

## **Studies on Fleischmann-Pons Calorimetry with ICARUS 1**

Toshiya Saito, Masao Sumi, Naoto Asami, and Hideo Ikegami\*  
New Hydrogen Energy Laboratory, The Institute of Applied Energy  
3-5 Techno Park 2, Shimonoporo, Atubetu-ku, Sapporo 004, Japan

\*National Institute for Fusion Science, Nagoya 464-01, Japan

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### **Abstract**

The Fleischmann-Pons calorimetry (FPC) is examined with the ICARUS 1 system, which is identical to the original cells which they designed for their calorimetry. In the present experimental studies, a critical evaluation is made of their original method (FPC) and a modified version of FPC is proposed. Its usefulness and validity is experimentally examined by detecting and regenerating artificial heat pulses regarded as heat excess.

### **1. Introduction**

The calorimetry which M. Fleischmann and S. Pons developed and have used with their cold fusion cells has been considered to determine the absolute power of heat excess, without any degradation of the time response caused by the heat capacity of the system. Their method depends entirely upon a mathematical analysis of the heat balance equation which is designed for their electrochemical calorimetry<sup>(1)</sup>. The method may be applied to various calorimetric systems other than electrochemical cells. The validity of their method has, however, seemingly not well been accepted, a possible reason of which will be discussed later on, in particular concerning their claim of excess heat from cold fusion.

Controversy on the Fleischmann-Pons Calorimetry (FPC) centers on the effective radiative heat transfer coefficient ( $k_R$ ). With any electrochemical calorimetry, when temperatures are measured, the temperature inhomogeneity in the cells is always a matter of great concern, and is normally observed in the present experiments to be less than a percent. With the FPC method, the temperature inhomogeneity, as well as conductive heat losses, is automatically woven into the effective radiative

heat transfer coefficient ( $k_R$ ) in the process of its determination. In their papers Fleischmann and Pons give a detailed description of their calorimetry; however, it is not clear how they actually estimated excess heat production. They seem to be too concerned with the precise determination of  $k_R$  to the exclusion of other factors. This leads one to wonder, on analyzing actual experimental data, how accurately and precisely the heat excess can be detected by their method, with the use of such a carefully determined  $k_R$ .

This is the context, in which the evaluation was made on FPC with the ICARUS 1 system (Fig.1), which was installed in February 1994 at the New Hydrogen Energy (NHE) Laboratory in Sapporo, in a close collaboration with Dr. S. Pons, IMRA Europe S. A..

## **2. The Principle of Fleischmann-Pons Calorimetry (FPC)<sup>(1)</sup>**

Their basic power balance equation determines the cell temperature  $\theta$ , which is the temperature of the electrolyte in the cell, to be given by

$$MC \frac{\partial \theta}{\partial t} = E - H + Q - k_R (\theta^4 - \theta_{\text{bath}}^4) \quad (1)$$

where  $CM$  is the heat capacity,  $E$  denotes the ohmic part of the electric power input,  $H$  gives the enthalpy carried away by the gas stream consisting of water vapor and electrolysis products. Any other generated heat in the cell is given by  $Q$ , and the last term represents radiative heat losses from the cell to the surrounding bath water across the vacuum gap of the Dewar in the unsilvered lower part of the cell (Fig.1), where  $k_R$  is the effective radiation heat transfer coefficient into which any other unknown heat losses, positive or negative, are considered to be woven. With the Dewar cell structure employed in the present experiments, conductive losses are assumed to be negligibly smaller than the radiative loss, but they do influence  $k_R$ , as will be discussed in the later section.

