Characteristics of Excess Heat in Pd|D$_2$O+D$_2$SO$_4$ Electrolytic Cells Measured by Seebeck Envelope Calorimetry

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Abstract. Pre-electrolysis at the boiling point in open Pd|D$_2$O cells is an effective method to activate a palladium cathode, which can produce excess power in subsequent electrolysis in closed systems for several months. The reproducibility is 23/45. Another characteristic of excess heat is the apparent resistance of electrolytic cell changes irreversibly with temperature.

1. Introduction

In previous works [1−3], anomalous excess thermal power in Pd|D$_2$O cells was observed using Seebeck Envelope Calorimetry (SEC). Two phenomena were found for reproducibility of excess heat. One is that the temperature increment during electrolysis must be high enough; otherwise no excess heat will be produced [2]. Another is that the second run always gives more excess heat than in the first under the same condition as shown in Table V in Ref. [2]. After reviewing the data of past experiments, it is found that the samples Pd-A and Pd-E in Ref. [2], which gave the maximum excess power (~ 1 W, about one order greater than others), have the same histories. Both of them had been electrolyzed at the boiling point in open cells due to mistakes (Exp. #041110 for Pd-A and Exp. #050829 for Pd-E). After that, these two samples become active in excess heat production in electrolysis. All these phenomena inspire the author to intentionally use pre-electrolysis at the boiling point in open cells to activate samples. Experimental results show that this procedure is effective to some extent as reported below. At the same time, it is found that the apparent cell resistance changes irreversibly with temperature when excess heat occurs.

2. Experimental set-up

Electrolytic cells used in most experiments described in this paper are modified versions of pervious experiments [3]. Copper tube leads were replaced with platinum wires to avoid contamination, and H$_2$SO$_4$ is replaced with D$_2$SO$_4$ for a similar reason. A schematic and a photo of the electrolytic cell are shown in Figs. 1(a) and 2(a), respectively. The cell is a cylinder of borosilicate glass (ϕ_{in} 42 $\times$ ϕ_{out} 45 $\times$ 142 mm^3, capacity ~190 ml). A PTFE male cap has three parts: the top part is ϕ 41 $\times$ 4 mm^2 for fixing the cell by a metal frame as shown in Figs. 1(b) and 2(b); the middle part is a hexagonal prism with side length 32 mm and thickness 13 mm; the bottom part is ϕ 41 $\times$ 24 mm^2 with a groove of 4 mm width and 2.5 mm depth in the middle for O-ring. 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 cap against the inner wall of glass cylinder. The cap has two holes, 1 mm diameter each and 20 mm apart, for the electrode lead wires. A PTFE plate (ϕ 41 $\times$ 8 mm^2) is used to suspend the recombination catalyst. It has 57 holes of ϕ 2 mm to pass gases (D$_2$ and O$_2$) and vapors (D$_2$O). A PTFE rod (ϕ 6 $\times$ 40 mm^2) is fastened to the perforated plate and the cap. This ensures that the perforated plate being at a fixed distance above the electrolyte. Before and after every electrolysis, the cell was weighed with a Mettler balance (PM1200, 0.001 g readability) since June 06, 2009 (Exp#090605). Before that time, cells were weighed only with chemical balances.

The metal frame is used to clamp the PTFE cap into the cell as shown in Figs. 1(b) and 2(b). These arrangements ensure that the electrolytic cell is a closed system. The metal frame and cell is partly embedded in a Styrofoam base (ϕ 15 $\times$ 12 cm^2), which is placed in an enamel jar (ϕ 15 $\times$ 16 cm^2). The enamel jar can weaken the impact of cell explosions in the calorimeter and prevent corrosion caused by

