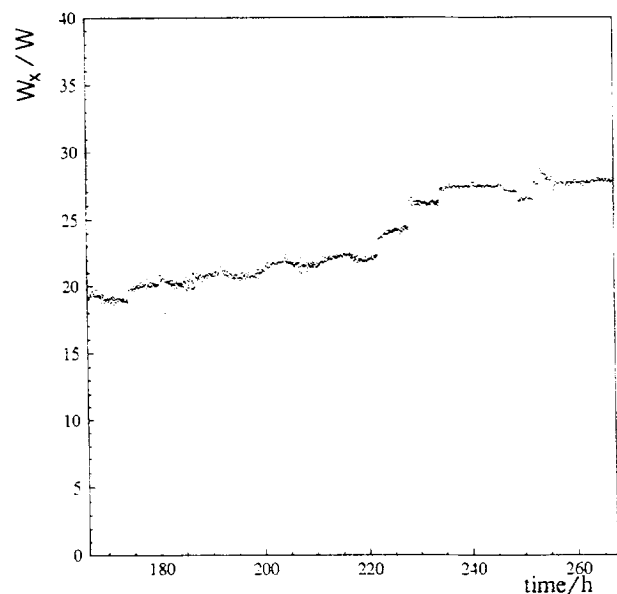


Fig. 10. Excess power vs. time for run 3. The typical error for this run is about 2.0 W.

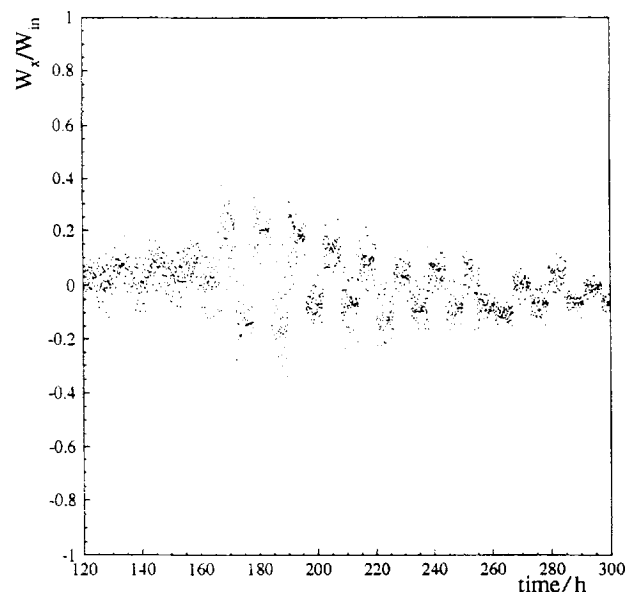


Fig. 11. Efficiency, defined as $\epsilon = W_x / W_{in}$ vs. time for the blank run.

the inhomogeneity of the calorimeter that may make the dissipation coefficient depend strongly on x_0 , the point at which the cell temperature is recorded. Finally, Figs. 8, 9 and 10 show the excess power for the three experiments, as obtained from the energy balance, and Figs. 11, 12 and 13 show the efficiencies in the three experiments, defined as the ratio between the excess power and the input power. The quoted errors for the excess power are due to:

- (i) the unavoidable errors that affect the experimental data of the various quantities that enter Eq. (26);
- (ii) the errors in the determination of the dissipation coefficient, which are mostly due to the statistical

