

# **The Method and Results Using Seebeck Calorimetry**

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## **ABSTRACT**

The characteristics of and errors associated with Seebeck calorimeters, as applied to the Fleischmann-Pons Effect, are described. This type of calorimeter as well as a flow type calorimeter were used to measured apparent excess energy from the same sample of platinum plated with palladium and other materials.

## **I. INTRODUCTION**

Acceptance of the Pons-Fleischmann effect<sup>1</sup> has depended on acceptance of anomalous heat production. Proving this claim involves use of a calorimeter. At least five different basic kinds have been used. Naturally, each design has its own set of errors and characteristics needing evaluation. Besides having only a small error, a calorimeter used to study cold fusion also must be very stable because the studies usually last for a long time. In addition, heat generated by the electrolytic process needs to be removed to avoid having the cell get too hot. Because this background energy can be large and the anomalous energy can be small, the calorimeter needs to be very sensitive over a wide range of heating power. No single design is ideal in meeting these requirements. Nevertheless, the Seebeck- or Kelvin-type comes close. This type of calorimeter measures power. Energy of a reaction is obtained by integrating the power over a period of time. This paper will describe the construction, operation, evaluation, and some results obtained using such a calorimeter. Other authors have also used and described the method.<sup>2-16</sup>

## **II. DESCRIPTION OF THE METHOD**

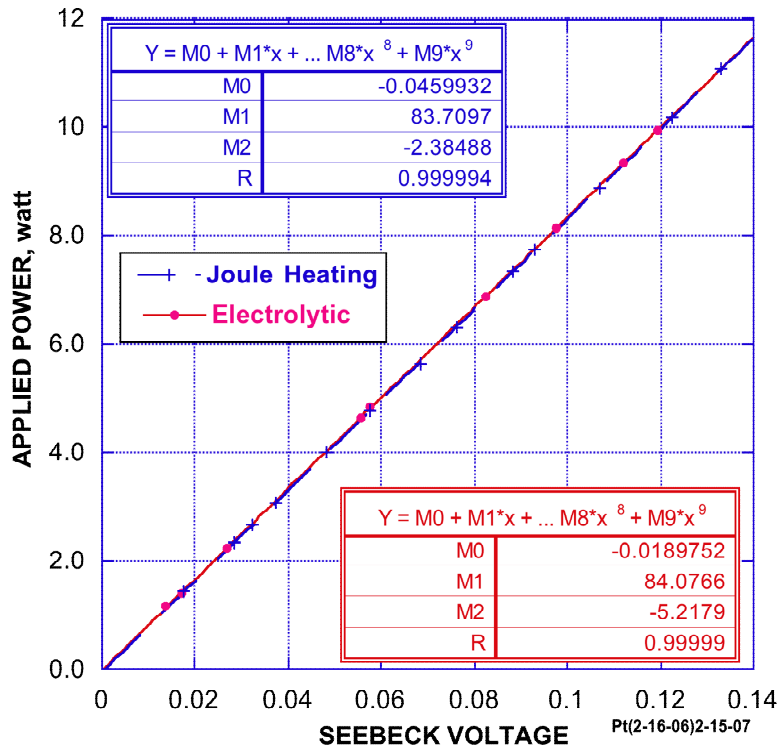
Heating power can be measured by causing the heat to pass through a thermal barrier, a process that generates a temperature difference across the barrier. When this method is used, the calorimeter is called an isoperibolic type. This temperature difference can be measured using various detectors, but usually only at a few locations. In contrast, a Seebeck calorimeter has a thermal barrier containing many temperature sensors, even to the extent of using a barrier made from a commercial thermoelectric converter assembly. When thermocouples are used, they are electrically connected in series so that their generated voltages add, thus providing a voltage having easily measured magnitude. This arrangement provides an accurate measurement of temperature difference at every location on the surrounding enclosure. When the outside is kept at constant temperature by flowing water, the generated voltage is proportional to the average power flowing through the walls. As a result, the calorimeter is relatively insensitive to where the source of heat is located. However, use of a fan within the envelope is advised to insure uniform temperature.

The amount of power (W) being generated within the Seebeck envelope is equal to

$$W = A + BV + CV^2 \quad \text{Equation 1}$$

where A, B, and C are constants obtained from a calibration using a known source of heat and V is the generated voltage. The simplicity of this defining equation makes the measurement easy to understand and to evaluate. Normally, the “A” term is very close to zero. However, small errors in the voltage measurement or small heat leaks into the envelope through penetrating wires can produce a small value. The “B” value gives the sensitivity of the calorimeter in units of watt/volt. The C term corrects for the nonlinearity of the thermal barrier, thermoelectric converter or thermocouples. Normally, the contribution of this term is very small.

Although the temperature is well known, accurate values for power can only be obtained after the temperature within the calorimeter has reached a constant value. The time required for the temperature to become constant after a change in produced power is called the time constant of the calorimeter, which is usually between 1 and 2 hours. An apparent power calculated using the calorimeter is not accurate until sufficient time has lapsed for the temperature within the cell to become constant.



**FIGURE 1. Typical calibration**

Figure 1 shows a typical calibration using two sources of heat. One set of calibration values was obtained using an electrical heater located within the electrolytic cell (Joule). The second resulted from heat generated by electrolytic action in a cell containing a recombining catalyst and an inert cathode. Notice that these two independent sources of heat show only a small difference.