the acidic electrolyte after an explosion. Three explosions occurred during the past year. These were caused by incomplete recombination, due to variability in the effectiveness of the recombination catalyst. The polystyrene box shown in Fig. 2(b) of Ref. [3] was broken into pieces in one explosion (Exp. #090219) earlier this year.
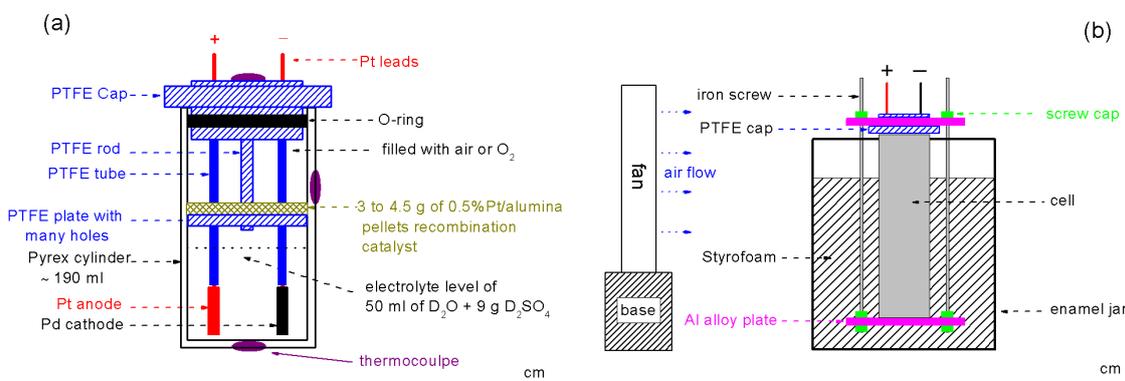

Fig. 1. - Schematics of electrolytic cell (a) and parts outside the cell (b).
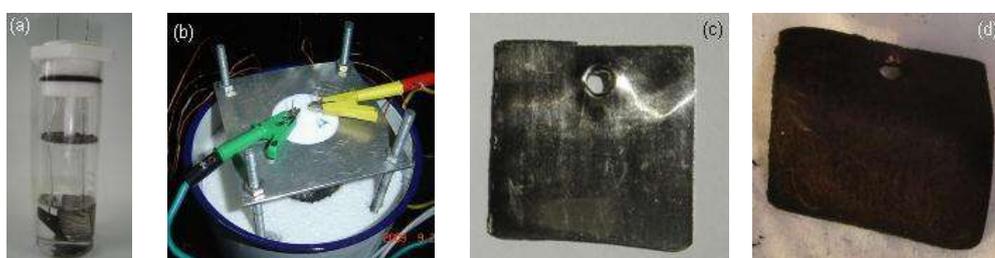

Fig. 2. - Photos of bare electrolytic cell (a), cell in the SEC (b), fresh Pd #1 (c) and Pd#1 after electrolysis as cathode for 285 hours and anode for 14 hours at 3 to 3.5 A (d).

Four different palladium samples are used as listed in table 1. Both Pd #1 (see Figs. 2(c) and (d)) and #2, provided by John Dash, Portland State University, are from Alfa Aesar, Stock #11514, Lot #G15Q17, 99.9% purity. Pd #3 is from General Research Institute for Nonferrous Metals (GRINM), 99.95% purity. Pd #4, provided by Da-Lun Wang, Institute of Nuclear Physics and Chemistry, CAEP, is from Kunming Institute of Precious Metals (KIPM). All these samples are weighed using an Ohaus AR2140 balance. Before the first electrolysis, all Pd samples were immersed in concentrated sulfuric acid to remove surface contamination, and then washed with de-ionized water several times.

Table 1. Parameters of different palladium samples used in experiments.

