DESCRIPTION OF A SENSITIVE SEEBECK CALORIMETER USED FOR COLD FUSION STUDIES

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A sensitive and stable Seebeck calorimeter is described and used to determine the heat of formation of PdD. This determination can be used to show that such calorimeters are sufficiently accurate to measure the LENR effect and give support to the claims.

Introduction

Heat production is an essential feature of the cold fusion effect and its measurement has been a frequent object of criticism[1]. Since 1989 when Profs. Fleischmann and Pons (F-P) [2] first revealed their observations, calorimetry has evolved from the simple isoperibolic design and become increasingly accurate[3] with use of the Seebeck type[4-7].

A Seebeck (Kelvin) calorimeter consists of thermal-electric converters that completely surround the source of heat. Temperature at the outside of these converters is held constant while temperature at the inside is allowed to increase. The average temperature difference generates a voltage that is used, after calibration, to determine the rate at which heat passes through the thermal barrier created by the converters. Because the design is very simple, operation is easy to understand and potential errors are easy to determine.

When used in a study of cold fusion, a gas-tight glass cell containing an electrolyte and electrodes is placed in the enclosure. Because the measured voltage represents an average of heat loss through all parts of the barrier, the device is only slightly sensitive to where the cell is placed within the enclosure. A fan is used to distribute heat more evenly and to reduce the cell temperature by removing heat from it more rapidly. The calorimeter is completely insensitive to where heat is being generated within the cell.

A calorimeter suitable for measuring the cold fusion effect must be sufficiently sensitive to detect a few tens of milliwatts superimposed on tens of watts. In addition, it must remain stable over long periods of time. The method of calibration must define the same characteristics as when heat is produced by an unknown source. Power production can be calibrated by generating heat using a resistor contained in the device. A dead cell or conditions expected to produce no anomalous energy can also be used. If the calorimeter is sufficiently sensitive, the total amount of energy given off by a known chemical reaction can also be measured. In this work, power is calibrated using a resistor in the cell or by using a Pt cathode and a quadratic equation, watt = $A + B*V + C*V^2$, shows the relationship between generated voltage (V) and applied watts (W). In addition, the calorimeter is used to measure the total amount of energy absorbed when a Pd cathode is loaded with D. Because this quantity is well known[8, 9], the method gives further demonstration that the calorimeter is indeed accurate and able to detect small amounts of energy.

Defining the accuracy of a calorimeter using a few numbers is not practical because several different and independent potential errors exist. Because of bubble action at high current, the amount of power being applied to a F-P cell is noisy. In addition, use of a fan adds additional noise, especially at low applied current as is the case during this study. This causes random fluctuations in measured power which are as much as ±10 mw during this study. If this fluctuation is too great, it can mask small changes in anomalous power, but it does not introduce an error that might be interpreted as anomalous power. On the other hand, the calibration constant or the sensitivity of the calorimeter can change with time. These changes can be produced by changes in reference temperature, in room temperature, in the amount of recombination taking place in the cell, or in physical parameters when new samples are placed in the cell. This potential drift is the main source of incorrect results. These potential errors are explored in this work.

Description

The device described here is made by gluing together commercially available thermoelectric converters, as shown in Fig. 1, using waterproof epoxy glue.
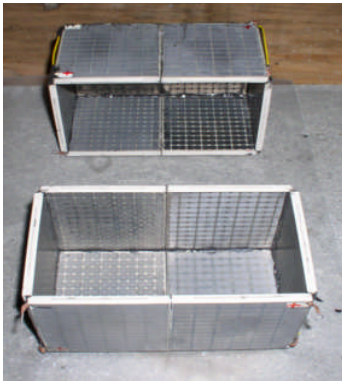

Figure 1. Glued panels assembled into two haves of a calorimeter. The length is 13.9 cm, the width is 6.9 cm and the total depth when assembled is 14.8 cm.