There are two unknowns in Eq.(1), namely  $MC$  and  $k_R$ , which can be simultaneously determined experimentally by introducing a square test heat pulse into the cell. Integrating Eq.(1) from the front time ( $t = 0$ ) of the square heat pulse input ( $\Delta Q$ ) to the time  $t$  and rearranging it with respect to  $MC$  and  $k_R$ , we will obtain the following equation.

$$\frac{\int_0^t (E - H + \Delta Q) dt}{\int_0^t (\theta^4 - \theta_{\text{bath}}^4) dt} = k_R + CM \frac{\theta(t) - \theta(0)}{\int_0^t (\theta^4 - \theta_{\text{bath}}^4) dt} \quad (2)$$

It will be easily seen that using two quantities, X (t) and Y (t), defined by

$$X(t) = [\theta(t) - \theta(0)] / \int_0^t (\theta^4 - \theta_{\text{bath}}^4) dt \quad (3)$$

$$Y(t) = \int_0^t (E - H + Q) dt / \int_0^t (\theta^4 - \theta_{\text{bath}}^4) dt \quad (4)$$

we can rewrite Eq.(2) as

$$Y(t) = k_R + CM X(t). \quad (5)$$

At each time of t, Y (t) and X (t) are calculated to show a linear relation as given by Eq. (5), where the slope indicates the heat capacity, CM, and the intercept of the linear line on the Y axis gives the effective radiative heat transfer coefficient,  $k_R$ .

Inserting the values of MC and  $k_R$ , thus determined, into Eq.(1), we can obtain the heat generation Q (t) in the cell simply by rewriting Eq.(1) as

$$Q(t) = CM \frac{d\theta}{dt} - E(t) + H(t) + k_R \{\theta(t)^4 - \theta_{\text{bath}}^4\} \quad (6)$$

Now, if we artificially assume that no excess heat is generated within the cell under the condition where the excess heat is actually present, i.e. with  $Q(t) > 0$ , the "imaginary" radiative heat transfer coefficient (denoted by  $k_{R1}$  hereafter) should be observed to be smaller than the "real" radiative heat transfer coefficient (denoted by  $k_{R2}$ ). Then the excess heat must be given by

$$Q(t) = (k_{R2} - k_{R1}) \{ \theta(t)^4 - \theta_{\text{bath}}^4 \} \quad (7)$$

The problem is how the "real" radiative heat transfer coefficient  $k_w$  can be determined. For this, Fleischmann and Pons use the following technique. At time  $t = 0$ , just before the test heat pulse is applied, they assume that Eq.(1) should satisfy the following condition,

$$\left[ CM \frac{d\theta}{dt} \right]_{t=0} = 0 = E(0) - H(0) - k_{R2} \{ \theta(0)^4 - \theta_{\text{bath}}^4 \} + Q_f \quad (8)$$

Putting  $Q = Q_f + \Delta Q$  in Eqs.(1) and (8), where  $Q_f$  denotes unknown heat excess, and integrating Eq.(1) in time from the front time ( $t = 0$ ) of the test heat pulse,  $\Delta Q$ , we will obtain the following expression for  $k_{R2}$ , by canceling  $Q_f$  in combination with Eq.(8) with the assumption that  $Q_f(t)$  is constant.

$$k_{R2} = \frac{\int_0^t [\{E(t) - E(0)\} - \{H(t) - H(0)\}] dt - CM \{ \theta(t) - \theta(0) \} + \Delta Q t}{\int_0^t \{ \theta(t)^4 - \theta(0)^4 \} dt} \quad (9)$$

where  $\Delta Q$  is also constant in the time period  $[0, t]$ . Putting the thus determined  $k_{R2}$ , into Eq.(7) together with  $k_{R1}$  determined by Eq.(2), one should be able to detect the averaged excess heat  $Q_f$ , only in each time period during which the test heat pulse is applied, under the further assumption that the excess heat  $Q_f$  is constant in time, — something which would be difficult to tell.

### 3. Experimental Evaluation of FPC

In the present experiments, efforts were made first to determine both  $k_{R1}$  and  $k_{R2}$  with a platinum rod cathode ( $2\phi \times 12.5$  mm) electrolyzing 0.1 M LiOD electrolyte in the identical cell (Fig.1) as used and operated by Pons and Fleischmann, which they named ICARUS 1. Since there would be no so-called excess heat anticipated in this blank experiment with the use of the platinum cathode, we should expect  $k_{R1} = k_{R2}$ , and the difference between them is considered to give a measure of errors, that is, a minimum detectable amount of heat output. Normally in the present experiment, those radiative heat transfer coefficients, determined by the method described in the previous section, were observed to scatter to give  $|k_{R1} - k_{R2}|/k_{R2} = 10\%$  as shown in Fig.2. A minimum detectable power may be estimated from

$$\delta Q = \delta k_R T_{\text{bath}}^4$$

to be unexpectedly as large as approximately  $\pm 0.3\text{W}$ , since the principle assumes the radiative heat loss to be a dominant loss. The main error source was found to be generated in the process of determining  $k_{R2}$  as would be anticipated from its way of deduction with Eq.(9).