At 1 watt total power, the difference is about 32 mW and about 35 mW at 8 watts total power. Temperature gradients are not the cause because the difference is nearly independent of applied power. If temperature gradients were the cause, bubble action, which increases with applied electrolytic power, would cause the gradients to change, hence cause the difference between the two calibrations to change. Nevertheless, the persistence difference over a wide range of applied power gives the final calibration an uncertainty of perhaps 35 mW. Because this difference is variable and not clearly related to any particular condition, a comparison should be made in an attempt to find the cause. If the source of bias cannot be identified, a doubt is created as to which of the two methods for calibration is correct. Consequently, the resulting excess power will contain an unknown bias. The existence of excess power can only be accepted if the amount is significantly greater than this bias.

Excess power is determined by subtracting the amount of applied electric power (cell volt x current) from that calculated using Equation 1. If the same resistors and measuring circuits are used for both the calibration and the measurement of excess power, many errors cancel, resulting in much less uncertainty. If different resistors and/or measuring circuits are used, the bias that is generated can give a false indication of excess power that can be hard to identify. Consequently, a dual calibration using both Joule and electrolytic power is important.

### III. CALORIMETER DESIGN

A picture of an open Seebeck envelope ( $7" \times 7" \times 7"$ ) containing a small electrolytic cell and several small fans is shown in Fig. 2a. This version is available from Thermoionics (<http://www.thermoionicscorp.com/>). Figure 2b shows a small Seebeck made by cementing commercial thermoelectric panels together. In this case, the top is a simple insulator. Constant-temperature water circulates around the outside of the converters.

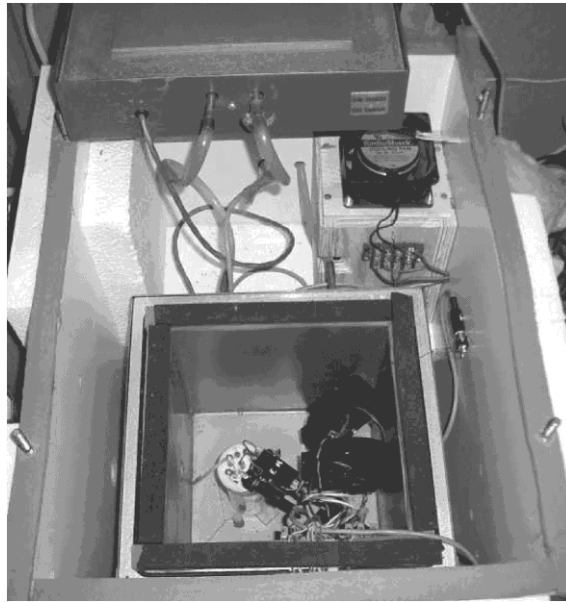
Figure 2c shows a Seebeck calorimeter using 1000 thermocouples placed in a polyethylene water pipe that serves as the thermal barrier. A fan is provided on the lid to circulate air within the enclosure. Water flows outside of the thermal barrier. A water-proof paint is used to electrically insulate the thermocouples from the cooling water.

Figures 2d and 2e show the outside and inside of a calorimeter made using commercial thermoelectric converter plates having high efficiency. In this design, the top is also active and water-cooled. This is only an example of possible designs. The method can be used to create enclosures of any size and a sensitivity greater than any other method.

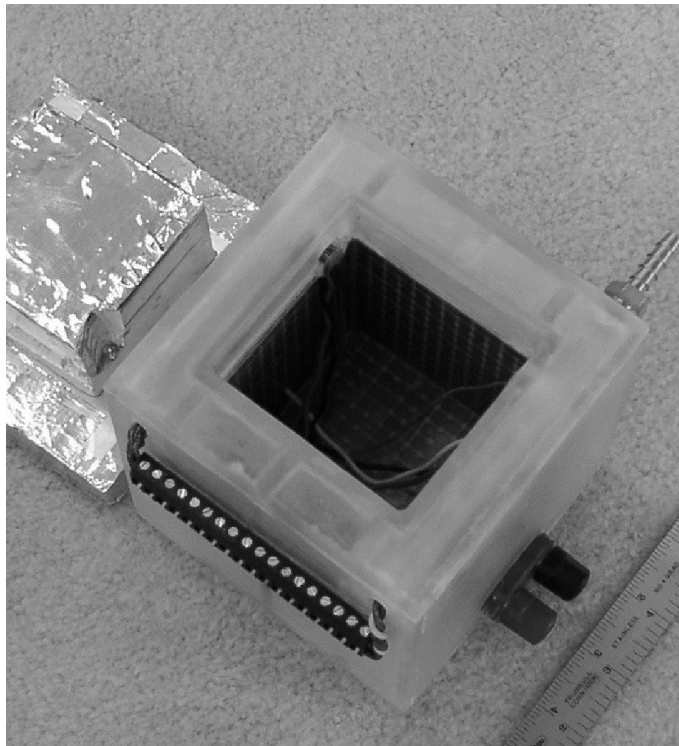
When constructing such a calorimeter, it is important to have all walls as identical as possible with respect to thermal conductivity and conversion efficiency from heat to voltage. In addition, the entire surface of the thermal barrier outside of the enclosure must be held at the same constant temperature regardless of the amount of power being generated within the enclosure. Therefore, water cooling, in contrast to air cooling, is the better method. If these conditions are not met, the calorimeter will be nonlinear and will be sensitive to where within the enclosure heat is generated. Water cooling also allows the temperature within the box to start well below room temperature if this should provide an advantage.

When used to measure heat generated by an electrolytic cell, the sensitivity and accuracy will be reduced somewhat by random variations in applied power caused by bubble formation. Bubbles change the resistance of the electrolyte, which causes random variations in voltage

measured across the cell. Hence random variations in applied power are produced, especially at high applied current.



