

Description of a Dual Calorimeter

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ABSTRACT

A dual calorimeter is described which can be used to study electrolytic processes. Experience with this instrument has revealed several deficiencies inherent in the isoperibolic calorimeter design that apply to all calorimeters of this type when used to study the cold fusion effect.

I. BACKGROUND

A calorimeter has been designed to measure heat energy produced in a Pons-Fleischmann type electrolytic cell. Two independent methods to determine heat production are used. This redundancy increases the reliability of the results as well as providing a method to study possible errors associated with conventional isoperibolic calorimetry. The design was constrained by the need for a small time constant, the ability to make changes easily, and limited resources. Provisions are made for computer control of the instrument. This is a first generation design, pictures of which can be seen at <http://home.netcom.com/~storms2/index.html>. A third generation design is presently being used and will be described in future articles.

Unfortunately, the design of the isoperibolic mode is not similar to that used in a stand-alone isoperibolic calorimeter. Normally, the reference temperature outside of the cell is constant and uniform in a stand-alone device. In the dual mode, the reference temperature is variable because the jacket temperature is used as the reference temperature. In addition, this reference temperature has a gradient between the top and bottom of the jacket. These differences make the isoperibolic mode more unstable than a stand-alone device. Nevertheless, this calorimeter can be used to study several limitations of the general isoperibolic design, limitation which workers in the cold fusion field need to understand.

II. GENERAL DESCRIPTION

The calorimeter determines energy production using the temperature change of water flowing through a surrounding jacket and by using the temperature difference across the cell wall. In addition to measuring heating power, the apparatus is capable of measuring the D/Pd ratio, the open-circuit-voltage (OCV), and the overvoltage of the cathode (OV) using two different reference electrodes. Calibration can be achieved by using electrolytic power or an internal heater.

The D/Pd ratio is determined as shown in Fig. 1. The amount of unrecombined oxygen produced when deuterium is retained by the cathode is determined from the amount of oil displaced from a reservoir onto a balance (0-600g, ± 0.01 g). Because the cell contains a recombiner (Pt on carbon cloth), any oxygen not associated with combined deuterium is

removed by forming D_2O . Hence, as long as the recombiner is working properly, very little oil is displaced. An additional recombiner is placed external to the calorimeter in the gas line. A temperature change of this recombiner is used to diagnose any failure of the

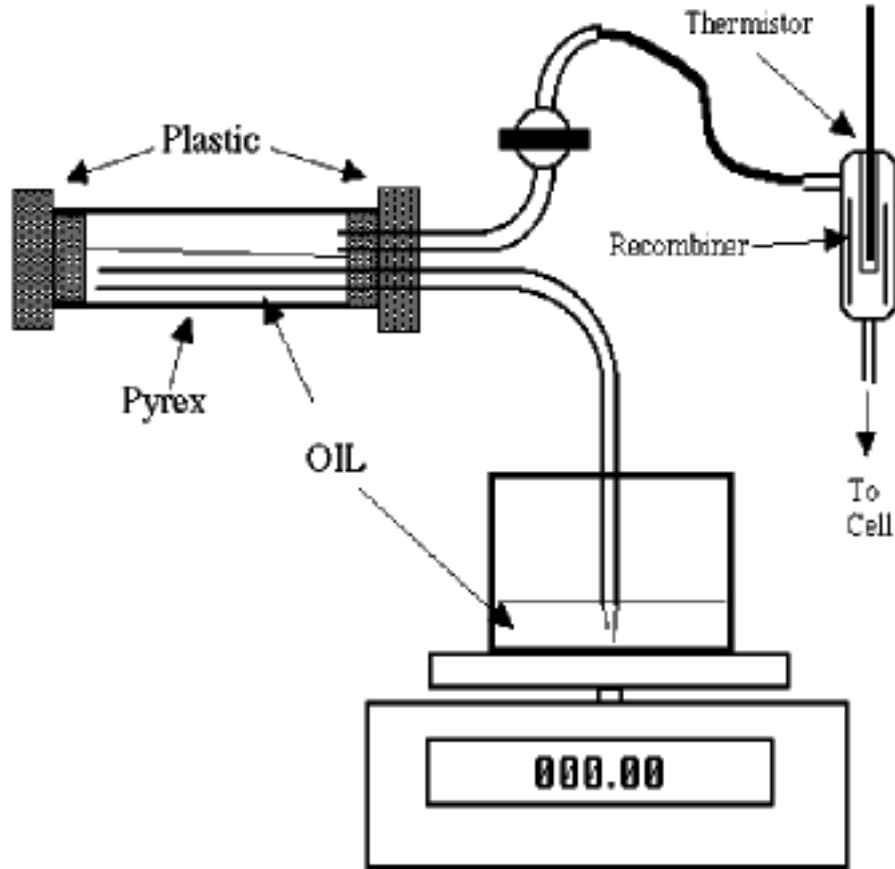


FIGURE 1. Drawing of a device used to measure the D/Pd ratio of the cathode.

internal recombiner. This device was also used to study the recombination process at the electrodes after the recombination catalyst was removed.

The Pyrex electrolytic cell is surrounded by a jacket through which water flows at a constant rate of 18-27 g/min ($\pm 0.2\%$) with a temperature of 20-50° ($\pm 0.02^\circ$). Temperature ($\pm 0.02^\circ$) is measured where the water enters the jacket and where it leaves. A mixing chamber is provided at the exit to insure uniform temperature. Temperature within the cell is measured at three locations. Thermistors are located immediately above the cathode, near the top of the electrolyte, and 2 cm below the top thermistor. A diagram showing the general positioning of the thermistors is shown in Fig. 2. Water flow to the cooling jacket is controlled by two valves shown in Fig. 3. Two operating conditions are used.

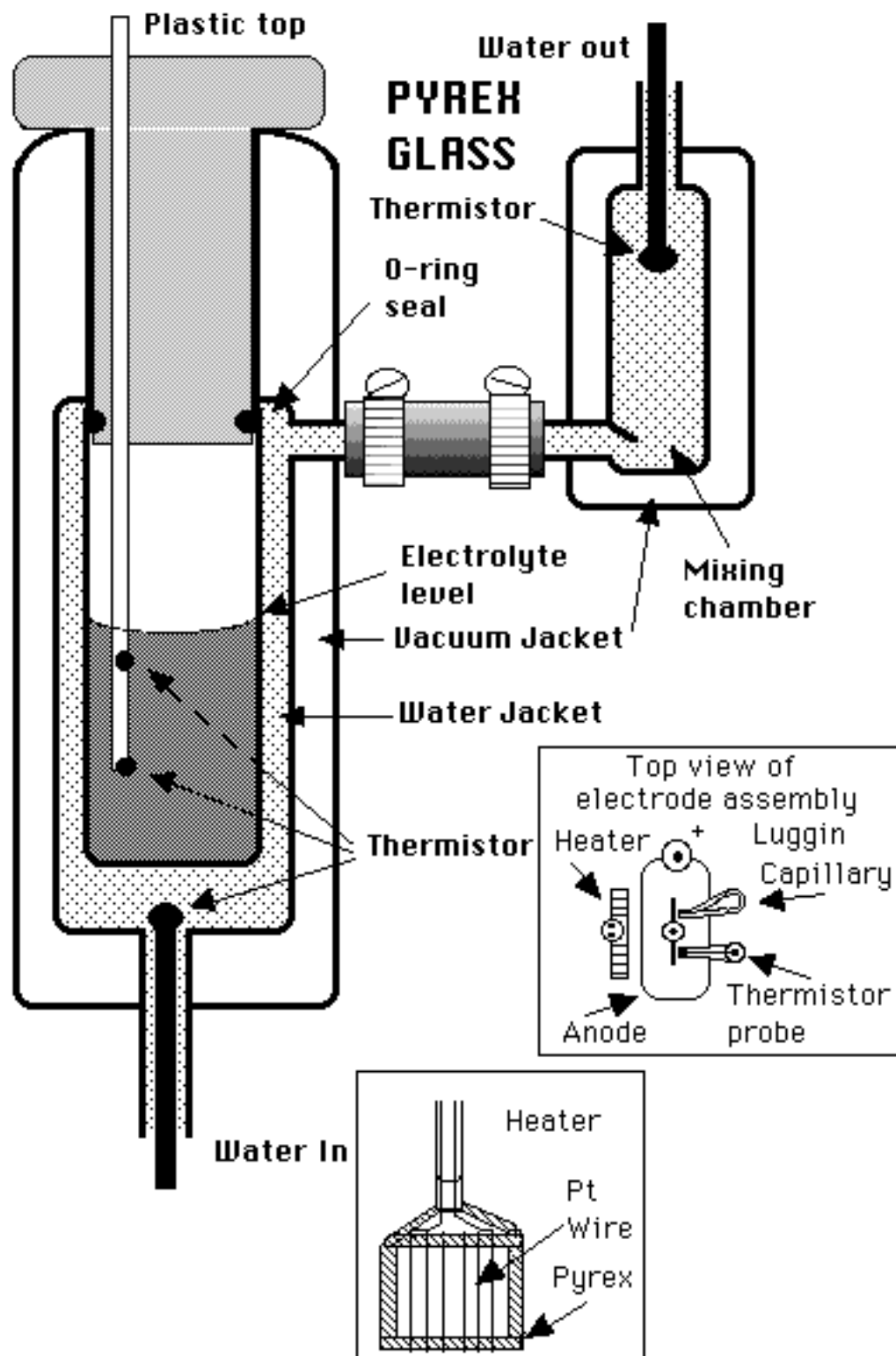


FIGURE 2. Cross-section of the calorimeter.