The panels are connected electrically in series. Once assembled, the outer surface is covered with an electrically insulating, waterproof epoxy paint. The electrical resistance of this coating must be tested and found to be high (>1 Mohm) before final assembly. If the resistance is too low, unwanted voltages will be generated by chemical reaction between the cooling water and the metal plates. These assemblies are placed within watertight plastic boxes that are designed to cause even water flow over the outside surface. When assembled, the two boxes are stacked one on top the other as shown in Fig. 2. Figure 3 shows a typical open calorimeter containing an electrolytic cell and
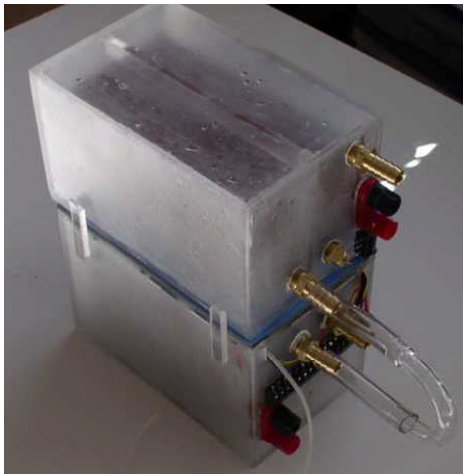

Figure 2. Assembled calorimeter with water cooling jacket in place. In this design, the wires pass out of the cell through plastic water cooled channels.

a small fan. Baffles are provided to insure air is passed over and around the cell.

Wires and plastic tubes are passed into the cell through channels that are in good thermal contact with the cooling water. In one design, these channels, visible in Fig. 3, are stainless steel tubes, which pass the length of the device within the cooling water. These wires carry current to the cell and fan and allow applied voltage to be measured at the calorimeter boundary. Circuits are arranged so that current and voltage used for calibration and for electrolysis are measured using the same resistor and

DA channels. In this way, any measurement errors caused by errors in the DA channels are cancelled. Measurements are made using National Instruments data acquisition boards and Labview.
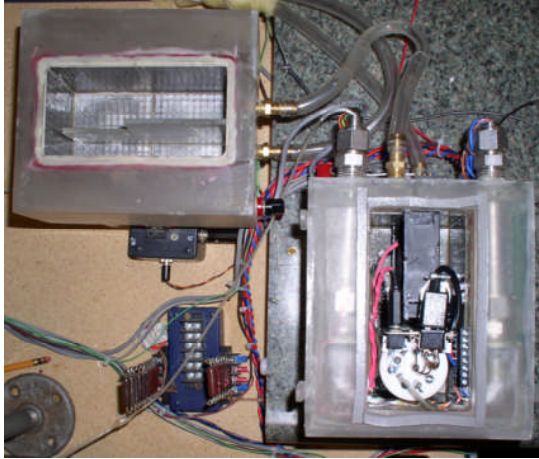

Figure 3. Completed calorimeter with cell and fan in place. Notice that the wires pass into the calorimeter through metal tubing so as to isolate the interior from changes in room temperature. The cell is attached to the calorimeter using plugs to allow easy removal. The stack of resistors at lower left are used to measure current through the cell and fan.

Switching from electrolysis to calibration can be accomplished by throwing one hardware and one software switch, which allows automatic calibration over the entire power range. A typical result is shown in Fig. 4. Table 1 lists calibration equations obtained over five months of examination. Experience and analysis of this information indicate that the uncertainty immediately after calibration is about ±16 mW, while drift caused by changes in room temperature and other factors can introduce an additional uncertainty of ±25 mW during long runs. If the average coefficients are assumed to be constant during the time shown in the table, the maximum uncertainty at 8.3 W of total power would be ± 60 mW. In other words, the calorimeter is stable to within ±60 mW or 0.7% over 5 months if no effort is made to recalibrate. Because calibration is so easy, these small drifts can be easily identified as error. At no time has anomalous power outside of this uncertainty suddenly appeared without being related to something done on purpose to the surface of the cathode. Notice also, that calibration values based on Joule heating of a resistor located in the cell agree very well with values obtained by using a platinum cathode. This shows that the location of heat production within the cell has no effect on measured values.
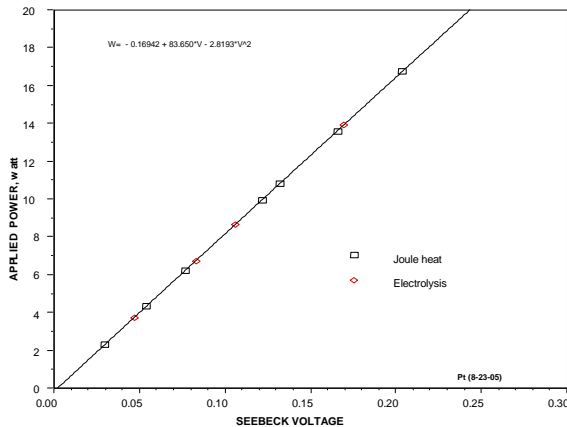

Figure 4. Typical calibration using an internal resistor. Four points are taken going up in power and four are taken going down, in sequence. The random error is the standard deviation of points from the drawn line. Data are taken after a delay of 90 min to allow the calorimeter to reach steady-state.