Pd #	Exp. #	size / mm^2	area / cm^2	mass / g	source	metallurgical treatment
1	081220-091002	$25 \times 25 \times 0.3$	12.5	2.1891	Alfa Aesar	30% cold rolled
2	090219-090612	$25 \times 25 \times 0.3$	12.5	2.1831		
3	090620-090624	$11 \times 31 \times 0.05$	7.25	0.2271	GRINM	cold rolled
4	090625-090723	$10 \times 30 \times 0.5$	6.28	1.7836	KIPM	unknown

The anode is a platinum foil, $31 \times 43 \times 0.02$ mm^3 with area of 26.7 cm^2. Two electrode lead wires made of Pt ($\phi\,0.8 \times 145$ mm^2) are covered with heat-shrink Teflon tubing. The Pt foil and wires are from GRINM (99.95% purity). These were annealed for easy machining. Ethyl α-cyanoacrylate instantaneous adhesive (502 glue) is filled into the gaps between the leads and the cap in order to prevent escape of the off gases from electrolysis. The cap is cooled with flowing air during electrolysis to prevent the failure of the glue at high temperature, as shown in Fig. 1(b).

The electrolyte is ~ 50 ml heavy water mixed with 8 to 10 g D_2SO_4. Both deuterium reagents are from Beijing Chemical Reagent Company (> 99.9% isotopic purity). The quantity of recombination catalyst varied from 3 to 4.5 g (~ 60 to 90 pellets), depending on its history and the applied current. In some cases, O_2 gas at 1 atmosphere is flowed into the cell to accelerate catalysis.

The calorimeter, power supply and data logging system are the same as before [3−5]. These will not be discussed here, except for some recent modifications.

3. Experimental results

3.1. Calibration of calorimeter and contrast experiments

The calibration was conducted with a 3.6 Ω electric heater, starting on May 19, 2009 (Exp. #090519). The heater is made of Tophet® alloy A wire (ϕ 0.3 mm) wound around cylindrical heat sink fins, which are located at the center of the measuring vessel of the calorimeter. The calorimeter was calibrated from 2 to 50 W (55 sets of data) 16 times in 13 months. It gives good stability and linearity between thermal powers and responses, as shown in Fig. 3(a) and the simulation equation (1) below:

$$P = -0.0355 \pm 0.0161 + (5.8961 \pm 0.0118)E - (0.0020 \pm 0.0016)\,E^2 \qquad (1)$$

with $\chi^2 = 0.1661$, $R^2 = 0.9997$, mean square = 0.0031. P is the input power in Watts and E is the output electromotive force of the SEC in Volts. This equation gives less accuracy than in Ref. [3] because the period is more than one year. Fluctuations of room temperature at different seasons affect the long term precision; however this calorimeter is calibrated every 2 to 3 weeks during experiments and it is enough accurate to give the real signal of excess power within the error of 20 mW for every calorimetry.
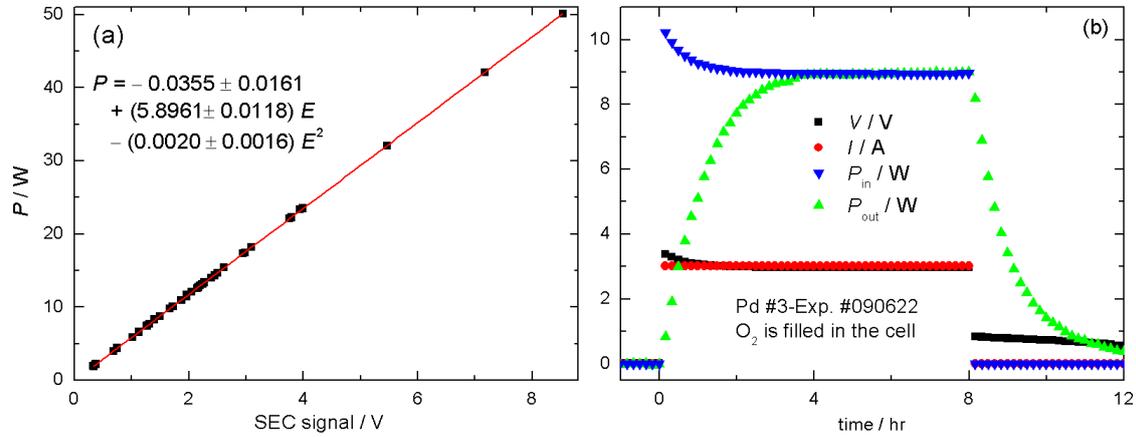

Fig. 3. - (a) Calibration of the calorimeter from 2 to 50 W, 55 sets of data, in 13 months; (b) Comparison of input electrolytic power with output thermal power of a Pd-D_2O cell. The fan's power is deducted from the total power.