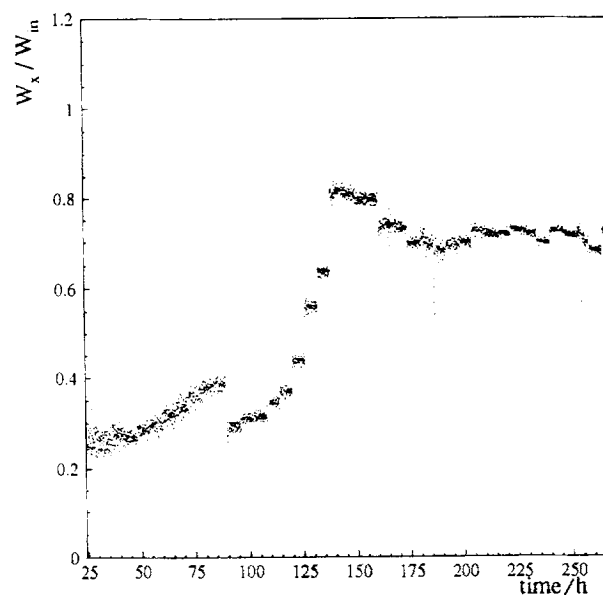


Fig. 12. As Fig. 11 for run 2.

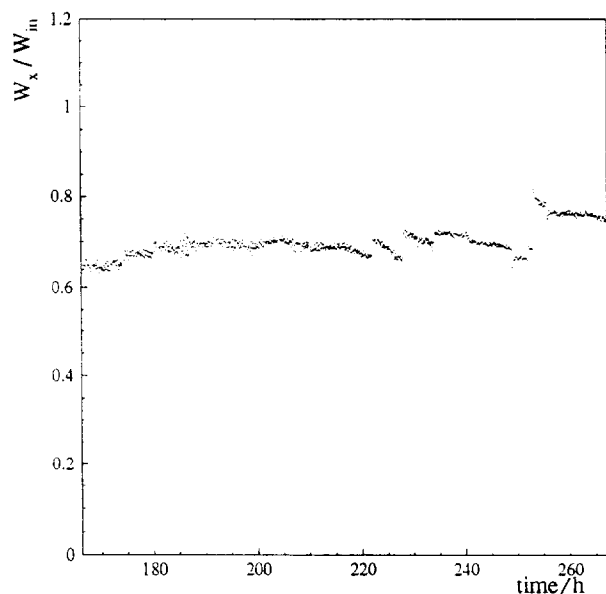


Fig. 13. As Fig. 11 for run 3.

uncertainties in the determination of the fit parameters.

4. Conclusions

The data we have analysed in this paper are just a small subset (and not a particularly significant one) of a set of data collected while experimenting on the modified FP-cells, alluded to in the Introduction. The reason why we have decided to publish them is two-fold: first to show that a reliable and accurate (isoperibolic) calorimetry can be carried out on cells where an unknown and time dependent enthalpy source, such as that expected from CF processes, is at work: second, to draw attention to the fact that other, more traditional calorimetries may well turn out to be inadequate. The reason for this is the non-negligible changes induced in the calorimeters by the large excess enthalpy produced in our ‘black’ cells. A comparison of Fig. 5 with Figs. 6 and 7 eloquently underscores this latter point, especially when we recall that the data of Figs. 5 and 6 refer to the same physical cell, the only difference being the cathode (Pt for Fig. 5 and Pd for Fig. 6).

However, in spite of these capricious changes, the graph in Fig. 8 does show that no excess enthalpy is found where none is expected, with an accuracy of 0.7 W and this over a period of six days, where all kinds of ‘bugs’ could have made their appearance should our analysis be fundamentally flawed (as the strange results of Figs. 6 and 7 would make some of the more traditional calorimetrists believe). Supported by such impeccable results (which also give us an accurate estimate of the size of the experimental uncertainties) we may now draw some conclusions as to the effectiveness in producing excess enthalpy of the new electrostatic configurations that we have tested in the

‘black’ runs 2 and 3 (see Figs. 9 and 10).

If we consider that in our analysis we have completely neglected the enthalpy losses in the gas flows from the cells (which we know are non-negligible due to their crucial role in the modification of the cell dissipation coefficient a), and therefore that our estimated excess enthalpy $w_x(t)$ is only a lower bound, we come to the following conclusions.

