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Construction of a Seebeck Envelope Calorimeter and Reproducibility of Excess Heat

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Abstract

A Seebeck Envelope Calorimeter (SEC) was designed and built. The inner volume is 17.6 L. Its outer wall temperature was controlled within 0.01°C. The device constant was 6 W/V and its time constant was 5 minutes. Dash-type cells were tested. Both an isoperibolic calorimeter and the SEC measured excess heat with the same Pd cathode of 25 × 25 × 0.3 mm^3. The SEC showed excess heat ranging from 0.15 ± 0.02 to 0.41 ± 0.03 W (average value 0.22 W) at applied current of 3 to 3.5 A (0.24 to 0.28 A cm^{-2}).

1. Introduction

A Seebeck Envelope Calorimeter (SEC) is a powerful tool for measuring excess heat in low energy nuclear reaction experiments [1–3]. In previous works we used an SEC made by Thermonetics Corporation [1,2]. However, this device had some intrinsic defects in our experience: (1) The device constant was unstable. We found that it shifted by 20% in three months; the SEC had to be calibrated before and after every experiment. (2) The heat insulation around the calorimeter was insufficient; thus the baseline and output signal shifted daily with the ambient temperature. This SEC had to be put into another, larger insulated box to prevent temperature fluctuations [1,2].

In this paper, we will describe a new SEC; its merits are simplicity, stability, and accuracy. Preliminary results on reproducibility of excess heat in the Pd-D_2O system are also reported.

2. Construction of calorimeter

A schematic of the calorimeter and accessories is similar to that which was published previously [1]. The calorimeter core consists of two aluminum alloy boxes. The inner box is the measuring vessel with interior dimensions of 26 × 26 × 26 cm^3 (17.576 L). The thicknesses of inner and outer box walls are 4 mm and 6 mm, respectively. Thermoelectric modules (TM, 5.4 × 40 × 40 mm^3), each with 127 thermocouples, are mounted between the inner and outer walls with screws. Thermal conductive silicone is wiped on both sides of each TM to improve thermal conductivity. 25 TMs are distributed uniformly on each wall, except for the two facing sidewalls which have 24 TMs because there is one hole in the center of each wall. Altogether, 148 TMs with a total of 18,796 thermocouples are used in this calorimeter. All of the TMs are connected in series. The heat flow during experiments is proportional to the measured emf (electromotive force) of the TMs. The two holes (ϕ = 2cm) in the two sidewalls mentioned above permit multi-functionality of this calorimeter; i.e., measurements of temperature, internal resistance and voltage of the unit-under-test (UUT). The thermal emf of the calorimeter and other signals of UUT are measured with a Keithley 2000 multimeter which is connected to a PC through a GPIB card, to automatically register the data.

The outer aluminum box is wired with copper tubing (ϕ_{in} = 8 mm, ϕ_{out} = 10 mm). Thermal conductive adhesive is used to mount the copper tubing and the aluminum walls. The outlet of the copper tubing is connected with the hose of a refrigerating/heating circulator (PolyScience 9112). The temperature range of this circulator is –20 to 200°C; the temperature stability is ± 0.01°C; and the pump outlet flow rate of the working fluid is 15 to 22 liters per minute. The inlet of the copper tube around the outer box is connected with a small cylindrical heat sink (ϕ_{in} 20 mm × h_{in} 50 mm); a remote, circular temperature probe is placed in it. This arrangement of the temperature probe ensures that the fluctuation of ambient temperature does not affect the calorimeter. The inlet of the small heat sink is connected to the circular probe with another hose. The hoses are wrapped with a polystyrene foam tubing to prevent heat losses. The calorimeter core is placed in a larger box with inner dimension of 70 × 70 × 70 cm^3. Heat insulation materials fill the gap between these two boxes.