Before presentation of anomalous excess heat, sample experiments are introduced to demonstrate the accuracy of the calorimetry and the reality of excess heat afterwards. Three types of experiments, i.e. Pt-D_2O, Pd-H_2O and dead Pd-D_2O electrolytic systems, were carried out. Each of them has only one component, i.e. cathode or electrolyte, being replaced with that in the active cell. All of Pt-D_2O (Pt cathode is a foil of $22 \times 28 \times 0.02$ mm^3) and Pd-H_2O systems were designed for contrast and did not give excess heat as shown in table 2. The inactive Pd cathodes also did not give excess heat especially for Pd #3 and #4.

Table 2. Parameters of different sample experiments carried out at 25 °C, 3 A.

Pd#-Exp#	system	t / hr	P_{in} / W*	P_{ex} / mW	Q_{in} / kJ*	Q_{ex} / kJ	Δm / g	$Q_{ex}+\Delta H$ / kJ
Pt-090824	Pt-D_2O	7	10.819(7)	1±24	278.20(6)	−0.29±1.25	0.084	0.95±1.26
1-091002	Pd-H_2O	9	8.824(4)	6±29	287.98(6)	−0.51±1.16	0.038	0.06±1.17
3-090622	Pd-D_2O	8	8.956(3)	0.4±26	262.38(5)	−0.55±0.90	0.022	−0.22±0.90

* The number in one set parentheses is the uncertainty of the last figure of the quantity before the parentheses.

Fig. 3(b) shows an example of calorimetric results for dead-Pd-D_2O electrolysis. The input and output powers are $P_{in} = 8.9556 \pm 0.0029$ and $P_{out} = 8.9552 \pm 0.0264$ W, respectively, during the steady state (5 to 8 hours of electrolysis time). They are consistent with each other within 0.004% although the calorimetric error is 0.29%. The input, output and excess energies are $Q_{in} = 262.38 \pm 0.05$, $Q_{out} = 261.83 \pm 0.88$ and $Q_{ex} = -0.55 \pm 0.90$ kJ, respectively. The mass loss of the cell in this run is $\Delta m = 0.022$ g. If this loss was caused by poor catalytic recombination, the corresponding energy correction (enthalpy change) is $\Delta H = 0.33 \pm 0.03$ kJ. The output energy after correction is $Q_{out} + \Delta H = 262.16 \pm 0.90$ kJ; the resulting excess energy is $Q_{ex} + \Delta H = -0.22 \pm 0.90$ kJ, corresponding to (-0.08 ± 0.34)% of the input energy. It means

there was no excess heat produced in the electrolytic cell and this calorimeter gave good accuracy (better than 0.1%) at power around 9 W running for 8 hours. Because this calorimeter is designed for power measurement, it gives higher precision for power than for energy, as shown in table 2.

3.2. Excess heat

As mentioned in the Introduction, effects of pre-electrolysis on excess heat are the main objective of this work. Seven runs with pre-electrolysis were carried out for 4 samples as shown in table 3. An example is shown in Fig. 4; this experiment was conducted at the end of 2008 using the cell described in Ref. [3]. Pd #1 was activated by pre-electrolysis on Dec. 20, 2008. The applied current was increased step by step: firstly 3.5 A for 2 hr, then 3.7 A for 1.5 hr and 3.9 A for 1 hr, 4 A for 0.5 hr at the end, as shown in Fig. 4(a). During the pre-electrolysis, the cell temperature was increasing and the electrolyte was boiling. The electrolyte level was lowering and the cathode surface was becoming exposed to the air. On the second day (Exp. #081221), more heavy water was added, and the cell was closed and electrolyzed. However, the excess heat was uncertain because of a poor seal and a great mass loss of 17.3 g. Two days later (Exp. #081223), the system was tested again and excess power was produced, as shown in Fig. 4(b). After electrolysis for 3 hr at 3 A, the calorimeter showed excess heat and its amplitude reached the maximum value of $P_{ex,max} = 220 \pm 16$ mW in 4.5 to 5 hr. After 5 hr electrolysis, P_{ex} keep the steady value of 120 ± 18 mW till the end of this experiment. In this experiment, there was no mass loss, within the error of measurement.