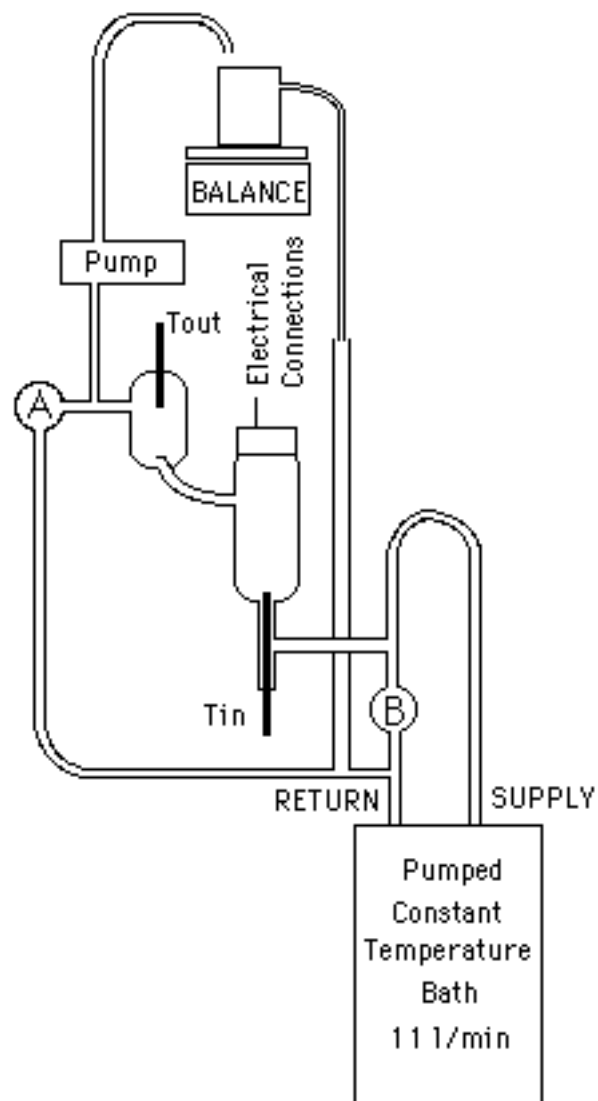


FIGURE 3. Plumbing diagram for cooling water flow path.

1. Thermistor calibration is done with valve A open and valve B closed. This allows cooling water to flow through the jacket at a maximum rate, thereby insuring uniform temperature.
2. Calorimetric measurements are made with valve B open, valve A closed, and the constant-flow pump turned on. This arrangement allows a small fraction of the constant-temperature water flowing through valve B to enter the calorimeter. The rate of flow is measured by filling a container, which is weighed by a balance. Upon filling, the container empties back into the constant temperature bath.

An exposed platinum-wire heater is located within the cell to allow Joule heat to be introduced at any time. This wire is also used as one of the reference electrodes when measuring the OCV, as explained in a later section.

The entire assembly is surrounded by an insulated box, which is maintained at constant temperature of 20° C ($\pm 0.02^\circ$). This temperature is referred to as "room temperature" in the text.

All temperatures are measured using linear thermistors (OMEGA 44202). These are calibrated against a mercury thermometer at $20 \pm 0.1^\circ\text{C}$, traceable to FIST, for absolute measurements. Relative calibration of the thermistors is obtained as follows: The temperature of the water flowing through the jacket and the temperature of the surrounding box are both made equal to $20 \pm 0.1^\circ\text{C}$. Under these conditions, the temperature at all thermistors is assumed to have the same value. The calibration equation of each thermistor is adjusted to reflect this assumption and the temperature coefficient supplied by the manufacturer is used to extrapolate the equations to other temperatures. A temperature increase or decrease of 10° from 20° will introduce an error of -0.05° , based on the coefficients supplied with the thermistors.

The cell voltage (± 0.001 V) is measured at the point where the current enters the cell and current (± 0.005 A) is measured using a known resistor (0.2 ohm). Both values are calibrated using a precision digital multimeter ($\pm 0.05\%$). The power supply is under computer control. Reported voltages are based on an average of 10,000 points and the resulting values are stored automatically using Labview.

III. CALIBRATION METHOD

Heat Transfer to Surroundings:

Calorimeters can not be completely thermally isolated from their environment. Therefore, not only must the temperature of the environment be constant, but this heat leak should be small and well known. The first problem is to determine the heat leak rate. Heat has two paths for exchanging between the cell and the room. It can pass through the plastic lid and/or it can pass through the vacuum jacket as radiation and gas conduction. It is necessary to determine which of these paths dominates in order that appropriate corrections can be made.

Electrolytic power was applied to the cell using a platinum cathode. The difference between the applied power and the power based on the temperature increase of water flowing through the jacket was determined. When this quantity is negative, the assembly is gaining energy, while a positive value indicates loss of energy. This value was compared to the difference between the room and the average jacket temperature in Fig. 4. As can be seen, the correlation between heat loss or gain, and the temperature difference between the jacket and the surroundings is found to be poor. In other words, heat flow does not change sign when the jacket and the surrounding are at the same temperature, a requirement if heat loss from the jacket through the vacuum space dominates. On the other hand, when a similar comparison is made using the difference between the electrolyte temperature and the surroundings, the correlation is excellent as shown in Fig. 5. Apparently, the heat leak between the electrolyte and the surrounding temperature is mainly through the plastic lid and amounts to $0.13 \text{ W/ } T$, where T is the difference between the environment and the average electrolyte temperature. This heat leak can also be determined by changing the temperature of the environment while

keeping the jacket temperature constant with no electrical energy applied to the cell. This approach gives $0.11 \text{ W/ } T$.

Calibration of the Flow-type Calorimeter:

Fluid passing through the jacket surrounding the cell picks up energy, thereby causing an increase in temperature. The flow rate times the temperature change times the heat capacity gives the rate of energy production within the cell. This method will be called the absolute method in the following discussion. When the absolute method is used, the heat loss correction, as determined above, would have to be applied. On the other hand, when the calorimeter is calibrated by applying known amounts of power, as shown in Fig. 6, this heat transfer effect is automatically taken into account. However, such an

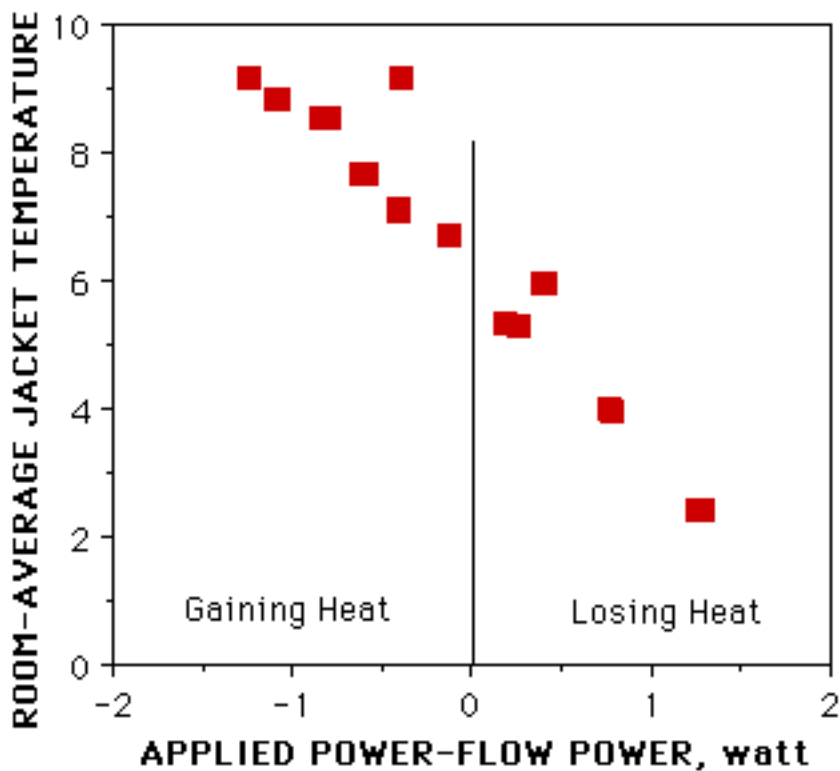


FIGURE 4. Effect of heat transfer between the jacket and "room temperature".

approach is accurate only when the environmental temperature is constant.. For this instrument, the environment is held to $\pm 0.02^\circ$. All errors combine to give a standard deviation of ± 0.05 watts based on many calibrations and studies of inert cathodes. Random variations and drift both fall well within this uncertainty.

Calibration can be done either by using power applied between the cathode and anode (electrolytic power) or by passing a current through platinum wire immersed in the electrolyte (Joule power). Good agreement is seen in Fig. 6 when power is applied using either method or in combination. Nevertheless, all measurements made during subsequent

studies of palladium are based only on a calibration using electrolytic heating. Joule heating is used only to determine whether any drift in calibration has occurred and to change the temperature of the cell independent of applied current.

Because an internal recombiner is used, all chemical energy is retained by the cell. However, if this recombiner should fail, the measured power could be in error by the amount of chemical energy leaving the cell. To determine whether this error is present, an external recombiner is placed in the gas line where its temperature can be measured, as seen in Fig. 1. Thus, any D_2 and O_2 that fail to recombine within the cell will do so in the external recombiner where this process can be recorded as a temperature increase. To calibrate the effectiveness of this system, the cell was electrolyzed after the internal recombiner was removed. As can be seen in Fig. 7, as little as 1 mW of chemical power