3. Calibration of the calorimeter

Calibration is conducted with a 6 ohm electrical heater. The four-wire Kelvin bridge method was used to eliminate lead resistance in the measurements. Applied current was measured with a 0.1 Ω (± 0.01%) standard resistor as shunt. A Sanyo Denki brushless fan (12 V × 0.21 A, 2.5 W) was used to make the temperature in the vessel homogeneous. The power of the fan was also measured in a similar manner. The calibration results are shown in Fig. 1. These results are simulated by a quadratic equation:

$$P/\mathrm{W} = -0.0743 \pm 0.0038 + (5.899 \pm 0.0053)E/V + (0.0017 \pm 0.0014)(E/V)^2 \qquad (1)$$

with $\chi^2 = 1.2 \times 10^{-4}$, $R^2 = 1$. P is the input power, and E is the output emf of the SEC. The device constant is about 6, or about 30 times more sensitive than the Thermonetics SEC. The device constant changed only 1.7% over a 9 month period. The time constant of this SEC is 5 minutes.

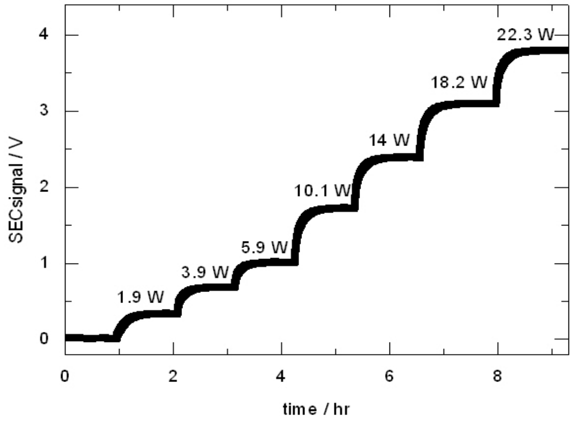

Figure 1 (a) SEC calibrations at 25°C.

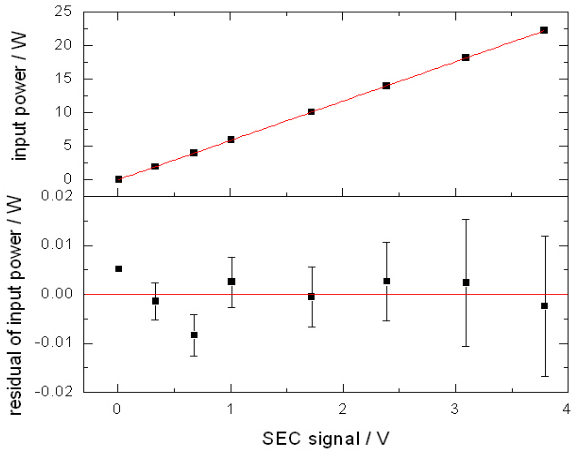

Figure 1(b) Simulation of calibrations.

4. Excess heat of Pd-D_2O system

A schematic of the electrolytic cell is shown in Fig. 2(a). The cell is a cylinder of borosilicate glass (capacity is about 250 ml, ϕ_{in} = 42 mm and ϕ_{out} = 45 mm, wall thickness = 1.5 mm, h = 180 mm). A PTFE male cap is tapered from ϕ47 × 5 mm^2 at the top, and ϕ41 × 15 mm^2 at the bottom. A groove of 4 mm width and 2.5 mm depth is made for O-ring in the middle of bottom part. The O-ring (ϕ_{in} = 31.5 mm, width = 3.55 mm) made of nitrile butadiene rubber (NBR, resistant to acid) is used to seal the top cap against the top inner wall of glass cylinder. The top cap has two holes, 7 mm diameter each, for the electrode lead wires. A PTFE plate (ϕ41 mm × 8 mm) is used to suspend the recombination catalyst above the electrode. It has 24 holes of ϕ2 mm for fluid (D_2, O_2, D_2O and its vapor) passing, and also has two holes, 7 mm diameter each, for the electrode lead wires. A PTFE rod (ϕ6 × 90 mm^2) is fastened to the perforated plate and the top cap ensures that the perforated plate is at a fixed distance above the electrolyte.

The Pd cathode was prepared from Alfa Aesar Stock # 11514, Lot # G15Q17, 99.9% purity palladium foil (metals basis). It was cold rolled from 15 × 25 × 0.5 mm^3 to 25 × 25 × 0.3 mm^3. Its surface area is 12.5 cm^2 and weight is 2.1891 g. The same Pd cathode was used for all experiments, with both isoperibolic calorimetry (IPC) and SEC.