Because the cell contains a recombiner, no gas (except orphaned oxygen) is expected to leave the cell. To determine if the recombiner is working and to measure the D/Pd ratio using the orphaned oxygen method, a small

plastic tube carries gas from the cell to a reservoir of oil. Any change in gas pressure within the cell is detected as a weight change of oil applied to a balance (±0.01g), as is visible in Fig. 5. This method allows the amount of orphaned oxygen resulting from D entering the Pd cathode to be determined and, from this, the D/Pd ratio. The method is calibrated by weighing the sample (±0.00005g) at the end of the study to determine the amount of contained deuterium. Because D_2 is lost from the sample once electrolysis stops, weight is measured as a function of time starting when current is stopped. The weight is plotted as a function of square root of time through which a least squares straight line is drawn, as shown in Fig. 6, which is extrapolated to zero time. A constant of 7600 g oil/mol contained D is typical when the measured contained deuterium is combined with the measured displaced oil.

TABLE 1

DATE	Coefficients in calibration equation			error, mW
	A	B	C	
2/14/05	-0.020	83.02	0.12833	7
2/17/05	0.006	82.85	2.012	17
2/21/05	0.001	83.04	0.366	17
2/26/05	0.001	83.35	-1.220	11
3/10/05	-0.051	83.18	0.325	24
3/15/05	-0.022	83.86	-1.927	10
3/21/05	0.002	83.30	-0.764	16
3/24/05	-0.027	83.76	-1.737	28
3/29/05	0.000	83.40	-1.556	19
4/29/05	-0.013	83.82	-1.998	16
5/7/05	-0.052	83.40	-1.516	24
5/19/05	-0.076	83.25	-1.258	10
5/22/05	-0.116	83.33	-0.841	5
5/26/05	-0.093	82.94	1.053	17
5/29/05	-0.065	83.04	0.587	16
6/1/05	-0.078	83.46	-2.371	13
7/2/05	-0.203	83.49	-1.940	15
average=	-0.047	83.323	-0.745	16

Figure 5. View of calorimeter and oil reservoir for measuring D/Pd ratio. The switch in the foreground allows change from electrolysis to calibration. Water is circulated using a pumped (1.5 l/min) constant temperature bath (±0.01° C).

When current is applied to a Pd cathode, the surrounding D_2O is

decomposed into D_2 at the cathode and O_2 at the anode, with D_2 and Pd reacting to produce β-PdD_x. This reaction is endothermic, as can be seen in Figure 7, because more energy is used to decompose D_2O
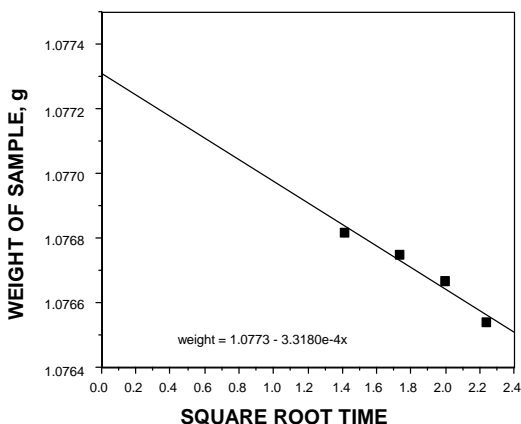

Figure 6. Determination of deuterium content of sample. Notice that the sample can be removed from the calorimeter and weighed within 2 min after turning off the current. The sample is dried quickly by washing with acetone.

than is produced when forming PdD. The greater the applied current, the more power is absorbed for a shorter time. This reaction uses energy, measured as power, that can be calculated from the reaction $(x/2)D_2O + Pd = PdD_x + (x/4)O_2$, where x is equal to the average D/Pd ratio. As the cathode takes up deuterium, the Pd converts to alpha-PdD followed by a layer of β-PdD of increasing thickness with a range of composition. Eventually, after most of the sample is converted to the final composition, reaction stops and conditions return to zero power (energy). At this time, the composition is in steady-state with a stable gradient and a constant rate of diffusion
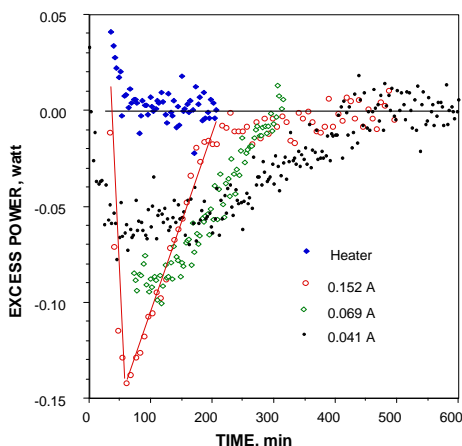

Figure 7. Power measurement during loading at various applied currents between the surface and random cracks where dissolved deuterium is lost as D_2 gas.