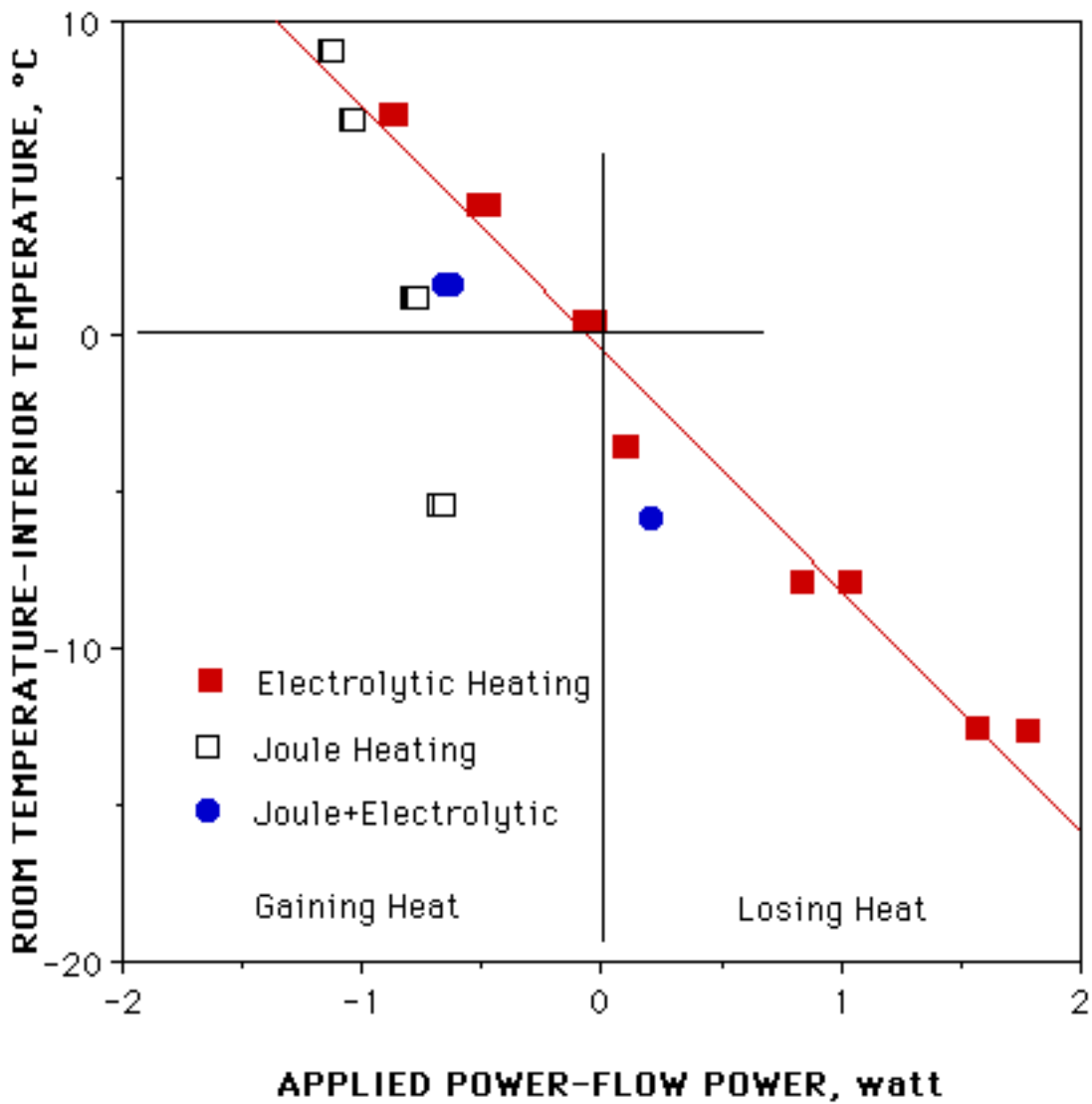


FIGURE 5. Effect of heat transfer between the cell electrolyte and the surroundings.

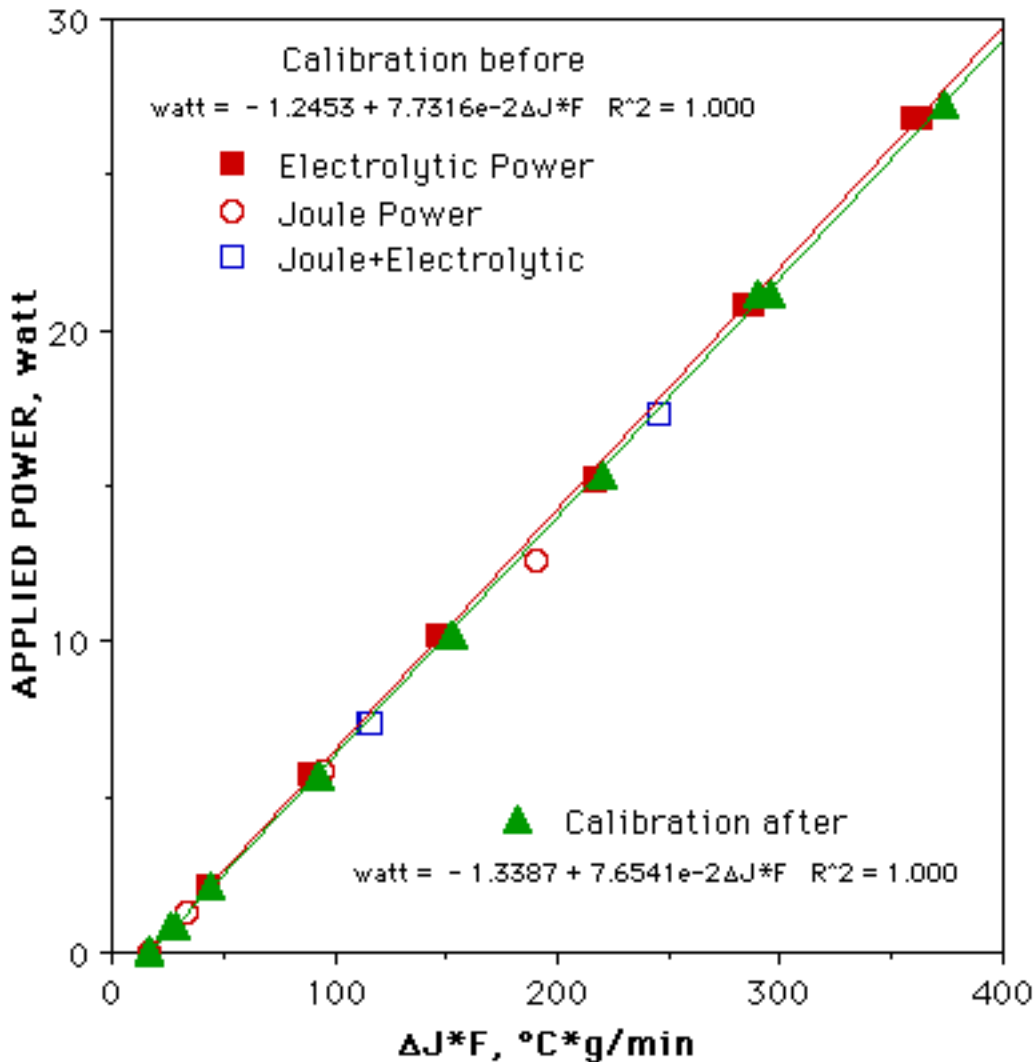


FIGURE 6. Calibration equation based on flow through jacket.

lost from the cell can be detected. In addition, if the both recombiners should fail, the loss of oil from the reservoir will be much greater than that produced by changes in the D/Pd ratio, hence easily observed.

Calibration of the Iso-peribolic-type Calorimeter:

Heat flow out of the electrolyte can also be determined by measuring the average temperature across the glass container. This method relies on knowing the true average temperatures of the cell wall at the inside and outside surfaces as well as the average thermal conductivity of the wall. These requirements can create large uncertainties as is described below.

Calibration is done by applying known power either as electrolytic current or as Joule heat, as described above. The resulting interior temperature is determined by averaging the temperature at the top and at the bottom of the cell. The average outer temperature is

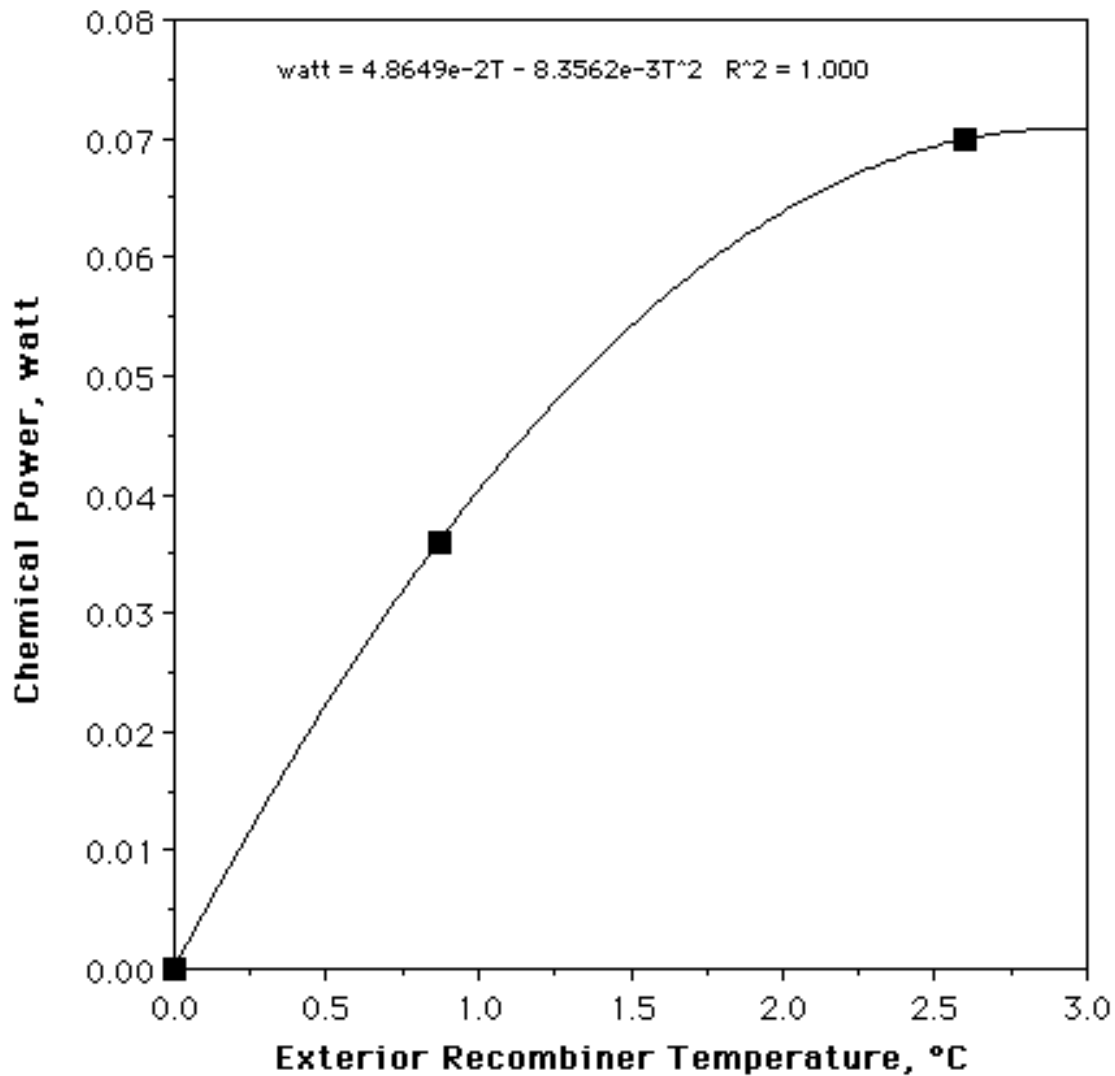


FIGURE 7. Effect of generated D₂+ O₂ gases on the temperature of the external recombiner.