Three platinum electrodes (two anodes and one cathode) are foils 22 × 28 × 0.02 mm^3, 11.5 cm^2 surface area. Four electrode lead wires are made of Pt (ϕ1 mm × 40 ~ 60 mm). The Pt foils (99.95% Pt) are from General Research Institute for Nonferrous Metals. These Pt leads are connected with copper tubes and encapsulated with glass tubes (ϕ_{in} = 2 mm, ϕ_{out} = 7 mm, length = 170 mm) as shown in Fig. 2(a). The gaps between the glass tubes and the PTFE cap are filled with glass cement.

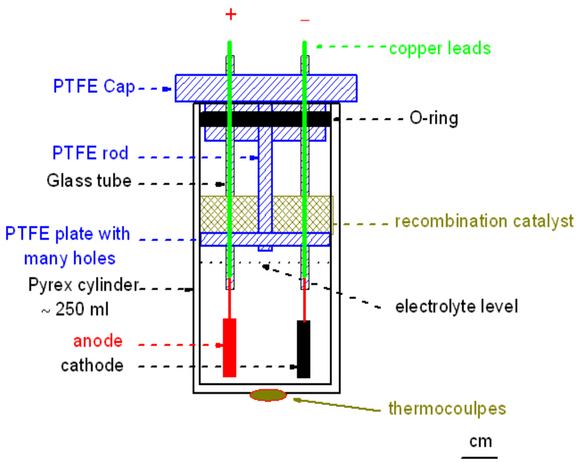

Fig. 2(a) Schematic of cell.

Fig. 2(b) Photo of isoperibolic calorimeter.

The electrolyte contains heavy water (Beijing Chemical Reagent Company, > 99.9% isotopic purity) mixed with H_2SO_4 in the mass ratio of 110:27.5 (20:3 of volume ratio or 20% of mass concentration). The catalyst contains 0.5% Pt on 1/8 inch diameter alumina pellets (Alfa Aesar). Three grams (62 to 64 pellets) are used in each cell.

4.1. Excess heat measured by isoperibolic calorimetry (IPC)

Before samples were tested with the SEC, excess heat production from the samples was first verified with an isoperibolic calorimeter (IPC) shown in Fig. 2(b). Two cells were connected in series: the E cell (experimental cell, heavy water electrolyte and Pd cathode) and C cell (control cell, light water electrolyte and Pt electrodes) [2,4]. The mass concentration of H_2SO_4 in light water electrolyte is 13%. The distance between two electrodes in the C cell is adjusted to make its voltage close to that of the E cell. These two cells are embedded in a 5 cm thick polystyrene block in a plexiglass box ($14 \times 18 \times 23$ cm^3, 4 mm wall thickness) as shown in Fig. 2(b). One K-type thermocouple was attached on the bottom of each cell to measure the temperature. The output power of the E-cell was calculated using the temperature difference between it and ambient, and the device constant deduced from the C-cell, as described in Refs. [2,4]. One example of excess heat is illustrated in Fig. 3(a) and all results are summarized in Table I. The excess power is 0.22 to 0.79 W in 7 runs. These results indicate this sample can produce excess heat during electrolysis at 0.24 A cm^{-2}.