Furthermore, as also shown in Fig. 2, another serious problem is found in the fact that in some cases  $k_{R1}$  was estimated to be larger than  $k_{R2}$ , which should not occur by any means according to their definition, unless  $Q(t)$  is negative, so that this casts a doubt on the validity of FPC.

After careful analysis of the FPC method, we had to devise our own alternative method of calorimetry by modifying FPC. Our method examines how the test heat pulse is regenerated, which could then be regarded as a pulse of artificial heat excess. This entails using an MC and  $k_R$  that have been predetermined by another test heat pulse in the manner described in the previous section [Eqs.(2) - (5)], that is, aside from FPC, what validity Eq.(6) would have in detecting the excess heat with the use of an MC and  $k_R$ , which have been predetermined under an assumption that no heat excess is then present. Should there already exist any unknown heat excess in the base line, it will not be directly detected by this method; however, the regenerated test heat pulse will be observed as a heat pulse with a smaller amplitude, since  $k_R$  then will have been estimated to be a smaller value than the "real" radiative heat transfer coefficient for  $Q_f = 0$ .

With the use of our modified method, each test heat pulse of  $0.25\text{W}$  was detected and regenerated as a heat pulse of  $0.25 \pm 0.002\text{ W}$ , as shown in Fig.3, for all 5 test pulses over 10 days of continuous electrolytic operation at  $200\text{ mA}$  with a cathode rod ( $21 \times 12.5\text{ mm}$ ) of  $\text{Pd}_{90}\text{Ag}_{10}$ . Those values,  $k_R = 0.7706 \times 10^{-9}\text{ W/K}^4$  and  $\text{MC} = 490.0\text{ J/K}$ , were determined at the time of  $2 \times 10^5$  seconds from the initiation of the electrolysis. The upward and downward spikes at the both edges of every regenerated pulse indicate errors due to  $\text{MC } d\theta/dt$ , that is, combined errors in determining both MC and  $d\theta/dt$ .

At the initiation of the electrolysis, a triangular decay of heat output may indicate the absorption heat of deuterium into the palladium cathode. One may also claim that some excess heat at a level of  $10\text{ mW}$  was continuously generated during the period of  $2.7 \times 10^5$  seconds (from  $1 \times 10^5$  to  $3.7 \times 10^5$  seconds), where the integrated heat excess amounted to  $2.7\text{ kJ}$ , or  $94.3\text{ kJ / cm}^3$ . This sort of excess heat generation may be overlooked by FPC which uses  $k_{R1}$  and  $k_{R2}$ , to detect an averaged heat excess only during the period of test heat pulses. However, such amount of heat excess as in the

level of 10 mW can be explained by a possible recombination of diffused deuteriums onto the anode surface. The observed power of 10 mW amounts to approximately 3% of the power spent to electrolyze the heavy water ( $E_{\text{thermoneutral potential}} \times I$ ), which is estimated in the present case to be  $\sim 300$  mW. This power has been taken care of in Eq.(1) by subtracting it from the total electric power input to leave only the ohmic power as denoted by  $E$ , however, the recombination (oxidization) has been neglected.

Repeated downward spikes indicate cooling (approximately - 300 J), by a supply of heavy water (approximately 4 cc) every 48 hours (172,800 sec.) of electrolysis and evaporation, at 200 mA. The spikes at the edges again indicate errors from the first term in the right hand side of Eq.(6), that is, combined errors in determining both MC and  $d\theta/dt$ .