Another example for sample Pd #2 is shown in Fig. 5. The current applied during pre-electrolysis was: firstly 3.5 A for 3 hr, then 3.7 A for 1 hr, 3.9 A for 1.3 hr, 4 A for 2.7 hr at the end, as illustrated in Fig. 5(a). Four days later, calorimetry with a closed cell was carried out. This sample gave excess power of $P_{ex} = 0.120 \pm 0.020$ W during 5 to 6 hr of electrolysis, as shown in Fig. 5(b).

Table 3. Summary of pre-electrolysis and subsequent excess heats.

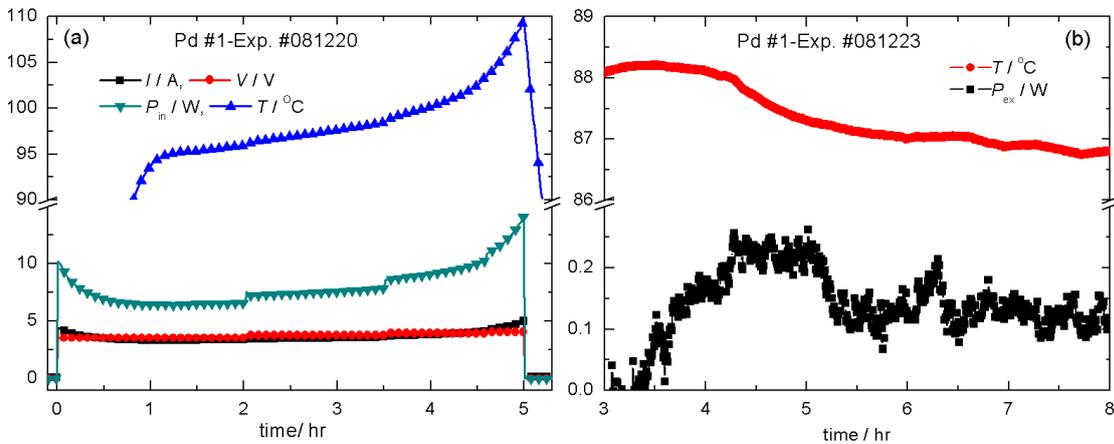| Pd #	pre-electrolysis			excess heats			total
	Exp. #	I_{max} / A	T_{max} / °C	Exp. #	$P_{ex,max}$ / mW	reproducibility	reproducibility
1	081220	4	110	081223	220 ± 16	8/15	17/35
	090808	4.5	97	090810	146 ± 24	4/4	
	090814	3	98	090828	66 ± 24	3/8	
	090915	4.5	108	090916	17 ± 22	0/1	
	090917	4.5	145	090919	31 ± 22	0/2	
	090921	4.5	127	090922	20 ± 15	0/1	
	090923	4.2	114	090927	152 ± 24	2/5	
2	090521	4	99	090525	120 ± 20	6/10	6/10
3	090620	3	97	090621	5 ± 24	0/3	0/3
4	090629	3	99	090721	3 ± 13	0/3	0/3