- (a) In run 2 we have reached a lower bound for the excess enthalpy of about $w_x \approx 25$ W. Considering that the volume of the Pd cathode is $V_2 = 8.15 \times 10^{-3}$ cm³, this means that in this run the specific excess power is

$$p_2 \geq 3 \text{ kW cm}^{-3} \quad (42)$$

- (b) As for run 3, taking $w_x = 30$ W and $V_3 = 8.35 \times 10^{-3}$ cm³, we obtain

$$p_3 \geq 3.6 \text{ kW cm}^{-3} \quad (43)$$

Such high power densities may seem quite exceptional, but in fact in other experiments (to be published) power densities ten to twenty times larger have been achieved.

Acknowledgements

We wish to thank Martin Fleischmann for many interesting discussions over the last few years and for useful comments on this paper.

Appendix A: Inhomogeneous calorimetry

Let us consider a calorimeter, consisting of a volume V of liquid electrolyte, bounded by the surface S (the cell). Let us suppose that inside the electrolyte V there is some localized enthalpy source (i.e. the cathode); the volume of these sources is negligible, while their boundary is A , so that

$$\partial V = S \cup A \quad (A1)$$

We can write the rate of enthalpy transfer from these sources to the calorimeter as

$$w_s(t) = - \int_A \mathbf{j}(\mathbf{x}, t) \cdot \mathbf{n} d^2\sigma \quad (A2)$$

where $\mathbf{j}(\mathbf{x}, t)$ is the heat flow and \mathbf{n} the unit vector pointing outwards from the cell surface.

Let $T(\mathbf{x}, t)$ be the temperature field inside the cell and $h(\mathbf{x}, t)$ the energy density. If $q(\mathbf{x}, t)$ is the power density produced by the sources inside the calorimeter (i.e. electrolysis) and $\rho c d\Delta T/dt(\mathbf{x}, t)$ is the power density stored in the system as enthalpy, the continuity equation reads

$$\frac{\partial h}{\partial t}(\mathbf{x}, t) - \text{div } \mathbf{j}(\mathbf{x}, t) = 0 \quad (A3)$$

where

$$\frac{\partial h}{\partial t}(\mathbf{x}, t) = q(\mathbf{x}, t) - \rho c_p \frac{d\Delta T}{dt}(\mathbf{x}, t) \quad (\text{A4})$$

By integrating the continuity equation, we have

$$\int_V d^3\mathbf{x} \frac{\partial h}{\partial t}(\mathbf{x}, t) - \int_{\partial V} \mathbf{j}(\mathbf{x}, t) \cdot \mathbf{n} d^2\sigma = 0 \quad (\text{A5})$$

The term

$$w(t) = \int_V d^3\mathbf{x} q(\mathbf{x}, t) - \int_A \mathbf{j}(\mathbf{x}, t) \cdot \mathbf{n} d^2\sigma \quad (\text{A6})$$

can be recognized as the total power released to the cell by all the sources, while

$$w_{\text{diss}}(t) = \int_S \mathbf{j}(\mathbf{x}, t) \cdot \mathbf{n} d^2\sigma \quad (\text{A7})$$

is nothing but the heat rate from the cell to the water bath, i.e. the dissipated power. In this way, the integrated continuity equation reads

$$\int_V d^3\mathbf{x} \rho c_p \frac{d\Delta T}{dt}(\mathbf{x}, t) = w(t) - w_{\text{diss}}(t) \quad (\text{A8})$$

In terms of the “mean temperature”

$$\overline{\Delta T}(t) = \frac{1}{V} \int_V d^3\mathbf{x} \Delta T(\mathbf{x}, t) \quad (\text{A9})$$

and writing, as usual

$$w_{\text{diss}}(t) = a(\overline{\Delta T})\overline{\Delta T}(t) \quad (\text{A10})$$

Eq. (A8) becomes

$$m c_p \frac{d\overline{\Delta T}}{dt}(t) = w(t) - a(\overline{\Delta T})\overline{\Delta T}(t) \quad (\text{A11})$$

which just looks like the balance equation for a homogeneous calorimeter and closely resembles Eq. (26).²

What can we say about Eq. (A11) if our thermistor records the value of the inhomogeneous temperature field at only one point, say \mathbf{x}_o [let $\Delta T_o(t) = \Delta T(\mathbf{x}_o, t)$]?