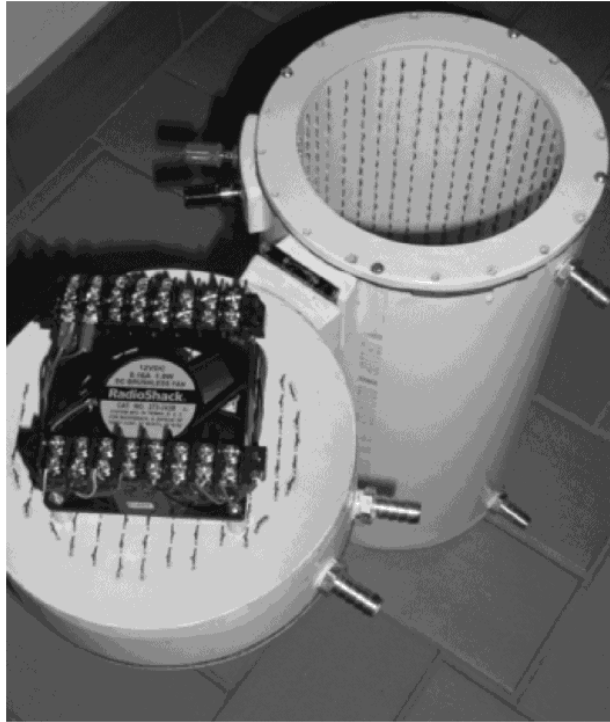
**FIGURE 2a.** Picture of commercial Seebeck Calorimeter. The calorimeter is contained in a constant temperature environment.



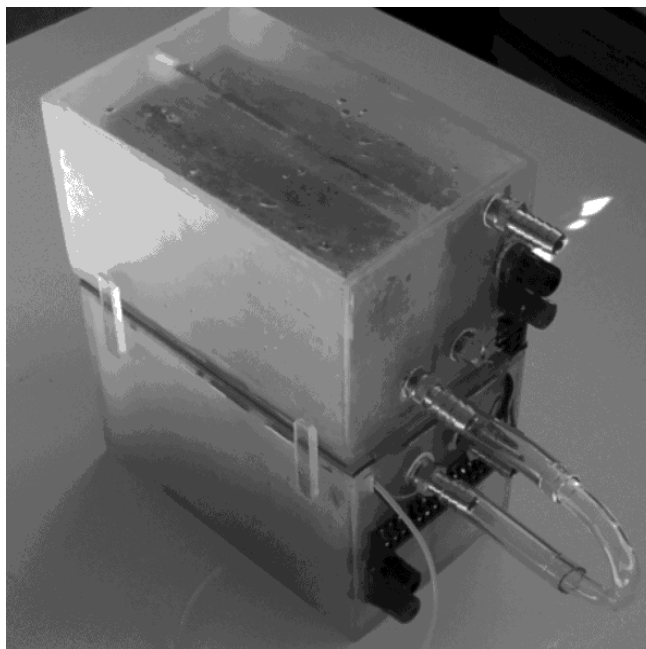
**FIGURE 2b.** Picture of small Seebeck calorimeter using thermoelectric converters as the thermal barrier, but with an inactive, insulating lid.

Although a well constructed Seebeck is relatively insensitive to changes in the room temperature, higher accuracy can be obtained by placing the Seebeck enclosure and all parts of the voltage and current measuring circuits in a constant temperature environment.

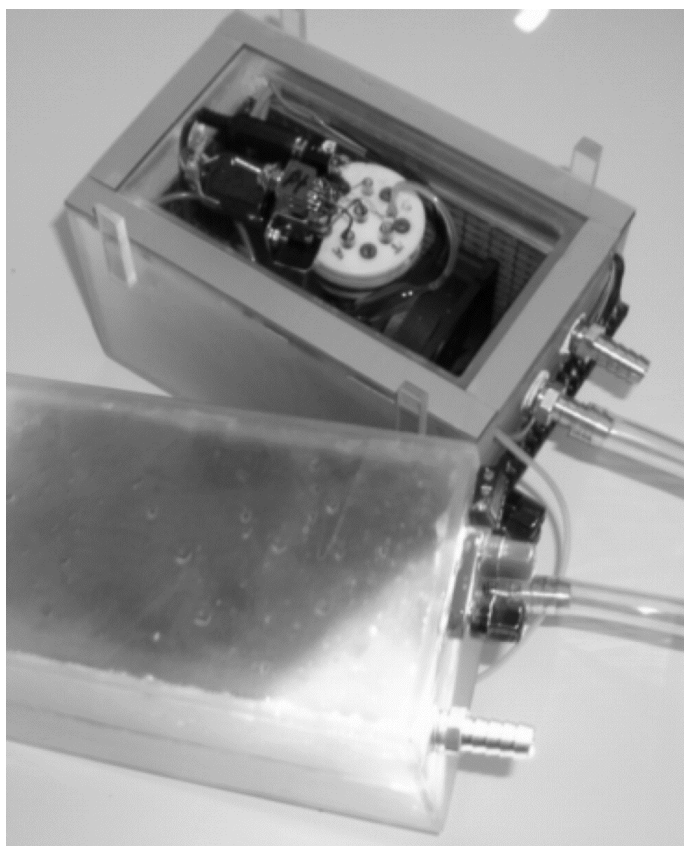
In general, the smaller and more compact the enclosure, the better. In general, a smaller enclosure has a faster response time and a higher sensitivity. In addition, it will have a lower cost.