During loading, deuterium is added to the cathode to produce the composition change shown in Fig. 8. Note that initially, all D_2 produced by electrolysis is combined with Pd. As the deuterium content increases, a smaller fraction of available D_2 is absorbed, with a sudden termination as a limit is reached. The remaining D_2 and O_2 are recombined by the contained catalyst and remain in the cell. If applied current is sufficiently small, the initial conversion to β-PdD becomes visible, as noted in Fig. 8.

Calculation of Enthalpy of Formation

The energy used during the loading reaction can be calculated by integrating data, such as shown in Fig. 7, between zero power and the curve drawn through the data points over the duration of the loading process. However, the shape of the curve is difficult to define unless slow loading rates are used. For this reason, the analysis will only be applied to a current of 0.041 A as shown in Fig. 9. This curve gives a value of -106 kJ/mol Pd. Termination of the reaction is assumed to occur at an average D/Pd of 0.8, the measured value for this sample, and at 460 min. The reaction equation becomes:

$0.4D_2O + Pd = PdD_{0.8} + 0.2O_2$, where $\Delta H_f(D_2O) = 294.6$ kJ/mol. Because Pd and O_2 are assumed to be at standard-state, their enthalpy values are zero. The enthalpy of formation

of $PdD_{0.8}$ is ΔH_f $(PdD_{0.8}) = -106 + 0.4 * 294.6 = 11.8$ kJ/mol. This value can be calculated from the published equation[9]:
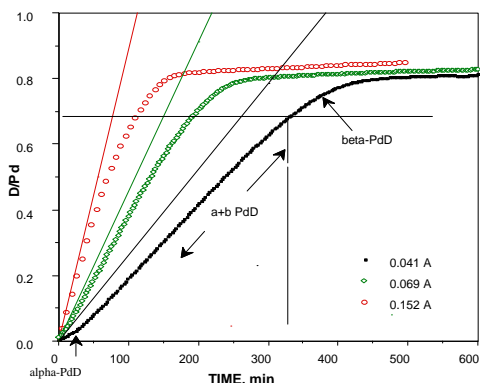

Figure 8. Composition of a cathode during loading. Note that at low current, loading of the alpha phase becomes visible. The lines show the loading rate if all D_2 produced by the current entered the Pd cathode. The horizontal line shows the published composition at the beta-PdD phase boundary at 1 atm D_2 and room temperature in the presence of alpha-PdD.

ΔH_f $(PdDx) = 44.99 - 41.89 * x = 11.5$ kJ/mol for x=0.8.

Because of scatter in the power measurements and because the sample does not have a uniform composition, the potential error in this measurement is about ± 2 kJ/mole. Agreement with the previous measurement is well within the possible error of both results, thereby demonstrating the potential accuracy of this calorimeter.
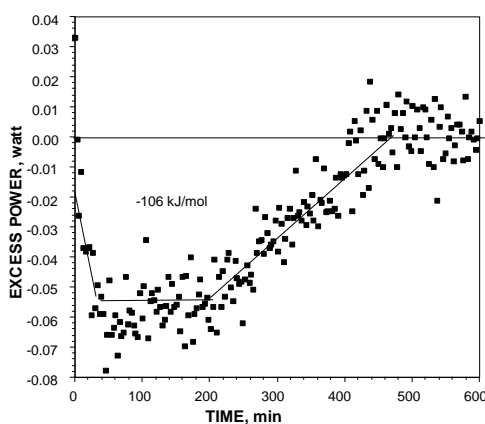

Figure 9. Data used to calculate enthalpy of formation of $PdD_{0.80}$ using 0.00974 mole of Pd. The first three points were taken while the calorimeter was approaching steady-state and must be ignored.

Summary

A Seebeck calorimeter can easily be constructed with characteristics that eliminate most errors thought to cause anomalous energy from cold fusion. In addition to being stable and accurate, the calorimeter is sufficiently sensitive to accurately measure the enthalpy of formation of PdD_x to give 11.8 kJ/mole using only 1 g of palladium.

References

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