A repeated change of slope in the base line in each period between the water filling time, indicates a change of  $k_R$  influenced by a change in conductive heat losses which have not been taken into consideration in Eq.(1). As the water decreases due to the electrolysis and evaporation, the water level descends and the distance of heat conduction through the glass wall, i.e. the distance from the electrolyte surface to the top of the cell increases, which turns out to suppress the conductive heat transfer, and there appears a periodic apparent heat generation. With the electrolytic currents of 400mA, the rate of descent of the water- surface level is faster than in the case of 200 mA, showing a larger apparent heat generation, with a steeper slope of sawtooth in the base line, as shown in Fig.4.

When the electrolytic currents increased from 200 mA to 400 mA, an additional change was observed that the base line stepped down by 0.07 W as also shown in Fig.4, as if a heat sink appeared in the cell. This could be explained as being caused either by lifting of the electrolyte surface level associated with a volume increase due to deuterium gas bubbles produced in the electrolyte, or by a voltage drop in the thin lead wire (0.25 mm $\varnothing$ ) of platinum to the cathode. Both are estimated to come in the same order of magnitude, sufficient to explain the loss of 70 mW, which is the amount of the base line down shift that was observed to be proportional to the electrolytic currents. In order to perform a proper calorimetry, the effective radiative heat transfer coefficient  $k_R$  must be re-estimated at each critical point such as when the electrolytic currents are changed. When the electrolyte boils, the surface level will change rather violently and the present method cannot be applied anymore.

Taking into consideration this experimental evaluation, we can claim that our modification of the FPC method makes it possible to detect any heat excess, by simply determining Eq.(6) with a properly determined  $k_R$ . With our modified method, we could easily detect any positive / negative amount of heat excess above approximately 30 mW over longer than a two month period, with the continuous use of the same  $k_R$  which has been determined at the initial stage of the electrolysis, when we could assume there to be no heat excess present. More precisely we may be able to claim from Fig.3 that

the power detectability with this method, under a low constant current operation, is better than a few mW during the first  $10^6$  seconds (approximately 10 days) after the determination of  $k_R$ .

#### **4. Conclusion**

The Fleischmann-Pons calorimetry (FPC) was examined with the ICARUS 1 system, which is identical to the original cells which they designed for their calorimetry. In our present experiments, their original method (FPC) could not reveal any satisfactory detectability to meet our expectation.

The most serious problem of FPC was found that in some cases  $k_{R1}$  was estimated to be larger than  $k_{R2}$ . This should not occur by any means according to the principle of the FPC method.

Our modified version of FPC proposes to use the basic power balance equation, Eq.( 1), and to estimate any heat excess with the use of an MC and  $k_R$  which have been predetermined in the earlier stage of the electrolysis under an assumption that no heat excess was present. The validity of our method is confirmed by regenerating a test heat pulse of 0.25W regarding it as an artificial heat excess. It was detected and regenerated as a heat pulse of  $0.25 \pm 0.002$  W for all 5 test heat pulses over 10 days of continuous electrolytic operation.

Our modified method of FPC could detect any excess heat, exceeding 30 mW under a low constant current operation for over a two month period with a continuous use of the same  $k_R$ , which was determined at the initial stage of the electrolysis, assuming that no heat excess was generated then. More precisely, the method was confirmed to show a power detectability as good as a few mW during the first  $10^6$  seconds (approximately 10 days) from the time of determination of  $k_R$ .