**FIGURE 2c. A Seebeck calorimeter made using 1000 thermocouples.**



**FIGURE 2d. Assembled calorimeter.**



**FIGURE 2e. Open calorimeter showing the electrolytic cell and a small fan. The cell has a universal design so that it can be exchanged with other cells when different experiments are undertaken.**

## IV. SOURCES OF ERROR

Although the measurement is not sensitive to where heat is generated within the electrolytic cell, it can be sensitive to where the cell is located within the Seebeck envelope. This effect arises when the outside of the thermal barrier is not cooled uniformly by constant-temperature water flow or if it does not have a uniform thermal conductivity. Consequently, better results are obtained if a small fan is placed in the envelope to distribute the heat. In addition, the fan cools the cell, resulting in a smaller temperature increase within the cell for the same amount of generated power. In the examples shown here, a 12V DC fan is used that consumes about 0.75 watts. This power is added to that being generated within the cell when the system is calibrated.

Unexpected differences in behavior can result when a large difference in the temperature at the cathode is produced by the same electrolytic power, such as results when different calorimeter designs are used. For example, Fig. 3 compares the temperature difference of the cathode in a flow-type and Seebeck calorimeter as a function of applied electrolytic power. This behavior is universal and needs to be acknowledged when results obtained using different calorimeters are compared. A special cell can be designed to lose heat more rapidly and reduce the cathode temperature, as pictured in Fig. 4.

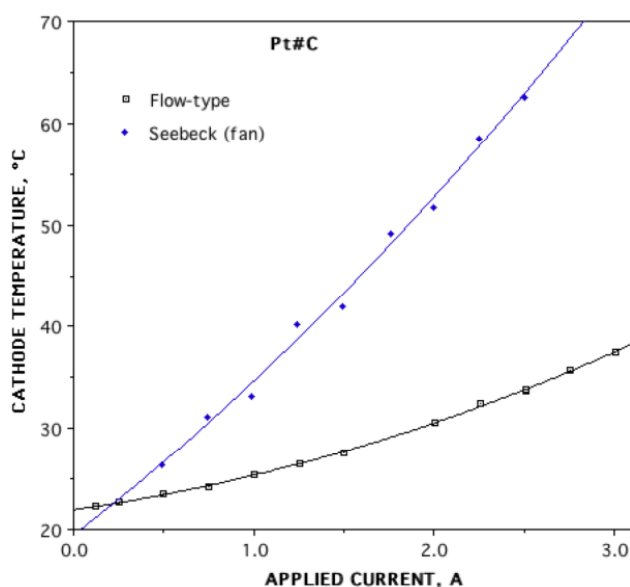


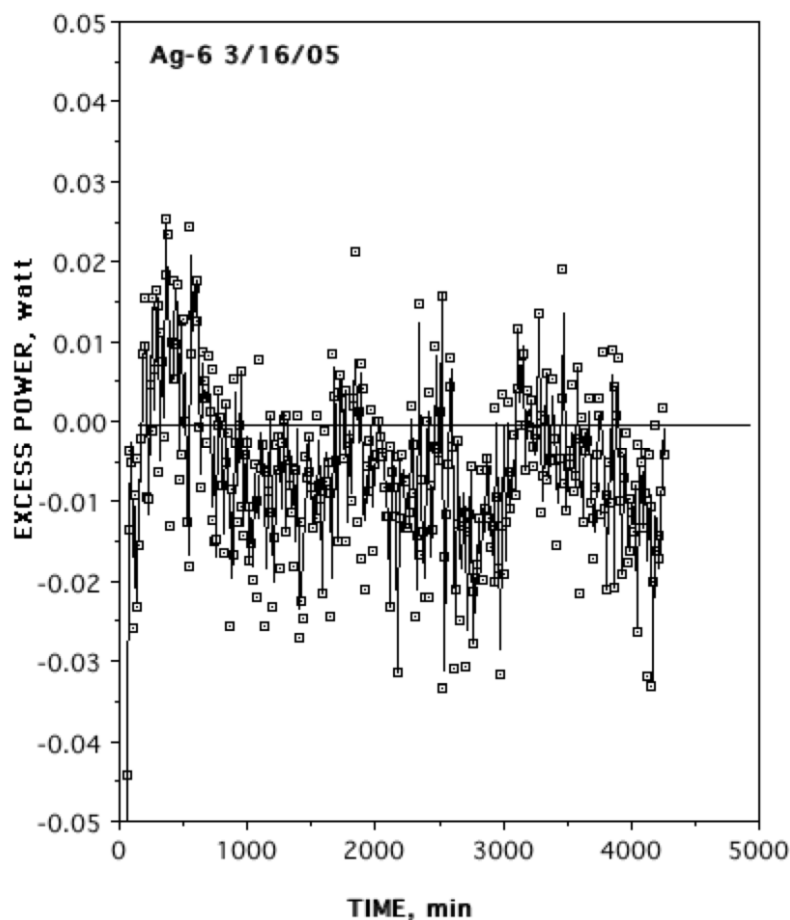
FIGURE 3. Comparison of cathode temperature vs applied current for a Seebeck and flow-type calorimeter.