determined by averaging the temperature of the water entering the jacket and that leaving. These temperatures are assumed to represent average conditions at the cell walls. The resulting calibration points are shown in Fig. 8 as applied power vs average T across the cell wall. A significant difference is seen in this case between the electrolytic and Joule methods. This difference is caused by different temperature gradients being present in the cell. The effect of this gradient is eliminated when some electrolytic power is applied along with Joule power. The magnitude of the temperature gradient between the top and bottom of the cell can be seen in Fig. 9 as applied power is increased. The absence of bubbles during Joule heating allows significant gradients to form. However, when some electrolysis is applied along with Joule heating, the gradient is greatly reduced as electrolytic current is increased, as seen in Fig. 10. The gradient also changes with time. Figure 11 shows the temperature difference between the top and the bottom of the electrolyte, and the difference between the top and the cathode position. These

changes demonstrates that convection currents are not stable even during electrolysis. Even a brief application of increased electrolytic power can shift the convection currents into a different pattern, thereby causing a change in temperature gradient. While these effects are small, they are real and need to be considered.

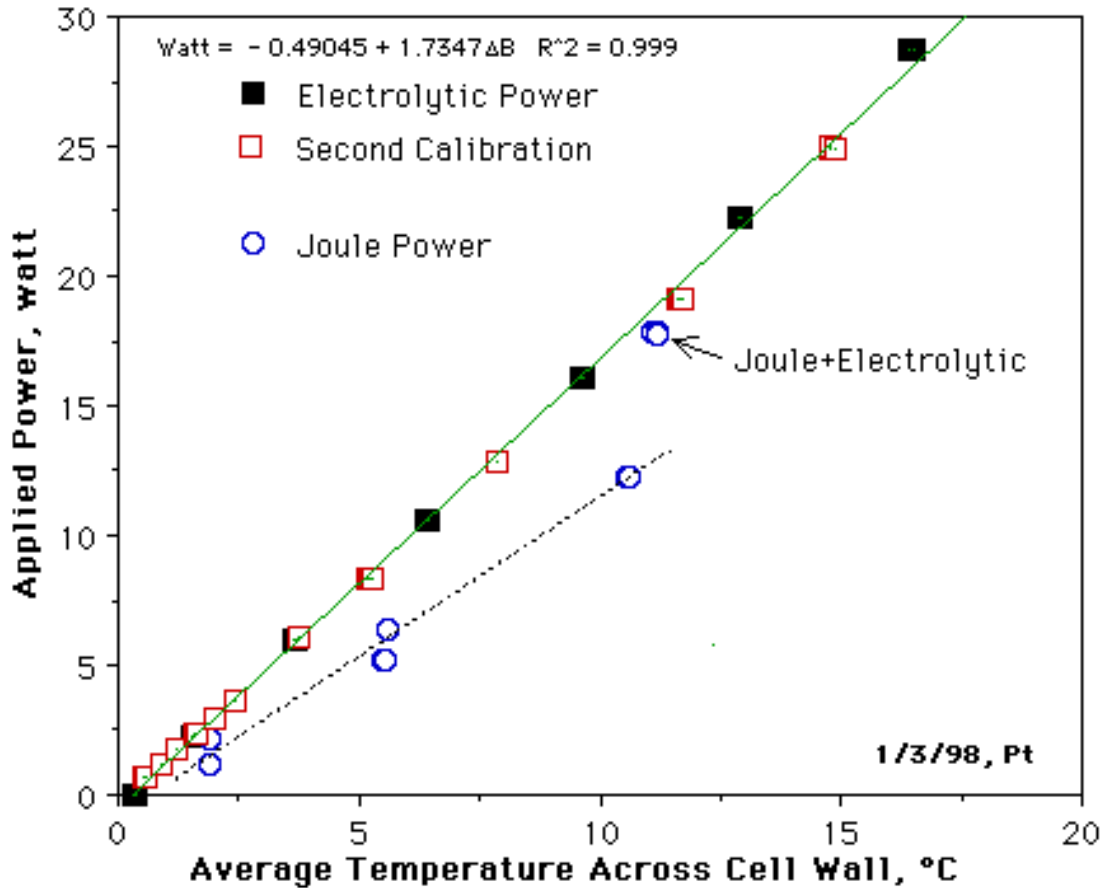


FIGURE 8. Isoperibolic calibration.

This time effect is thought to be caused by the following factors: Early in the electrolytic process, bubbles are small and numerous, while later they become fewer and bigger. This change is proposed to produce changes in the stirring patterns, hence changes in the gradient. This change also changes the calibration constant, hence the apparent presence of anomalous energy. In addition, changes in the position of the cathodes, as might occur when changing samples, also has a marked effect on this gradient. Production of anomalous energy at the cathode will also change the patterns, thereby adding an uncertainty to the magnitude of the extra energy.

Part of the difference between the isoperibolic calibration constant based on electrolysis and that based on Joule heating can be attributed to reduction of temperature gradient by bubble action. However, this is not the only factor. A stagnate layer of fluid exists at the cell wall and this layer has a variable thermal conductivity depending on the amount of

fluid convection. This variable was explored using a similar cell that could be stirred by rotating a magnetic bar with known rotational speed. The slope of applied power vs temperature difference across the cell wall was determined at various rotational speeds. The resulting values for the thermal conductivity of the cell wall are plotted in Fig. 12 as a function of rotational speed. This increase takes place even when the temperature gradient within the cell becomes very small as can be seen in Fig. 13. Clearly, the effect

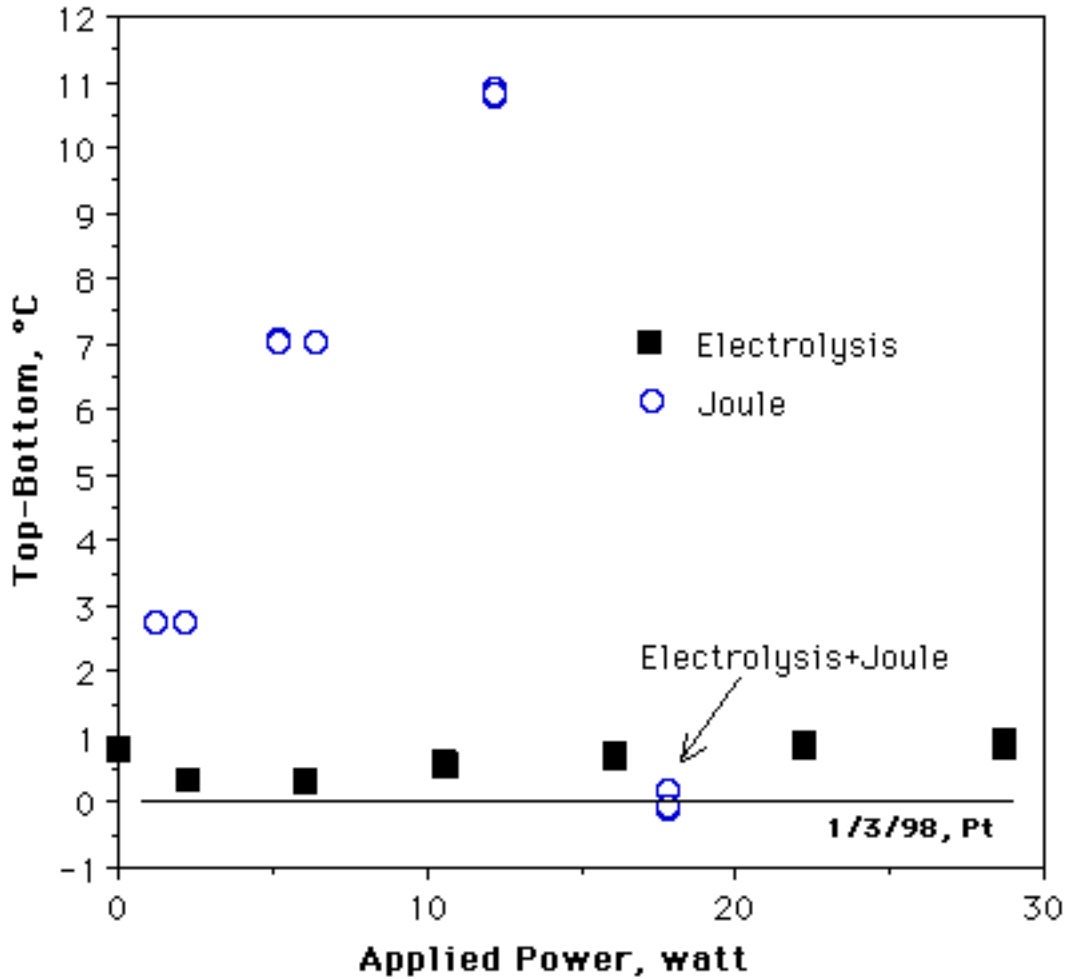


FIGURE 9. Gradient between the top and bottom of the electrolyte as a function of applied power.

is not influenced by gross temperature gradients within the cell. However, at low stirring rates or when only a small number of bubbles are being produced in the absence of mechanical stirring, the combined effect of gradient and stagnate layer can have a dramatic effect on the calibration constant. Even when high currents are applied or mechanical stirring is used, unpredictable behavior will be observed. In addition, growth of films on the glass surfaces caused by bacteria action or impurity deposition can further change the effective thermal conductivity during long duration studies.