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#### **Reference**

- (1) M. Fleischmann and S. Pons, Phys. Letters A 176 (1993) 118

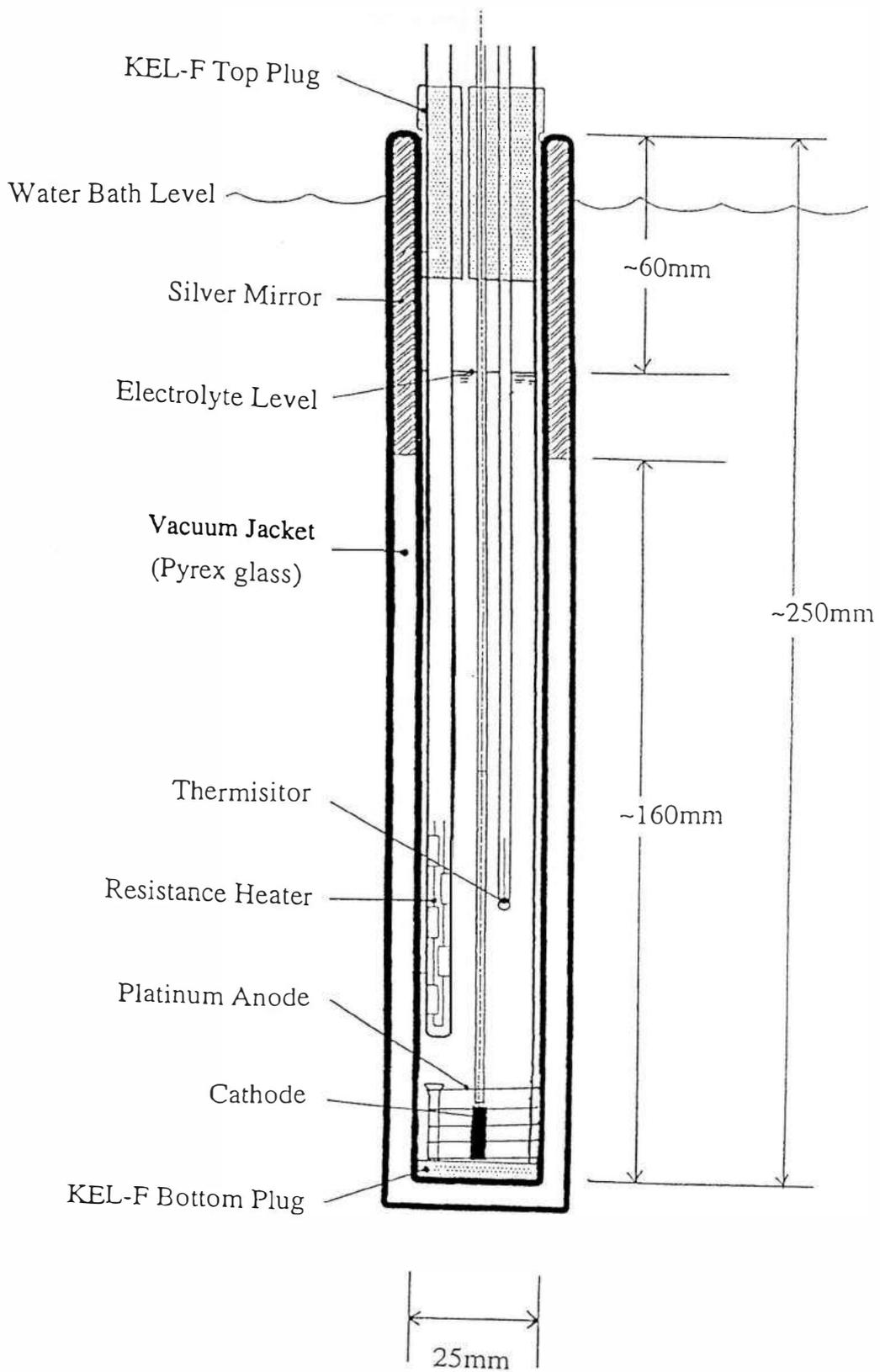