Fig. 4. - Example of effects of pre-electrolysis in an open cell in the first run on the excess heat production on the subsequent run in a closed cell. (a) Pre-electrolysis; (b) Excess power after activation. Parameters: $T_{SEC} = 25$ °C, 3 A × 8 hr, $P_{ex,max} = 220 \pm 16$ mW (4.5 to 5 hr); $P_{ex,stable} = 120 \pm 18$ mW (7 to 8 hr), $Q_{ex} = 2.46 \pm 0.33$ kJ. The mass loss during electrolysis $\Delta m = 0.0 \pm 0.2$ g.
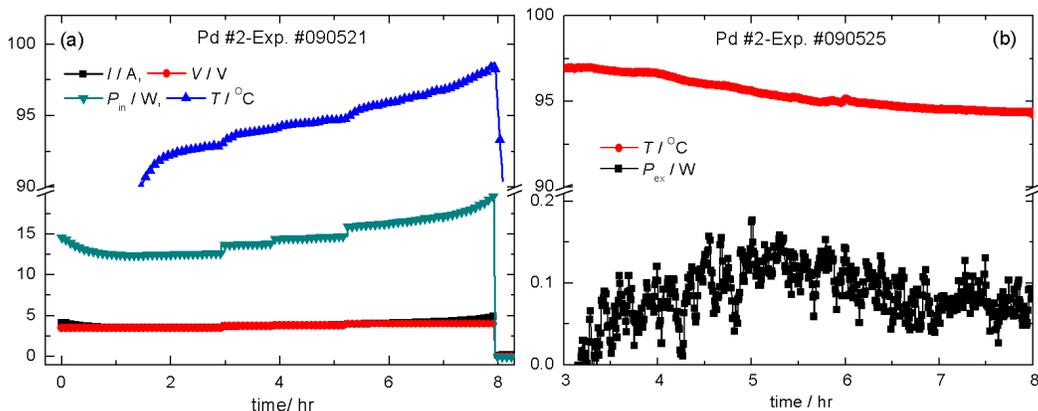
Fig. 5. - Another example of effects of pre-electrolysis in an open cell in the first run on the excess heat production in a closed cell in the subsequent run. (a) Pre-electrolysis; (b) Excess power after activation. Parameters: T_{SEC} = 25 °C, 3 A × 8 hr, P_{ex} = 120 ± 20 mW (5 to 6 hr). The mass loss Δm = 0.05 ± 0.02 g is not included in calculation of excess power.

Not every pre-electrolysis for every sample can stimulate excess power in subsequent experiments, as shown in table 3. For sample Pd #1, the effective ratio of pre-electrolysis is 4/7. For the other 3 samples, only one pre-electrolysis was tested and only one sample gave excess power; therefore, further research is necessary to determine other unknown factors which affect reproducibility.

Besides pre-electrolysis, other methods were used in attempts to stimulate increased excess heat production. These include reverse current activation in pre-electrolysis (Exp. #090814, 090915, 090921 for Pd #1), modifying cell temperature through changing the thickness of Styrofoam layers shown in Fig. 1(b) (85 to 102 °C, Exp. #090725 to #090731), stepwise increasing (ladder-like) current (Exp. #090825) were also tested to stimulate excess heat production as done before [1−3]; however, all these methods did not show clear evidence of positive effects. More work is needed.

From the history of Pd #1 shown in table 3, it seems excess heat from boiling-point electrolysis can be switched on or off like a light bulb. Another question is the lifetime of excess heat activity after pre-electrolysis. Pd #1 kept the activity for at least 7 months (Exp. #081220 to 090807). Sample Pd-A had kept the activity for at least 2 months (Exp. #041110 to #050111) and Pd-E kept the activity for at least 10 months (Exp. #050829 to #060706) in Ref. [2]. Therefore, pre-electrolysis should be an effective way to activate a Pd sample for several months.