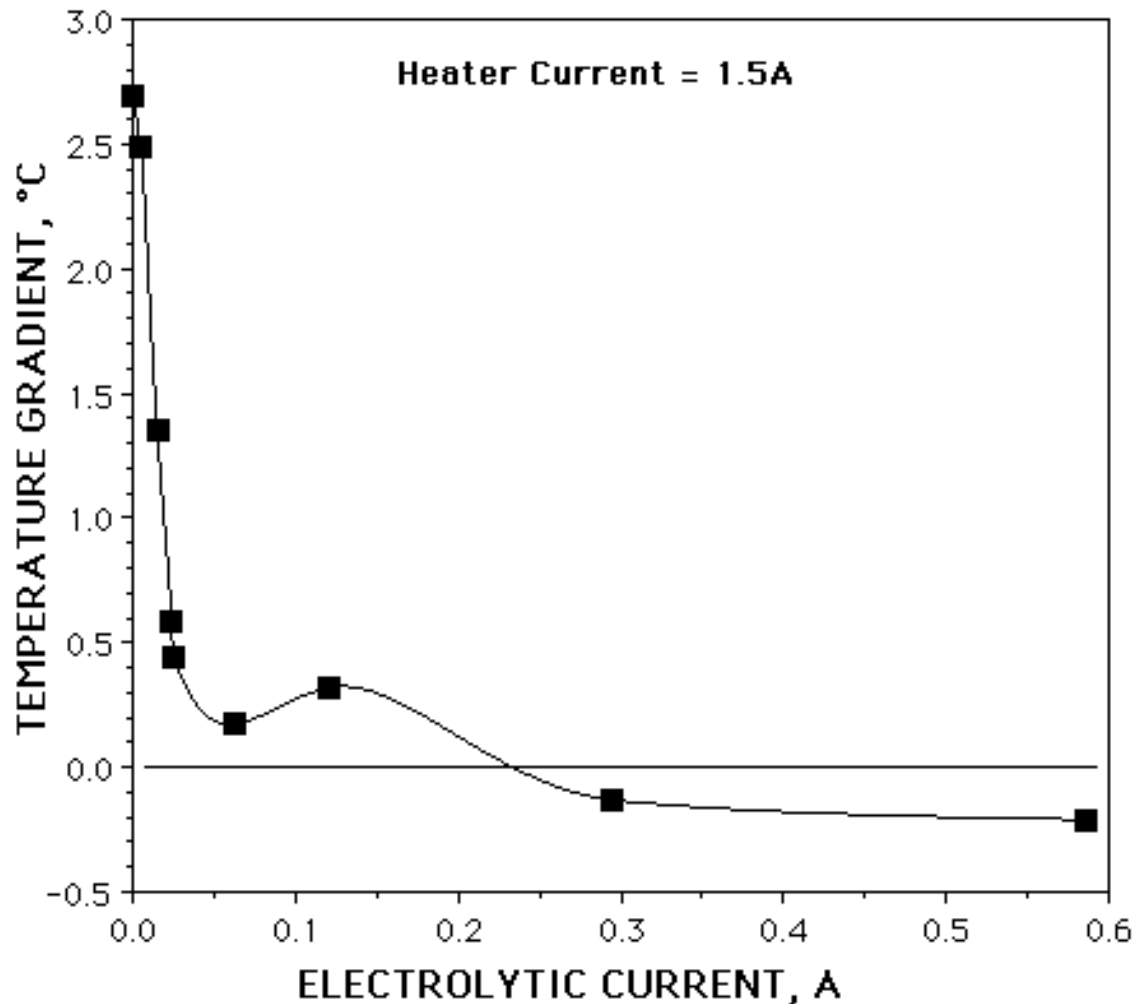


FIGURE 10. Reduction in gradient as electrolysis current is increased at a fixed heater current.

The total uncertainty in this method of heat detection is ± 0.5 W using the design described in this paper. Most of the uncertainty is caused by drift in the calibration constant caused by changes in bubble pattern and changes in the effective thermal conductivity of the glass wall. However, the short-term random error is much less, being about ± 0.05 W.

Mechanically stirred cells used previously by the author show a much smaller total uncertainty. Use of the double-wall isoperibolic method would eliminate these problems completely.

IV. OPEN-CIRCUIT-VOLTAGE

The voltage measured between the cathode and a reference electrode is proportional to the log of the chemical activity of hydrogen at the cathode surface. It also provides a way to determine the effective pressure of D_2 gas within voids, as shown in Fig 14.

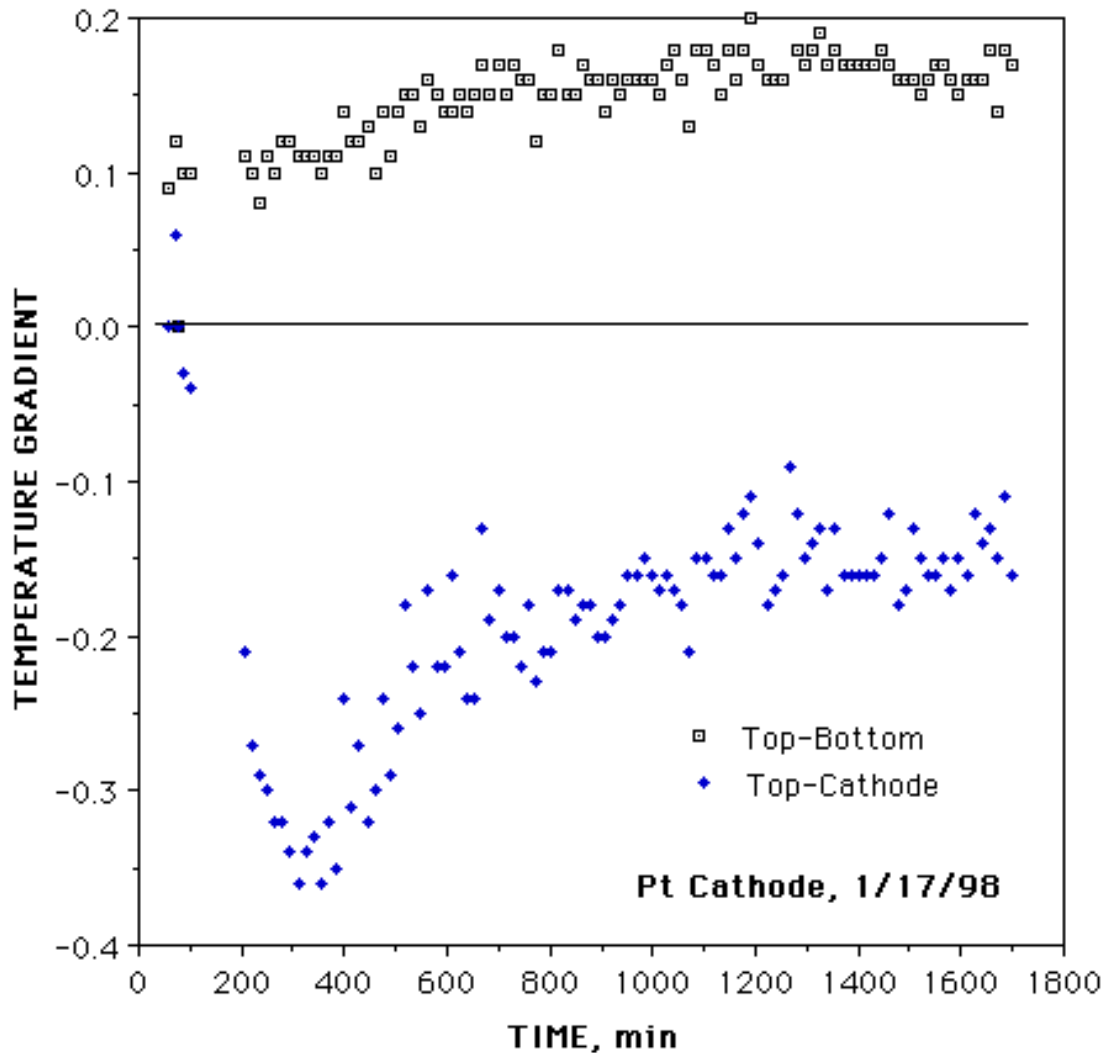


FIGURE 11. Temperature difference between the top and bottom thermistors, and the difference between the top and cathode thermistors.

This voltage can be determined when the current is briefly stopped and is called open-circuit-voltage (OCV). The voltage is called the overvoltage (OV) when it is measured while current is flowing. The latter situation is complex because the voltage is influenced by the IR effect produced in the electrolyte by the flowing current and by the voltage drop across any barrier at the cathode surface. Both voltages are measured using two methods. The value called "in" (Fig. 15) is obtained using an external platinum electrode which samples the voltage at a small spot on the cathode through a Luggin capillary placed within 1 mm of the surface. The value called "out" is obtained using a platinum wire (heater wire) immersed in the electrolyte outside of the cathode-anode structure. The latter method gives an average value for the entire cathode surface. Both reference electrodes are calibrated by comparing them to a clean platinum cathode. Figure 15 shows the change in OCV for a platinum cathode after being electrolyzed at 2 A. Once the applied current is turned off, the OCV voltage drops quickly as deuterium is lost from the metal surface. The "out" electrode shows the expected zero voltage after all deuterium