Fig. 1 Fleischmann - Pons Type Open Cell

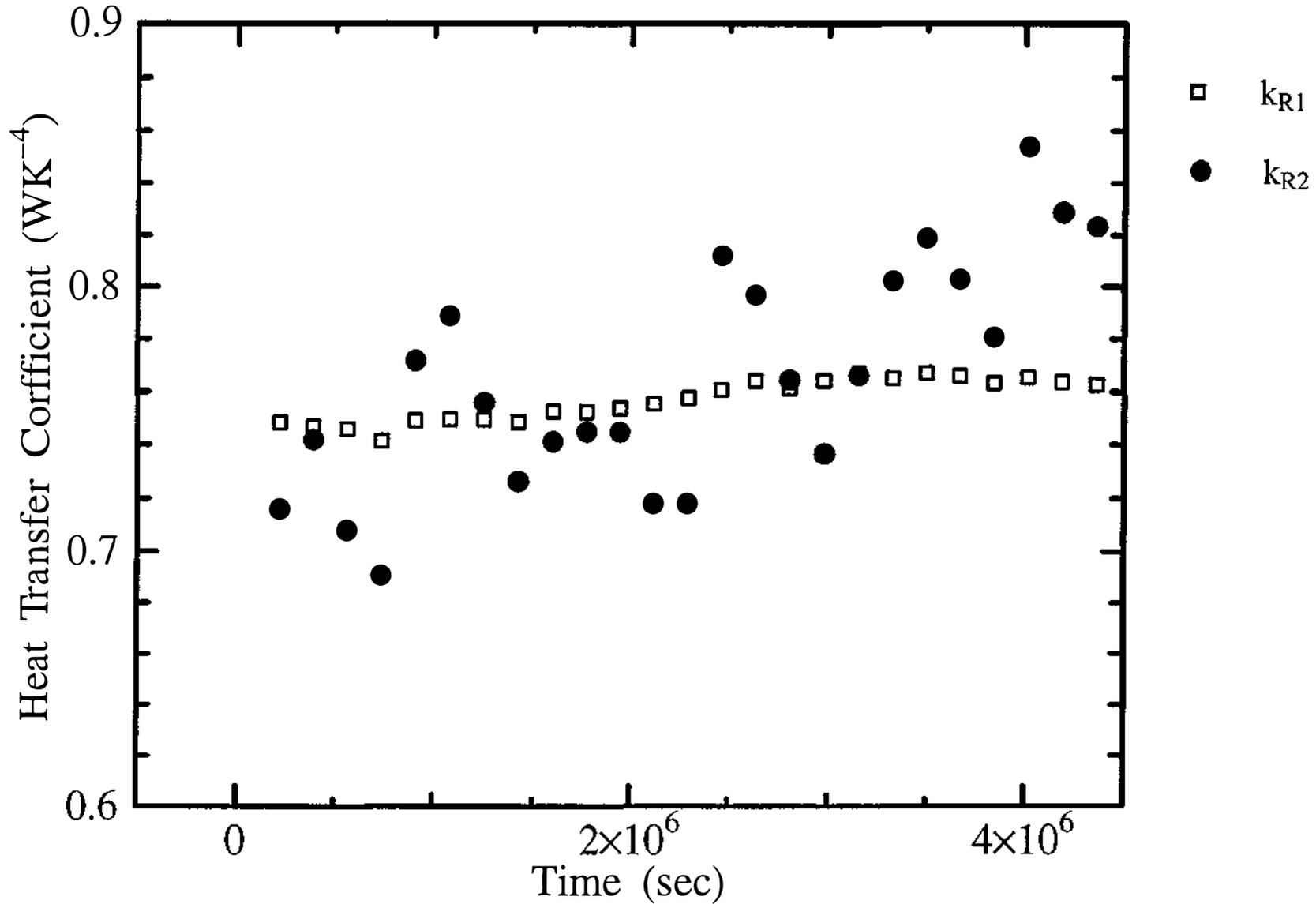


Fig.2 Heat Transfer Coefficient of exp.4711  
Electrode : Pd (J/M Bt.8023  $\phi$  2x12.5) Electrolyte : 0.1M LiOD