**FIGURE 4. Cell with cooling fins to reduce cathode temperature.**

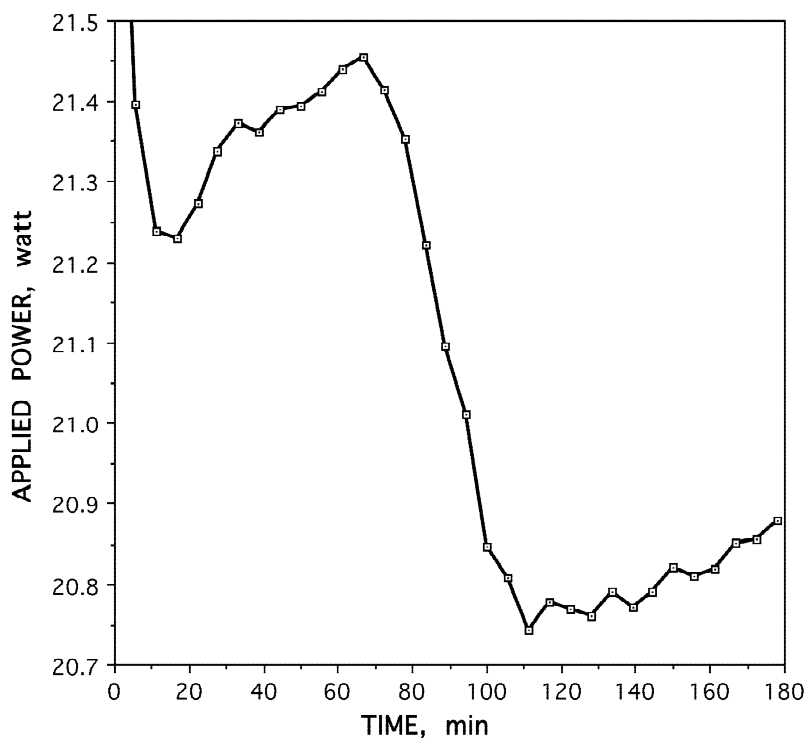
As long as power supplied to the fan and electrolytic action is constant, its value can be accurately measured. However, most fans of this type exhibit small variations in wattage that introduce about a  $\pm 5$  mW ripple on the value of calculated power (W). Bubble action adds an additional variation on the power being supplied for electrolysis. An example of how this rapid variation in applied power affects the apparent excess power is shown in Fig. 5. Other calorimeter types are expected to show the same behavior, the magnitude of which will depend on how long the signal is averaged to obtain the reported value. In this case, points are taken every six minutes and the data are averaged for about 30 sec.



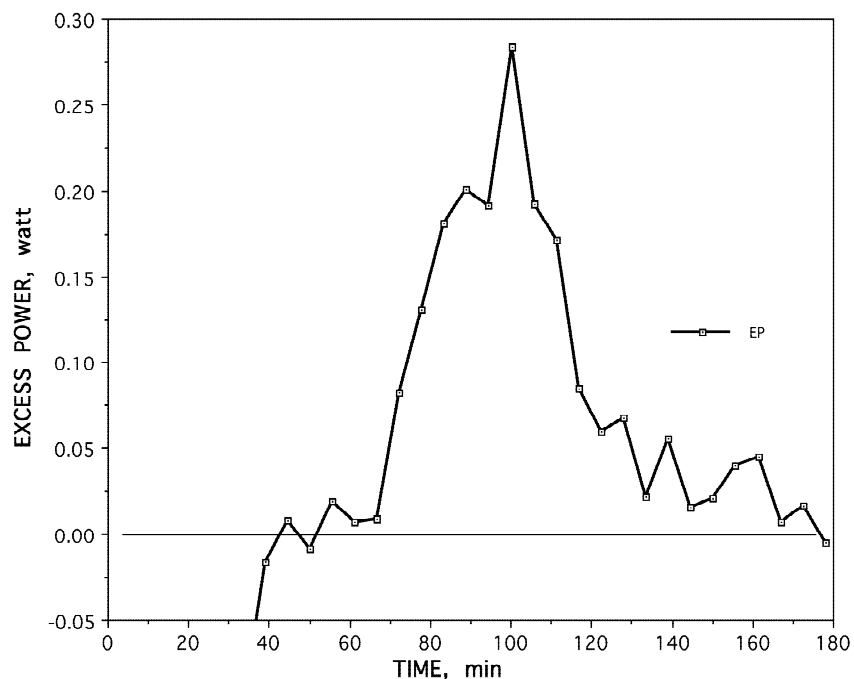


**FIGURE. 5. Examples of variations in apparent excess power.**

Apparent excess power can also be produced when applied power changes too rapidly for the calorimeter to remain in equilibrium. For example, if applied power is reduced as shown in Fig. 6, perhaps because the resistance of the cell changes, the calculated apparent power will have the behavior shown in Fig. 7. Unless this change in applied power were recognized, the result might be interpreted as a sudden burst of excess power. In fact, the calculated excess is only accurate when applied power and the resulting temperature within the cell are constant or change slowly compared to the time constant of the calorimeter. Similar behavior will be observed in all calorimeters that measure power production.