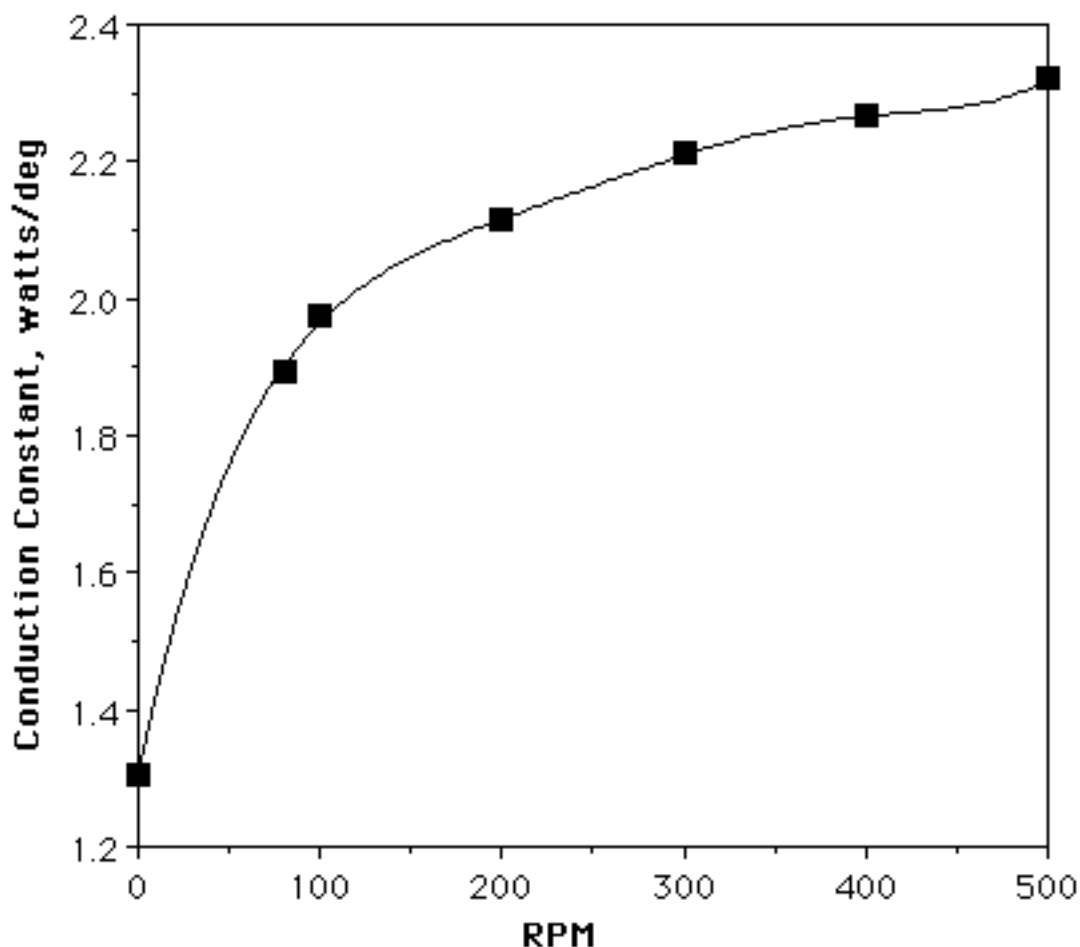


FIGURE 12. Thermal conduction of cell wall as a function of stirring speed.

is lost. However, the "in" electrode appears to have a -0.04 V bias that is evident both at the beginning and ending of the study. This bias is caused by small drifts in the reference electrode potential for which a correction needs to be applied if absolute values are required. However, useful information can be obtained using only relative values. This approach is in contrast to using a reference electrode held at a fixed hydrogen pressure of 1 atm, called a SHE (Standard Hydrogen Electrode), which can give absolute values for the voltage. However, the latter method is too complex to be useful in this application.

Deloading of palladium has a much different behavior. A thin coating of Pd on silver produces the behavior during deloading shown in Figure 16. A very rapid drop is seen until the composition of the surface enters the β region after which the OCV becomes relatively constant. Another rapid drop is seen after the β -phase has been completely converted to α -PdD. A reverse of this behavior is seen during loading. In addition, once the sample is mostly fully loaded, the OCV slowly rises as electrolysis is continued, as can be seen in Fig. 17. A similar deloading behavior is seen in Fig. 18, which shows the behavior of $4.8 \mu\text{m}$ Pd on Pt. In this case, the OCV drops very rapidly at first then shows

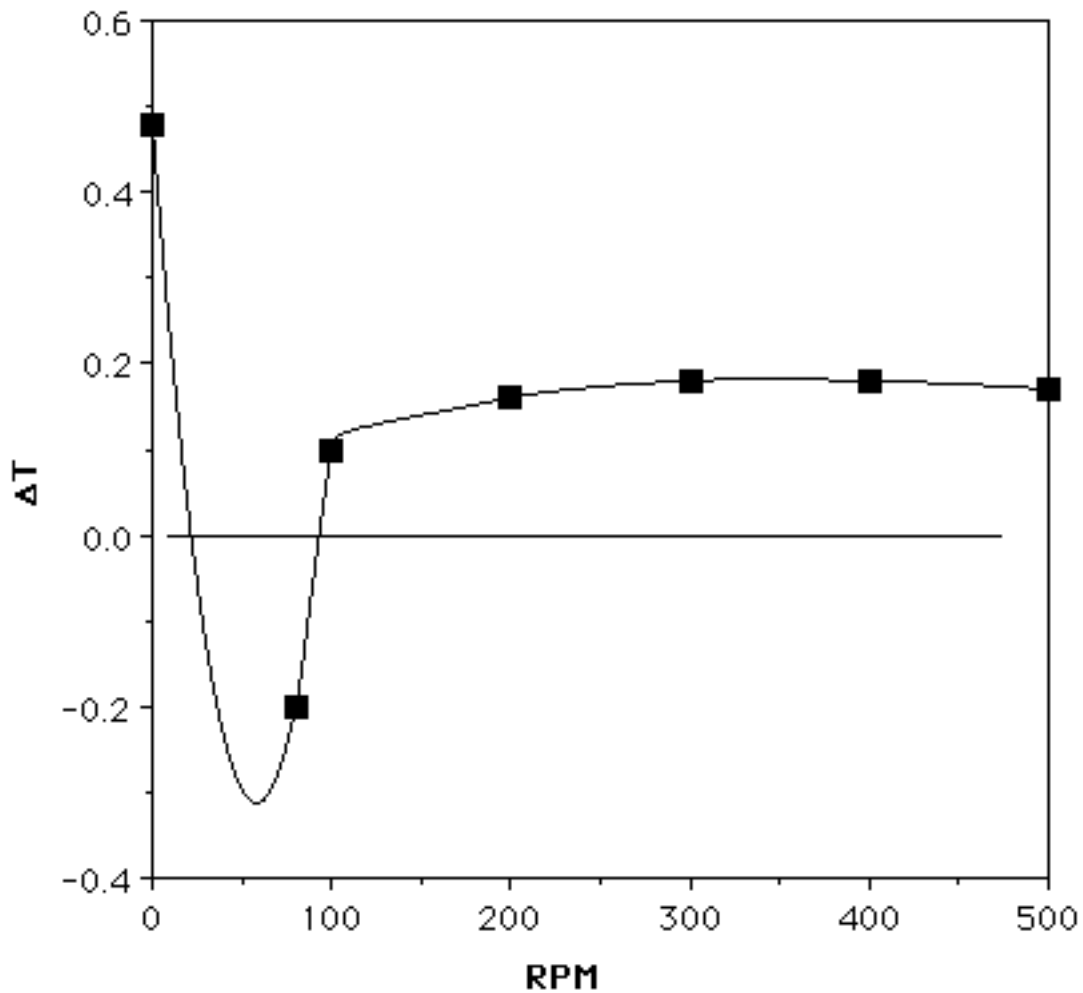


FIGURE 13. Temperature gradient between the top and bottom of the cell as a function of stirring speed.

a plateau for a brief time. Further deuterium loss causes a slow drop toward a value expected for the $-$ mixture. The time during which the surface is a two-phase mixture during deloading is proportional to the amount of Pd present. Presence of a second plateau above the $+$ region is characteristic of samples which produced excess energy, as was the case for this sample. Consequently, the shape of such curves gives important insight into the nature of the palladium surface and the eventual production of excess energy.

Because of the very rapid loss of deuterium from thin films, provisions are made to keep the delay time in measuring the OCV after current is turned off to between 0.1 and 0.5 sec. Nevertheless, significant deloading can occur during this time when the layer is very thin. In addition, regular measurements are made of the overvoltage, i.e. the voltage generated while current is flowing. Figure 19 shows a typical behavior of a fully loaded sample. The OV moves in concert with the OCV, but not always by the same amount.

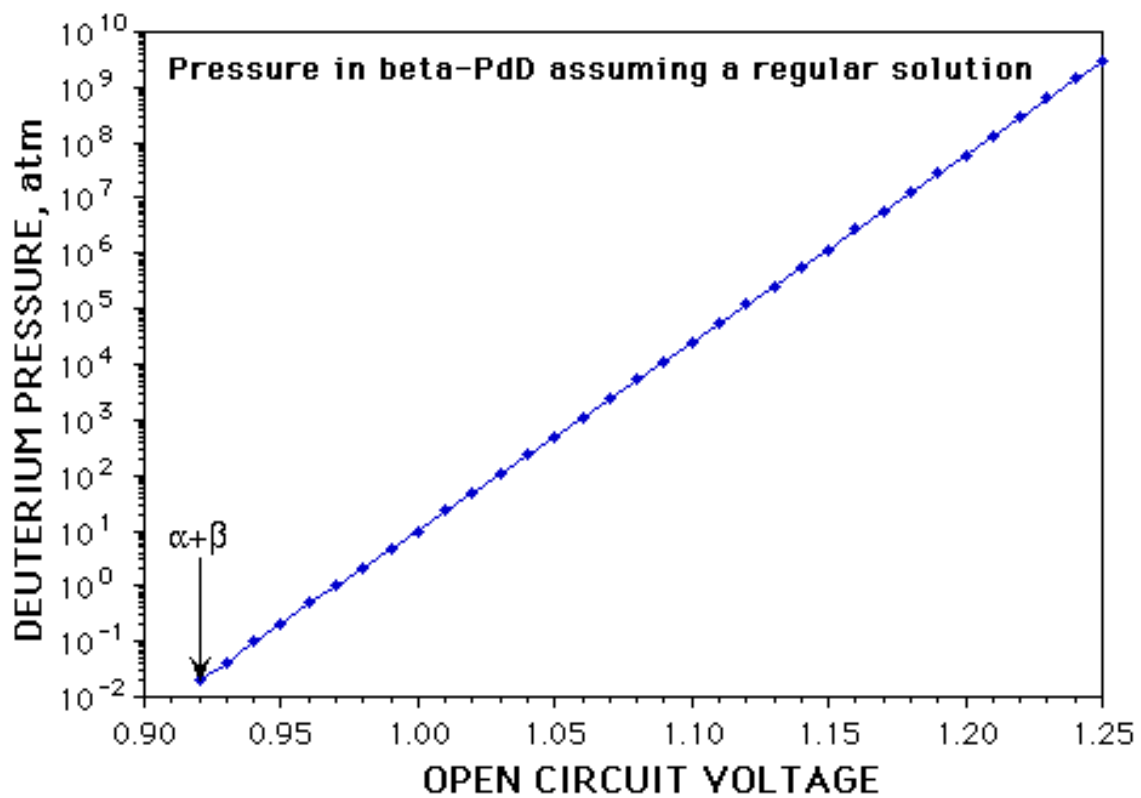


FIGURE 14. The OCV is measured relative to platinum exposed to the same electrolyte as the cathode. The effective pressure is calculated using the published thermodynamic properties of β -PdD and the Nernst equation.