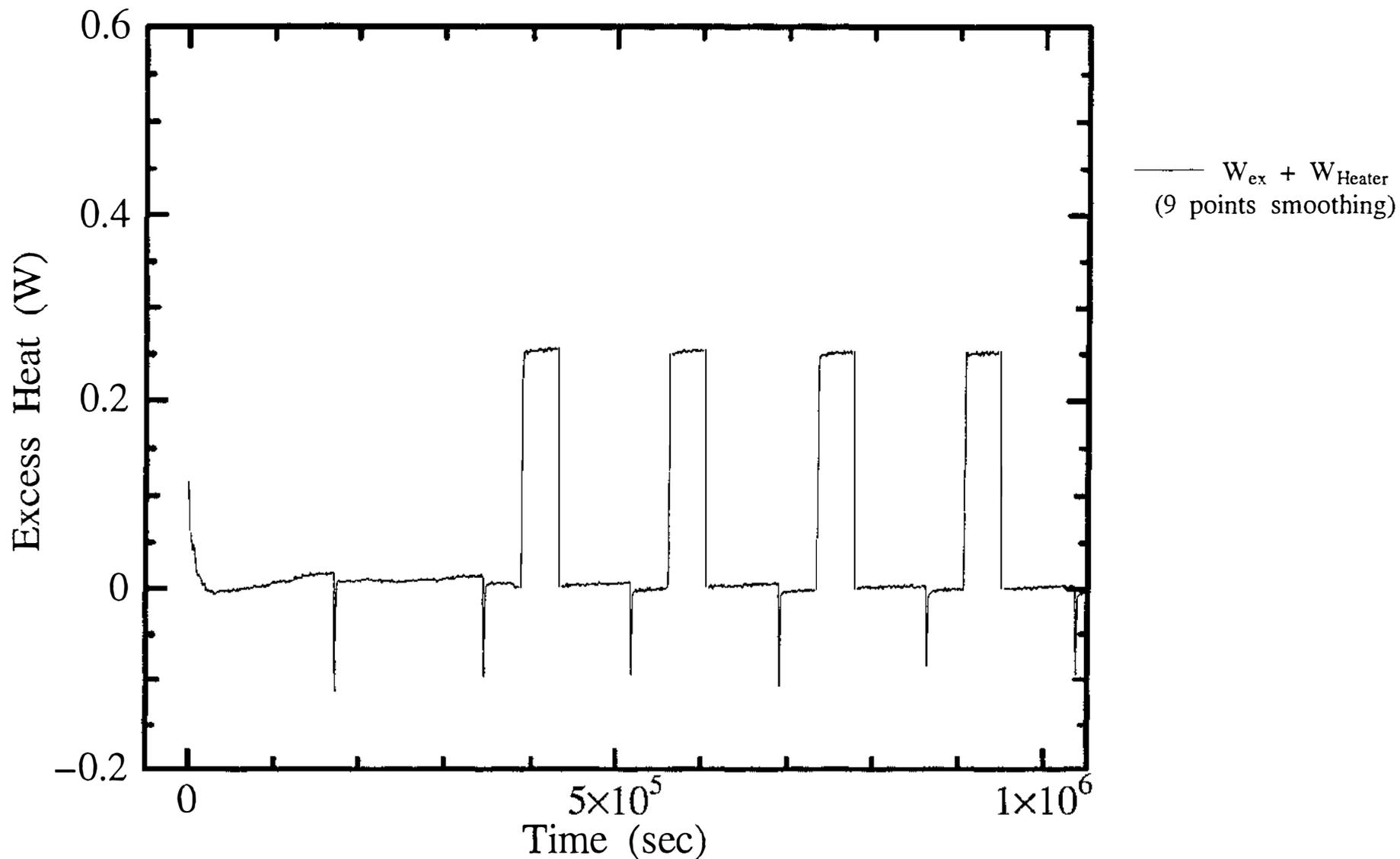


Fig.3 Change of Excess Heat (include Heater Input) of exp.4251

Heater inputs are reproduced as square pulses.