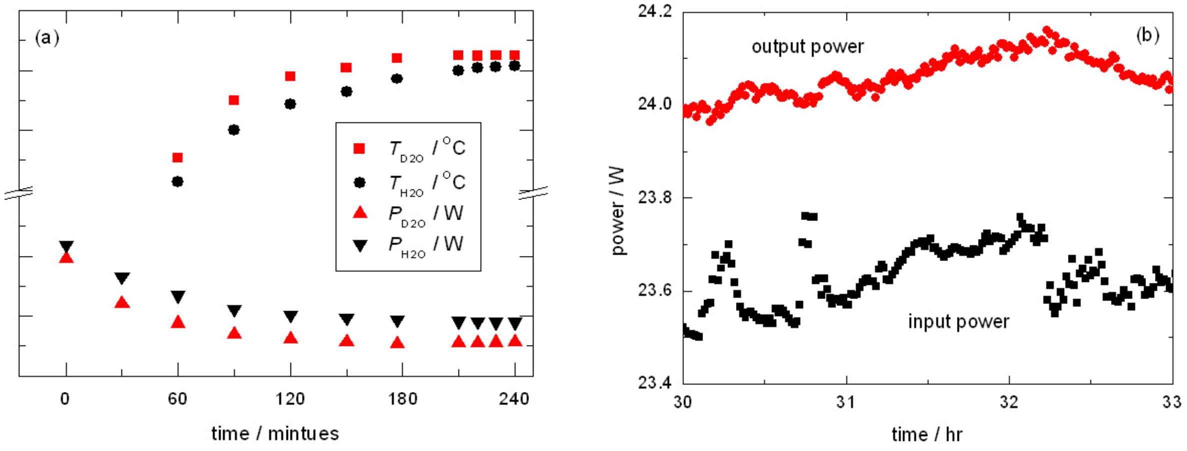

Fig. 3(a) Excess thermal power measured by IPC (Run #2 in Table I); (b) Excess thermal power measured by SEC at 0.28 A cm^{-2} (Run #6 in Table II).

Table I. Summary of excess thermal power measured by IPC.

No.	System*	Current and time	T_{room}/°C	P_C/ W	T_C/°C	P_E/W	T_E/°C	P_{ex}/ W
1	OC	-3A×2hr, 3A×3hr	22.0	4.77	59.5	4.21	60.4	0.44
2	OC	3 A × 5 hr	25.3	4.91	60.3	4.56	61.3	0.49
3	OC	3.5 A × 3.3 hr	24.9	5.84	67.3	5.66	67.0	0.22
4	CC	3 A × 4 hr	22.0	10.08	73.6	8.87	71.6	0.79
5	CC	-3 A × 1 hr 3 A × 7 hr	24.1	9.51	70.4	8.69	70.1	0.67
6	CC	3 A × 4 hr	30.8	9.86	77.0	9.18	76.2	0.50
7	CC	-3A×1hr, 3A×7hr	30.0	8.59	69.4	8.53	72.0	0.63

* OC is open cell; CC is closed cell; C is the control cell; E is the experimental cell.

4.2. Excess heat measured by SEC

After excess heat was verified with the IPC method, the entire isoperibolic calorimeter with the two cells installed in it (shown in Fig. 2(b)) was placed inside the SEC, where calorimetry was again performed. One example of excess heat is shown in Fig. 3(b). We performed 11 experimental runs. Six of these produced excess heat, ranging from 0.15 to 0.41 W, as shown in Table II. Run #3 had only the E (experimental) cell and not the C (control) cell; it also showed the excess heat. The total excess heat was 54 kJ and average excess power was 0.22 W in these 6 positive runs. Excess power measured by IPC and SEC were qualitatively consistent as shown in Table II.

Table II. Summary of 6 positive excess heat run measured by SEC at 25°C.

No.	System*	Current, time	ΔQ/kJ	P_{in}/W	P_{ex}/W	P_{in}/W		T/°C	
						P_C	P_E	T_C	T_E
1	OC, E+C	3 A × 6.33 hr	4.29	9.60	0.28 ± 0.02			59.6	58.9
2	OC, E+C	3 A × 7 hr	4.04	9.50	0.23 ± 0.02			59.8	59.6
3	OC, E	3 A × 7 hr	5.04	8.20	0.15 ± 0.02				59.9
4	OC, E+C	3.5 A × 6 hr	3.63	12.97	0.29 ± 0.02	6.55	5.48	66.2	66.1
5	OC, E+C	–3.5 A × 1 hr, 3.5 A×5.5 hr	8.18	13.16	0.22 ± 0.04	6.93	5.29	66.8	66.7
6	CC, E+C	3 A × 24 hr, 3.5 A × 36 hr	28.63[#]	23.67	0.41 ± 0.03	12.19	10.55	76.5	75.4

Note: All power and temperature values were taken when the values were stable.

* OC is open cell; CC is closed cell; E is E cell, C is C cell.

[#] Because the catalyst in the E cell did not work after 34 hrs electrolysis (mass losses of E cell and C cell were 32.7 and 0.4 g, respectively), this is a conservative evaluation.

5. Conclusion

A Seebeck Envelope Calorimeter was designed and constructed. It is sensitive; it has a fast response, and a stable device constant. Excess heat in Dash-type cells was verified with this calorimeter. Further work on this subject is in progress in our lab.

Acknowledgment

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