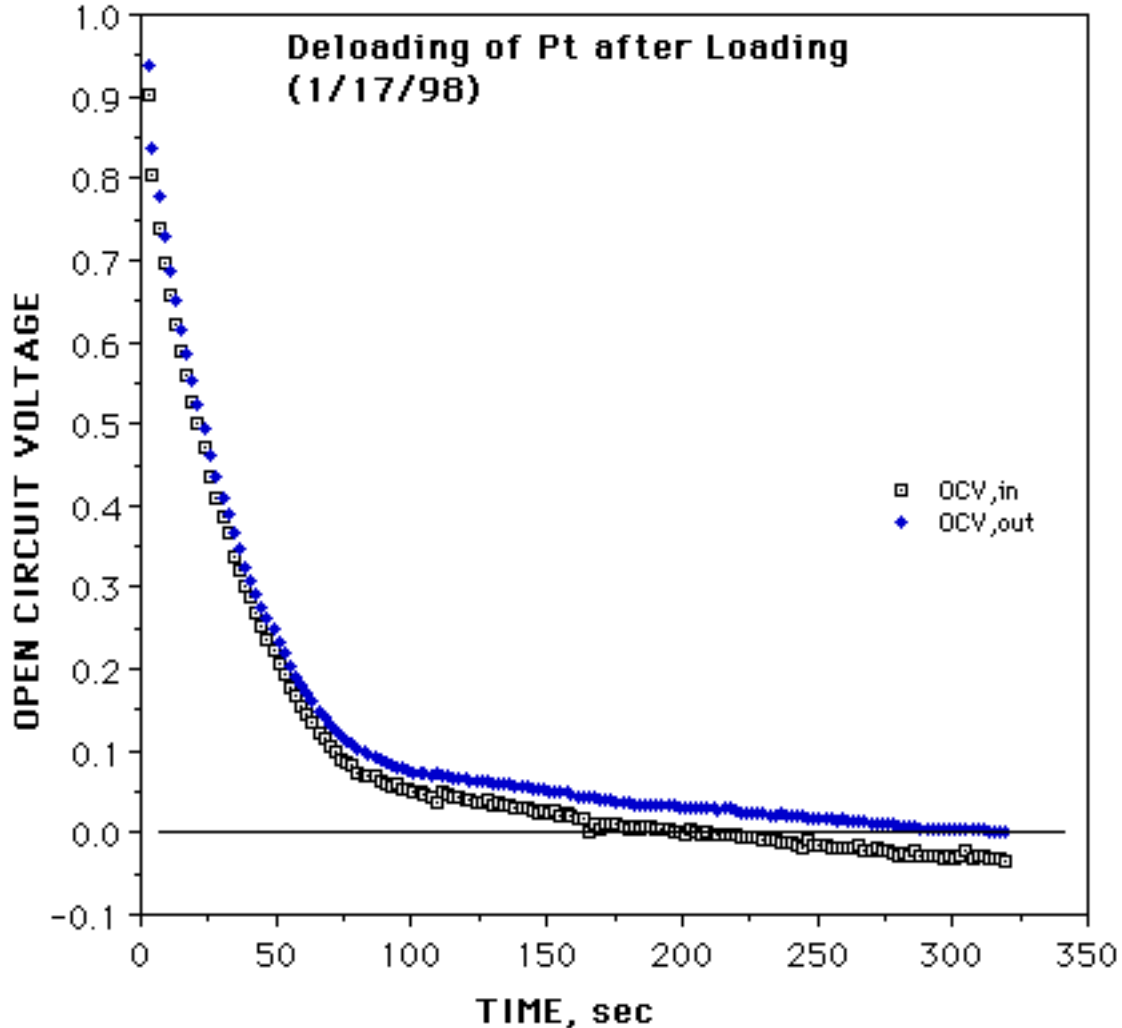


FIGURE 15. Open-Circuit-Voltage (OCV) of Pt as a function of time after a current of 2.0 A is interrupted.

CONCLUSIONS

1. Temperature gradients within the electrolyte are reduced by bubble stirring. The remaining gradient is variable, hence can change with time and with the position of the cathode with respect to the temperature sensors. However, a "normal" isoperibolic calorimeter will show a much smaller effect than detected in this study. Consequently, this error is not significant when evaluating such studies.

2. An unstirred, isoperibolic calorimeter can not be calibrated using an internal heater but must be calibrated using heat generated by electrolysis. Many workers use heater calibration while electrolytic current is flowing. This method greatly reduces the potential error associated with heater calibration alone. However, use of sufficient electrolytic current to eliminate the gradients must be demonstrated.

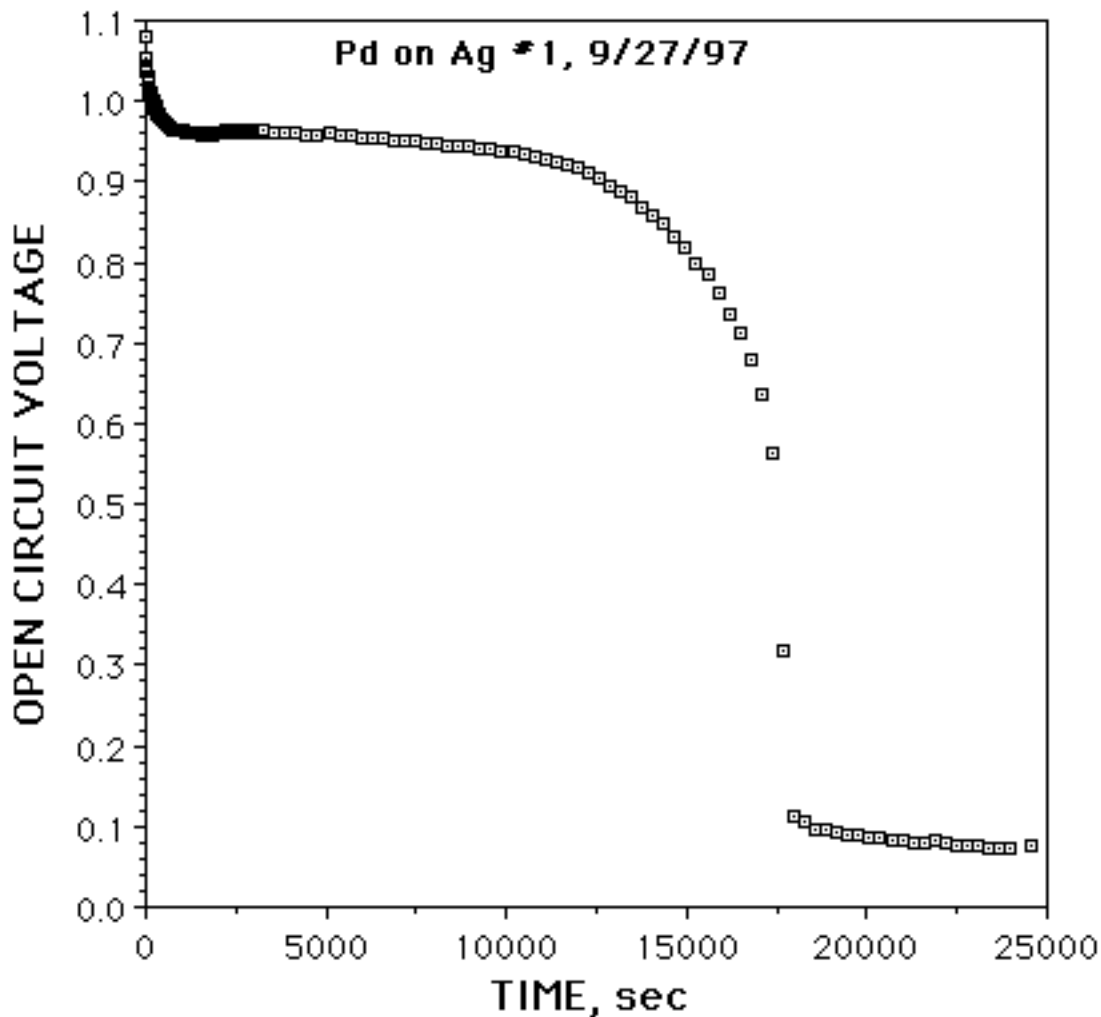


FIGURE 16. Open circuit voltage during deloading of Pd plated on silver.

3. A major source of error when using an isoperibolic calorimeter is caused by the stagnate layer of fluid on the cell wall. This layer changes the thermal conductivity of the cell wall in unpredictable ways, and is not removed by bubble mixing or by stirring. The layer is unstable with respect to time and is very sensitive to convection currents produced by bubbles. Cells using small currents are especially sensitive to errors produced by this effect. The isoperibolic method is also susceptible to significant drifting of the calibration constant caused by changes in stirring pattern. A single-wall isoperibolic calorimeter that loses most of its heat by radiation will not be affected by this problem.

4. The OCV is a sensitive method for investigating composition and phase changes at the cathode surface. However, the value can be lowered because of hydrogen loss during the measurement. In addition, this loss during such a measurement can prevent the surface from achieving the necessary high composition to achieve the CANR effect. Therefore, the technique needs to be used with caution.