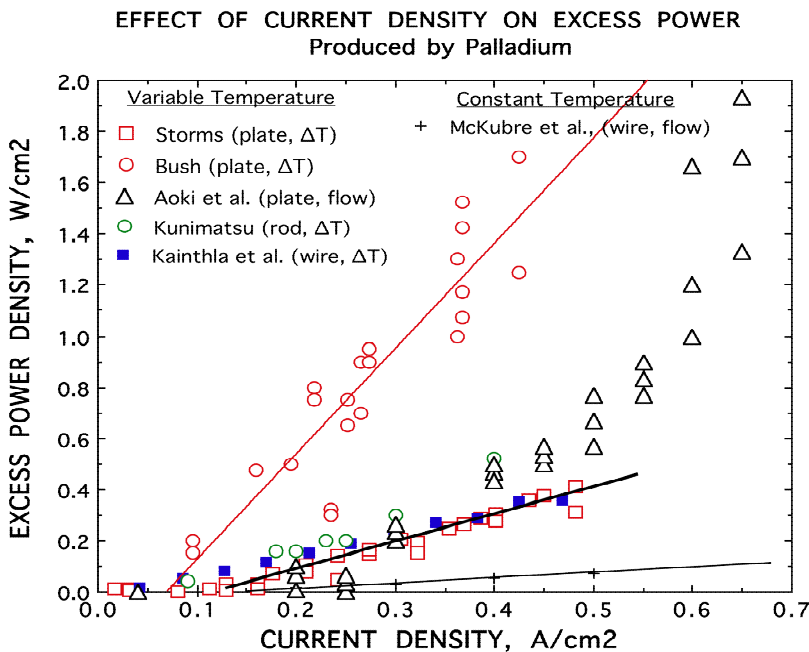
**FIGURE 6.** Example of a change in power applied to an electrolytic cell.



**FIGURE 7.** Result of power change shown in Fig. 6.

Apparent excess power can also be caused by a drift in the calibration constant. Unfortunately, this drift produces a behavior exactly like the one produced by production of excess energy. This error can be identified by changing applied current, first up and then down in value. Because the excess is a function of applied current, this change should show a repeated behavior. An example

of several studies showing this effect is provided in Fig. 8. Some samples show a very reproducible effect of current and some do not. If the apparent excess returns to near zero when current is reduced to zero, confidence in the calorimeter can remain high. On the other hand, if the excess does not return to zero, the data should be ignored even though life after death might be the explanation. At the very least, a recalibration needs to be done when expected behavior is not produced.



**FIGURE 8.** Change in apparent excess with applied current.

Another error results when the amount of recombination of  $D_2$  and  $O_2$  is unknown. If recombination is complete, because a catalyst has been placed in the cell, no error is introduced in the measured heat because all gas will be converted to the original  $D_2O$ . However, in the absence of a catalyst, the amount of recombination can be variable and must be measured. When applied current is above about 0.1 A, the amount of recombination is always small, as shown in Fig. 9. In contrast, smaller currents show a significant and variable amount of recombination that needs to be measured directly. This measurement can be made by attaching an oil reservoir to the sealed cell that captures gas leaving the cell, as shown in Fig. 10. By dividing the amount of gas leaving the cell by the number of electrons passing through the cell, the amount of recombination can be determined. When a constant value independent of current is found, it is safe to assume that no recombination is occurring in the cell, i.e. all generated gas is leaving the cell. However, when recombination occurs, the amount of gas leaving the cell is reduced and the calculated ratio is no longer constant. This behavior can be easily seen in Fig. 11 for various conditions. Stirring the cell, thereby causing bubbles to impact the electrodes, has no significant effect on this behavior. Therefore, bubble contact with the electrodes does not cause recombination.

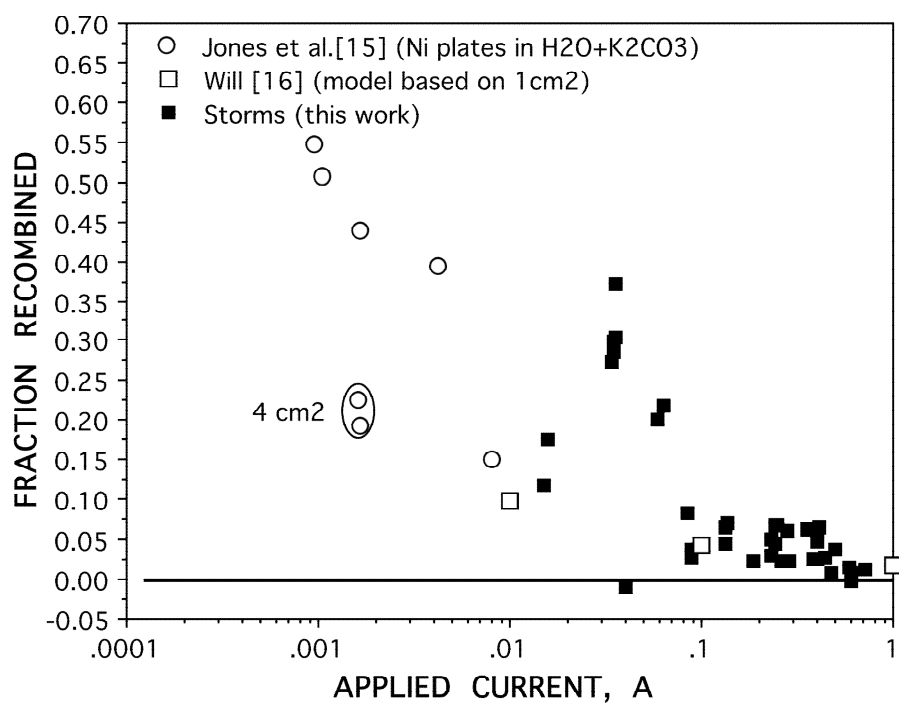


FIGURE 9. Fraction of gas recombined vs log of applied current.