3.2. *Irreversible change of cell's resistance with temperature*

During the emergence of excess heat, it was noticed that P_{ex} and cell temperature T approach to their maximum amplitudes and then decrease to the stable values as shown in Figs. 4(b) and 5(b). It means that
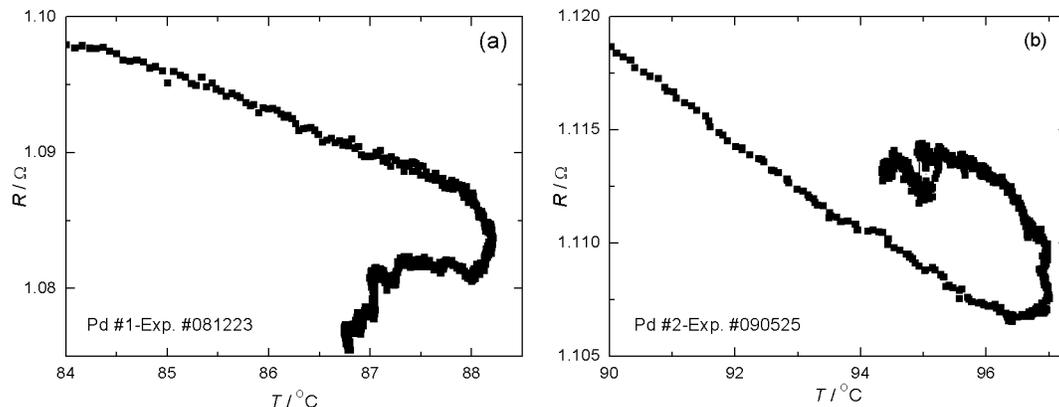

Fig. 6. - Apparent cell resistance R vs. temperature T for experiments in which excess power was produced.

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increment of excess power is suppressed in electrolysis due to a changing cell parameter. This parameter is the apparent cell resistance R. R vs. T with excess heat is shown in Fig. 6 and without excess heat in Fig. 7. It is found that there is obvious irreversible change of R vs. T when excess heats occur. These results indicate this change can be a collateral evidence of excess heat besides the calorimetry. However, this irreversible change is not fully understandable and predictable at present; it may be negative or positive as shown in Fig. 6(a) and (b), respectively.
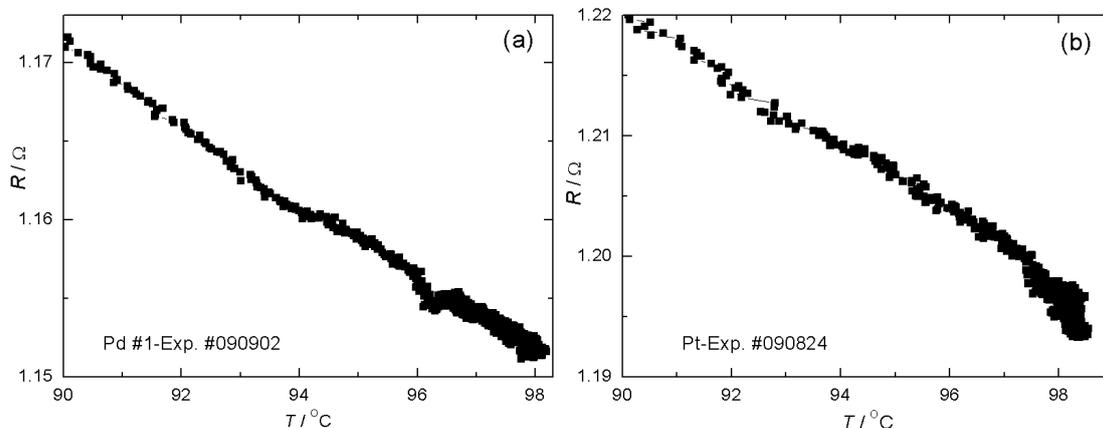

Fig. 7. - Apparent cell resistance R vs. temperature T without excess power.

4. Discussion

Pre-electrolysis activation of excess heat production reported here is similar to the heat-after-death effect observed by Fleischmann and Pons [6]; both situations work at the boiling point of the electrolyte. This phenomenon must be explainable by some mechanism which is activated by the high temperature. As concerns the irreversible change of cell resistance, it should be the intrinsic nature of excess heat because the state of cathode polarization must change in excess heat production at the cathode hot spots observed by Mosier-Boss and Szpak [7], and positive feedback of voltage and temperature observed by Fleischmann et al [8]. The author will study all these interesting phenomena in future work.

5. References

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