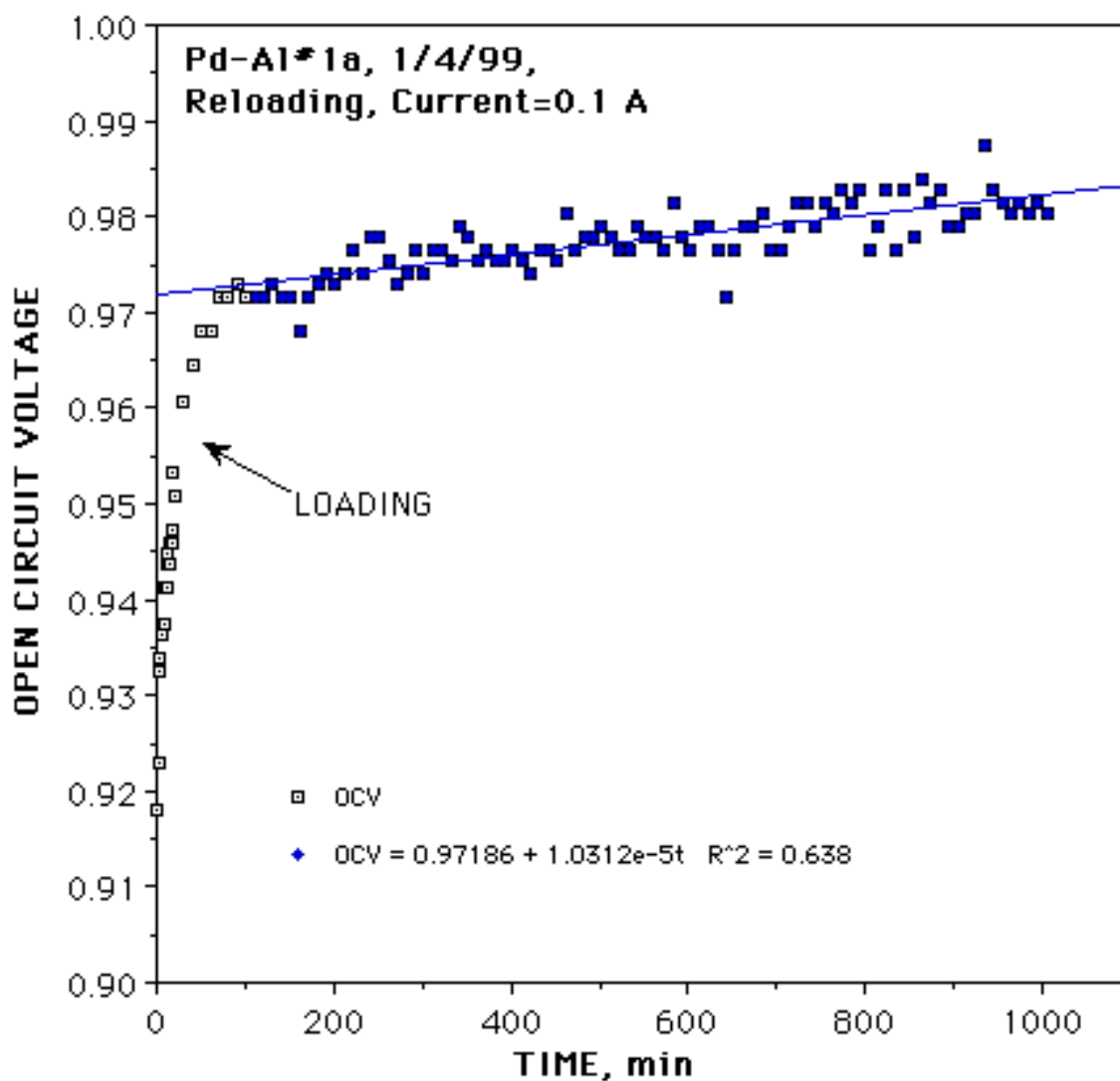


FIGURE 17. Behavior of the open circuit voltage during and after loading.

5. Although a flow-type calorimeter is not sensitive to temperature gradients within the cell, it does suffer from other errors that need to be revealed by appropriate calibration. For example, heat exchange through the lid can affect the results even though the rest of the cell is held at a constant temperature.

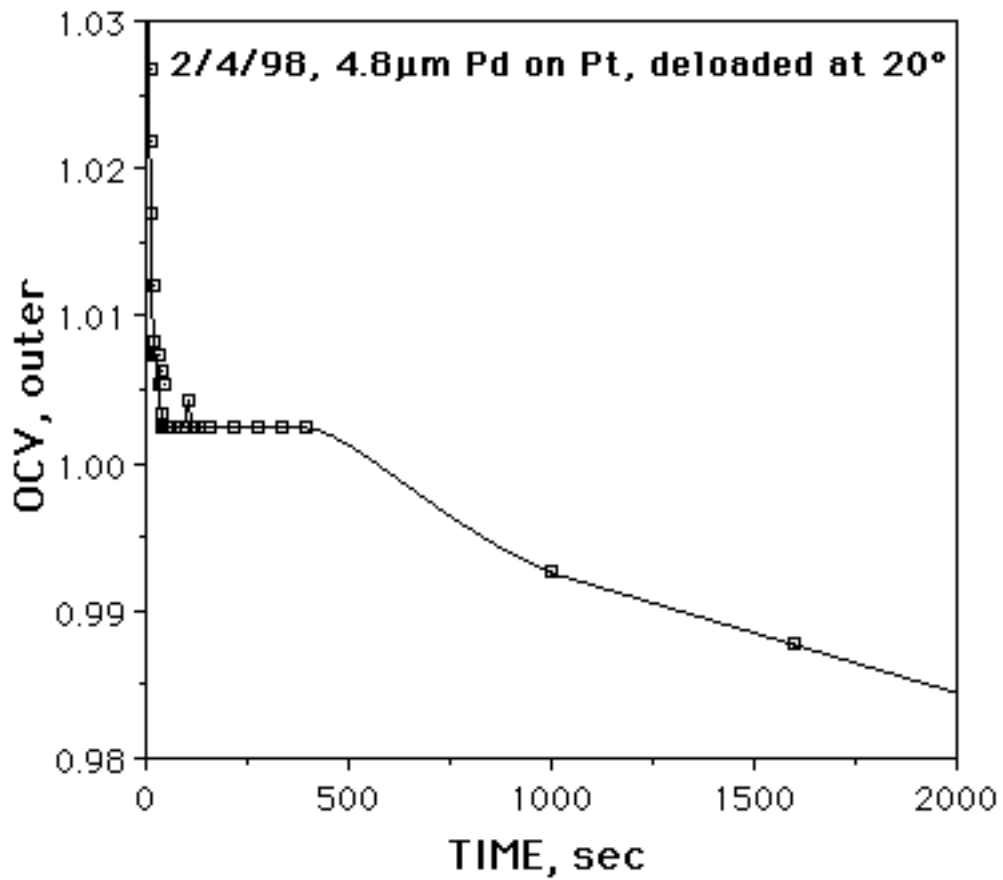


FIGURE 18. OCV as a function of time after current of 0.05A was stopped.

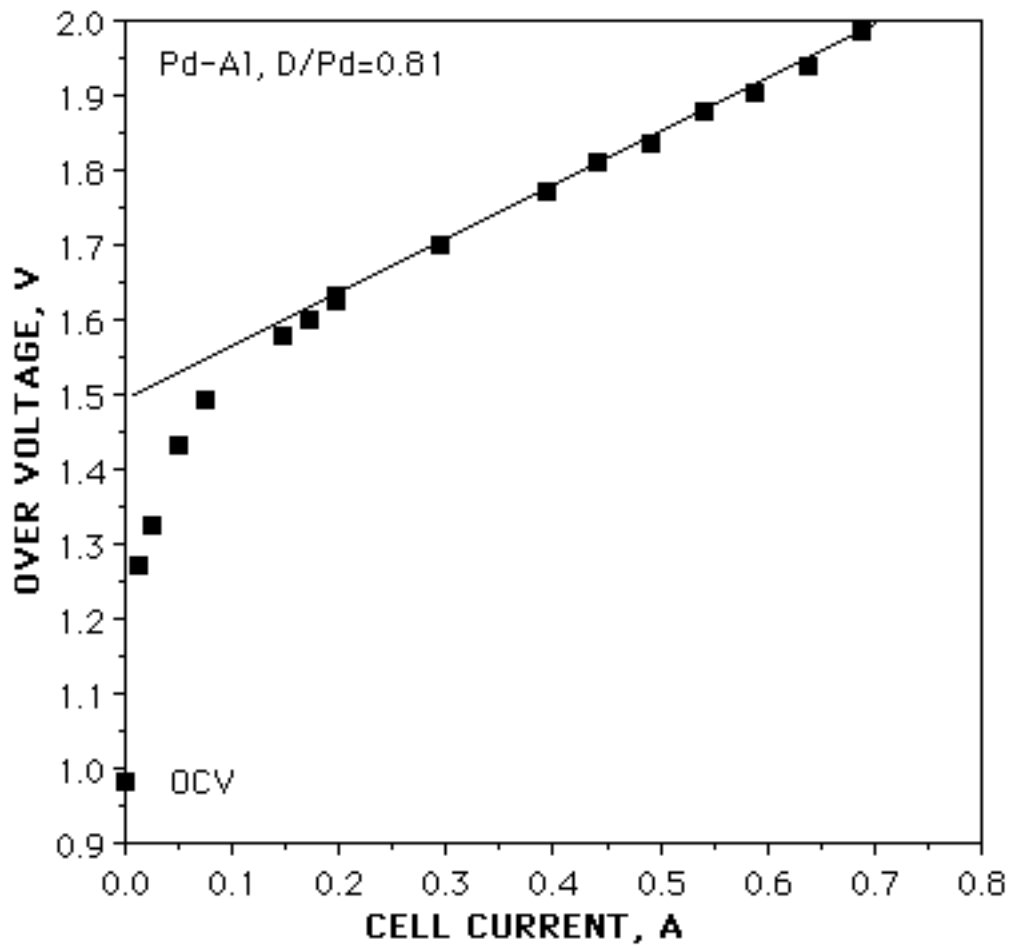


FIGURE 19. Typical behavior of the overvoltage as current is changed. The single value for open-circuit-voltage was obtained while the current was interrupted for 0.1 sec. Values are referenced to an external Pt electrode using a Luggin capillary. The line shows the effect of the voltage drop within the electrolyte produced by the flowing current.