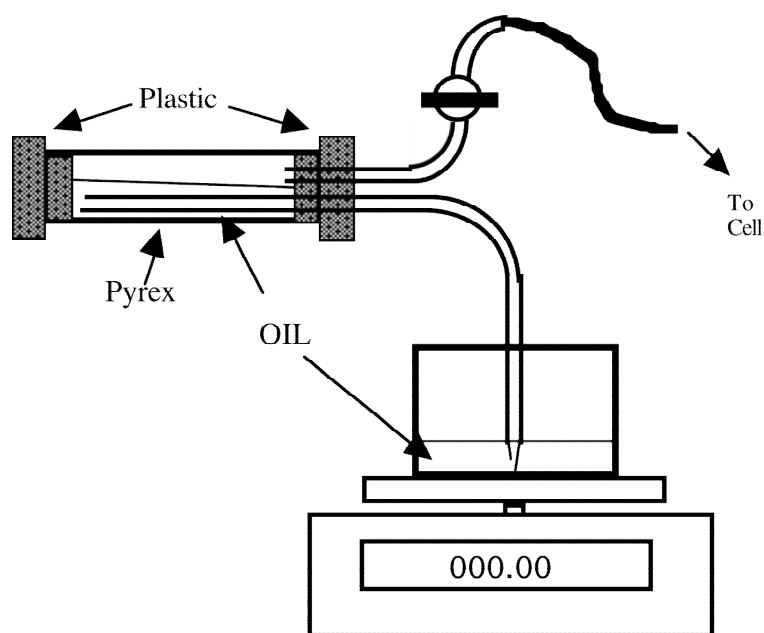
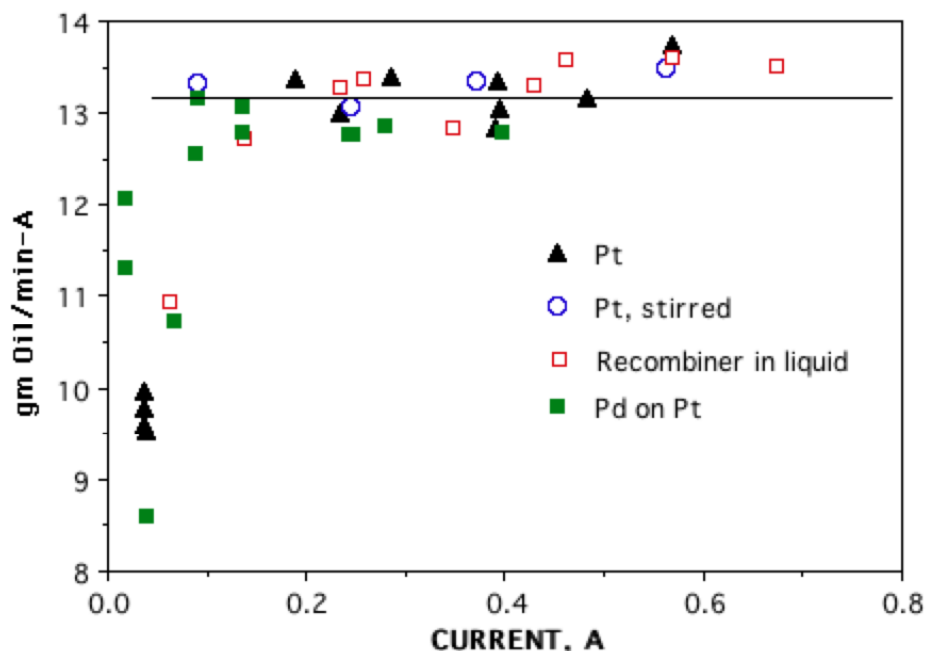


FIGURE 10. Drawing of oil system. Mineral oil is used.



**FIGURE 11. Oil weight/ampere\*minute vs current for various conditions.**

Recombination can also be determined less accurately by weighing the amount of  $D_2O$  lost from the cell or by measuring the change in electrolyte volume.

Errors can't be avoided, but techniques can be used to separate a real behavior from one produced by error. These techniques involve measuring two independent behaviors or by using two different kinds of calorimeters as discussed below.

When extra heat is produced by a reaction at the cathode, the cell temperature will increase. If this increase is associated with excess heat being produced, as shown in Fig.12, confidence in the reality of the excess heat is increased. As the figure shows, a slow initial drop in cell temperature caused no change in excess power. However, when an increase in cell temperature was detected at 1200 min, a corresponding increase in excess power was also measured. This excess remained constant while the cell temperature remained constant at the higher temperature. Because cell temperature is not used to calculate excess power, these values result from two completely independent measurements showing extra heat production.

If a sample shows similar behaviors using two different calorimeters, each having different errors, the reality of the measurement also increases. Figure 13 shows such a comparison using a flow-type and a Seebeck calorimeter. Figure 14 shows a different data set for the same sample using two different methods. During the study labeled "sweep" a data point was taken after which the current was changed. After a delay sufficient to allow the calorimeter to stabilize for about 90 minutes, another data point was taken. In contrast, each data point labeled "constant" is an average of data taken over several hours at constant current. As a result, random errors are reduced. In Fig. 14, the excess power obtained using the Seebeck, which had a larger cell temperature, was slightly greater than that produced in the flow-type in which the cathode had a lower temperature.