In general, we do not know how the “mean temperature” $\overline{\Delta T}(t)$ depends on the temperature field $\Delta T(\mathbf{x}, t)$, on the point \mathbf{x}_o , on the geometry of the sources, and so on.

Let us write

$$\overline{\Delta T}(t) = f[\mathbf{x}_o, t, \Delta T_o] = \lambda_o[t, \Delta T_o] \Delta T_o(t) \quad (\text{A12})$$

then Eq. (A11) becomes

$$m c_p \frac{\partial[\lambda_o \Delta T_o]}{\partial t}(t) = w(t) - a(\Delta T) \lambda_o \Delta T_o(t) \quad (\text{A13})$$

i.e.

$$m c_p \left\{ \frac{\partial \lambda_o}{\partial t} \Delta T_o + \frac{\partial \lambda_o}{\partial \Delta T_o} \frac{\partial \Delta T_o}{\partial t} \Delta T_o + \lambda_o \frac{\partial \Delta T_o}{\partial t} \right\} = w(t) - a(\Delta T) \lambda_o \Delta T_o(t) \quad (\text{A14})$$

If we define

$$m_o = m \left[\lambda_o + \frac{\partial \lambda_o}{\partial \Delta T_o} \Delta T_o \right] \cdot \frac{\partial \Delta T_o}{\partial t} \quad (\text{A15})$$

$$a_o = a \lambda_o + m c_p \frac{\partial \lambda_o}{\partial t} \quad (\text{A16})$$

we finally arrive at

$$m_o c_p \frac{\partial \Delta T_o}{\partial t} = w(t) - a_o \Delta T_o(t) \quad (\text{A17})$$

which is the key-point of our analysis.

Appendix B: Nomenclature

C_{p, D_2O}	heat capacitance of liquid D_2O
$C_{p, D_2O, gas}$	heat capacitance of D_2O vapour
C_{p, D_2}	heat capacitance of D_2
C_{p, O_2}	heat capacitance of O_2
L_{D_2O}	latent heat of evaporation of D_2O
Q_d	energy for the dissociation of one mole of D_2O
F	Faraday constant
I_{el}	cell current
T_a	reservoir temperature of the refilling system
T_b	bath temperature
T_c	cell temperature
ΔT	cell over bath temperature, $\Delta T = T_c - T_b$
$\Delta \dot{T}$	time derivative of ΔT
m	molar content of the cell

References

- [1] M. Fleischmann, S. Pons and M. Hawkins, *J. Electroanal. Chem.*, 261 (1989) 301; 263 (1989) 187.
- [2] M. Fleischmann and S. Pons, in T. Bressani, E. Del Giudice and G. Preparata (Eds.), *Proc. 2nd Annual Conf. on Cold Fusion*, Como, 29 June–4 July 1991.
- [3] M. Fleischmann and S. Pons, in H. Ikegami (Ed.), *Frontiers of Cold Fusion*, Proc. ICCF3, Nagoya, Japan, 21–25 October 1992.
- [4] M. Fleischmann, S. Pons, M. Anderson, L.J. Li and M. Hawkins, *J. Electroanal. Chem.*, 287 (1990) 293.
- [5] G. Preparata, *Cold Fusion 93: some theoretical ideas*, Proc. ICCF 4, Maui, USA, 6–9 December 1993.
- [6] C. Bartolomeo, M. Fleischmann, G. Larramona, S. Pons, J. Roulette, H. Sugiura and G. Preparata, Alfred Cöhn and after: the α , β , γ of the palladium–hydrogen system, Proc. ICCF 4, Maui, USA, 6–9 December 1993.
- [7] G. Preparata, *Alcune osservazioni sulla calorimetria di celle elettrolitiche del tipo di Fleischmann e Pons*, Milan, 1994, unpublished.

² In fact, if the calorimeter is a homogeneous one $\Delta T(\mathbf{x}, t) = \Delta T(t) \quad \forall \mathbf{x} \in V$ and Eq. (A11) reduces to Eq. (26).