Electrode : 10%Ag-Pd (J/M Bt.0.549  $\phi$  4x12.5) Electrolyte : 0.1M LiOD

$k_R = 0.7706 \times 10^{-9}$  ( $\text{WK}^{-4}$ ),  $CM = 490.0$  ( $\text{J/K}$ ),  $W_{\text{Heater}} = 0.2506$

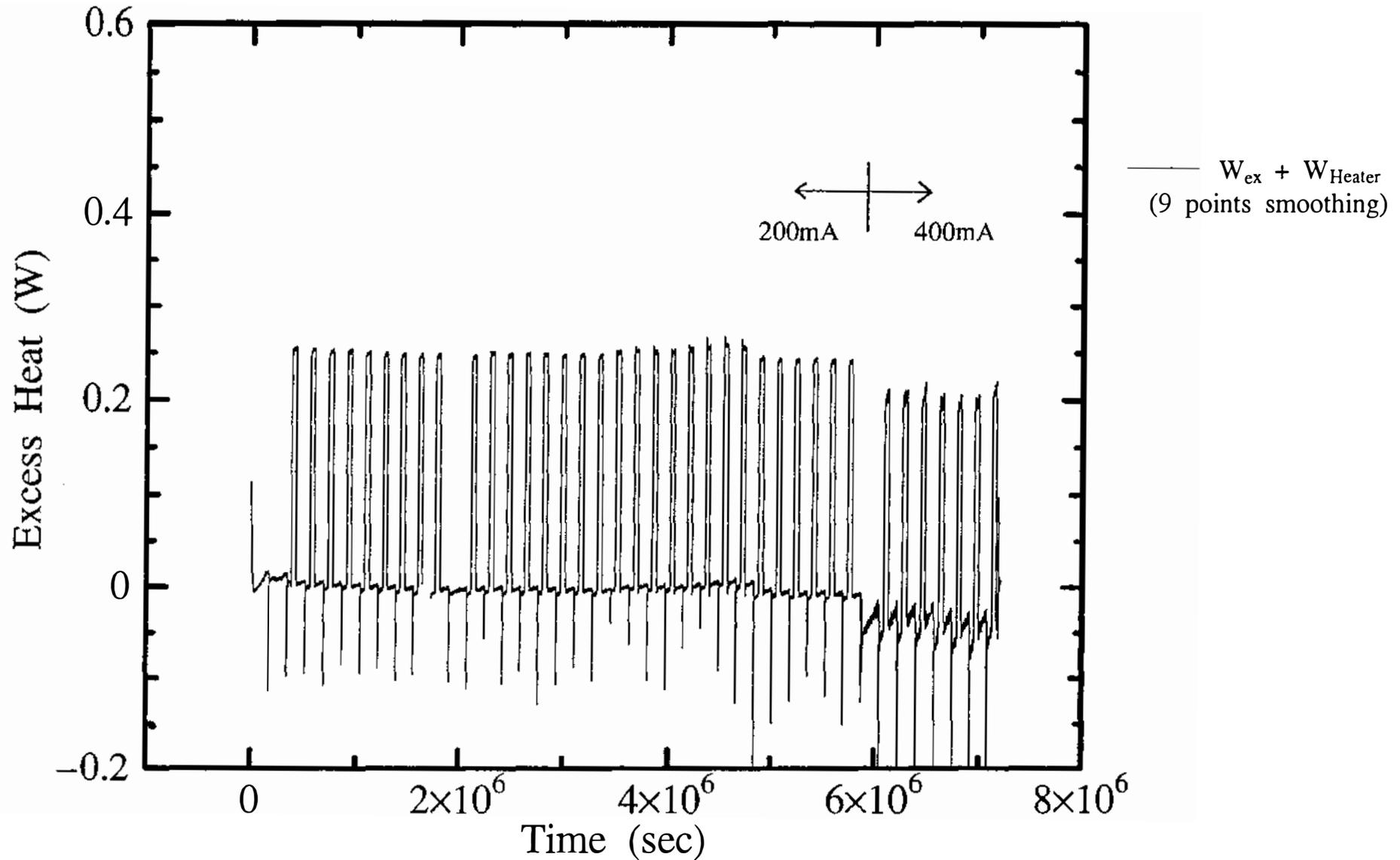


Fig.4 Change of Excess Heat (include Heater Input) of exp.4251

Electrode : 10%Ag-Pd (J/M Bt.0.549  $\phi$  4x12.5) Electrolyte : 0.1M LiOD

$k_R = 0.7706 \times 10^{-9}$  (WK<sup>-4</sup>), CM = 490.0 (J/K),  $W_{Heater} = 0.2506$