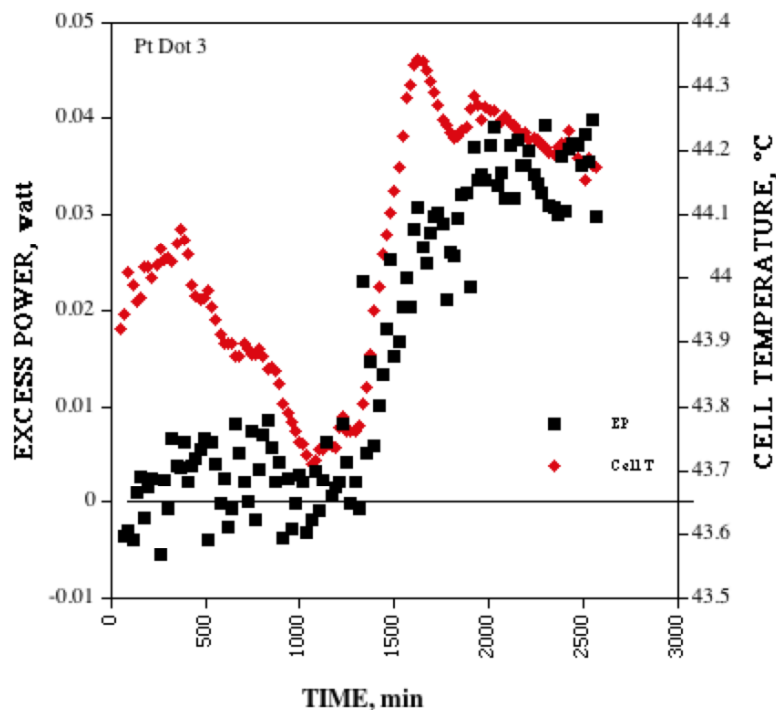


Figure 12. Simultaneous measurement of excess power and cell temperature using a Seebeck calorimeter.

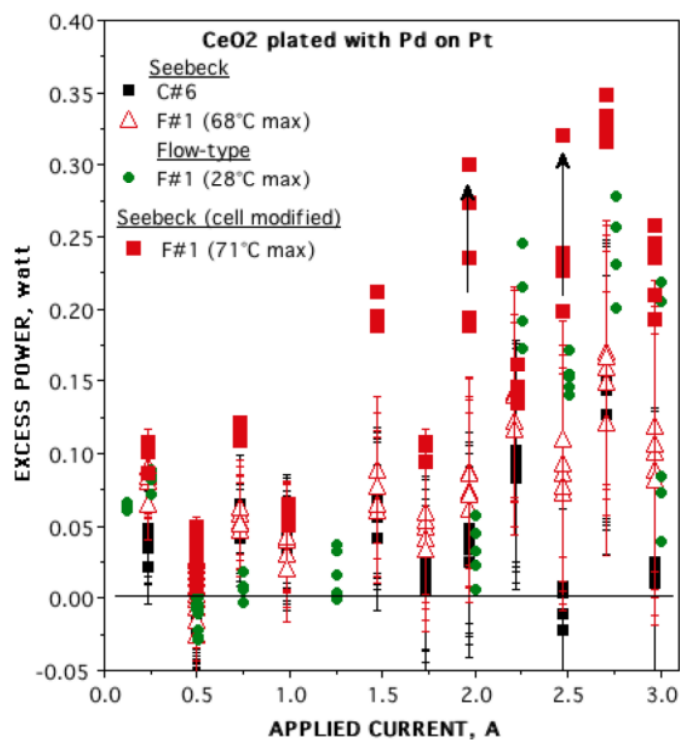
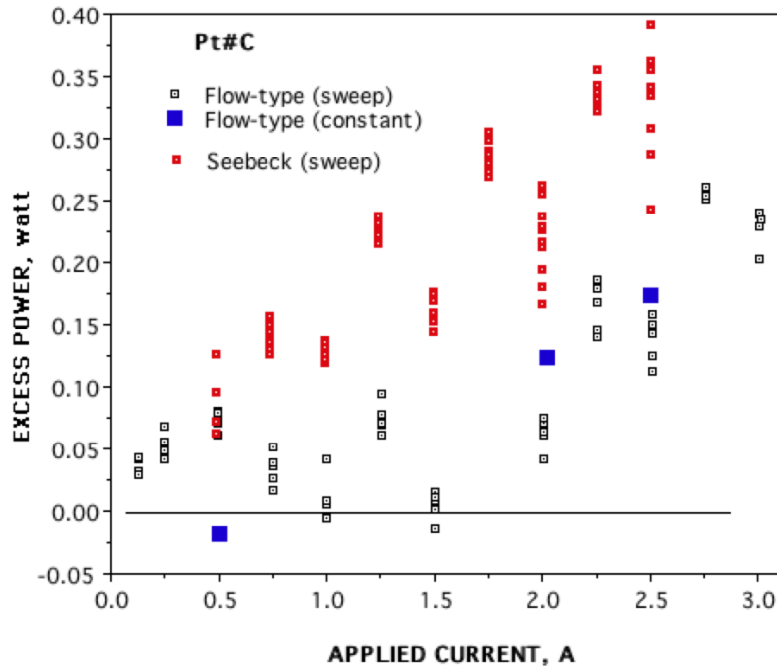


FIGURE 13. A comparison between excess power obtained by using a flow-type and a Seebeck calorimeter. The cathode was platinum plated with palladium using a bath containing a suspended powder of mixed oxides including CeO<sub>2</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO.



**FIGURE 14.** A comparison between excess power obtained by using a flow-type and a Seebeck calorimeter using the same cathode studied in Fig. 13.

## V. CONCLUSION

The Seebeck calorimeter is simple to use and to understand. It is very stable and is capable of accepting a wide range of power production within its envelope. The absolute accuracy depends on the design and the skill of the operator, as is required of all measurement methods. Nevertheless, this calorimeter allows the error to be easily identified and evaluated. Proper design of a measurement can reduce the absolute error in a power measurement to less than 30 mW and the relative error to less than 15 mW.

A study of the same sample using two different types of calorimeter demonstrates production of excess energy using an electrolyte containing D<sub>2</sub>O and a platinum cathode on which palladium and other materials have been plated. The behavior has the characteristics attributed to the Fleischmann-Pons Effect.

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