Characteristics of excess heat in $Pd|D_2O+D_2SO_4$ electrolytic cells measured by Seebeck Envelope Calorimetry

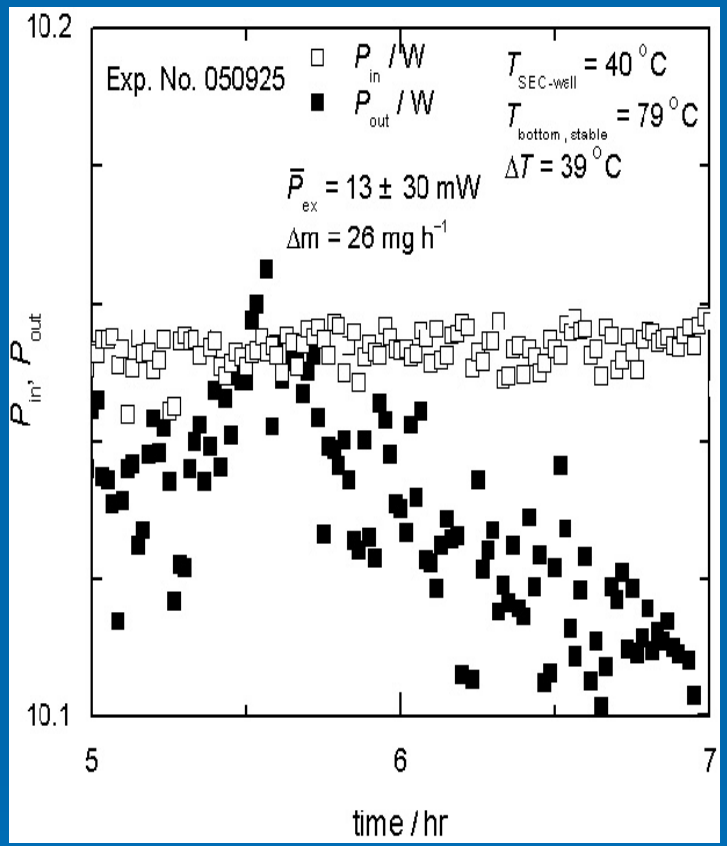
Wu-Shou Zhang
Institute of Chemistry, CAS, Beijing, China

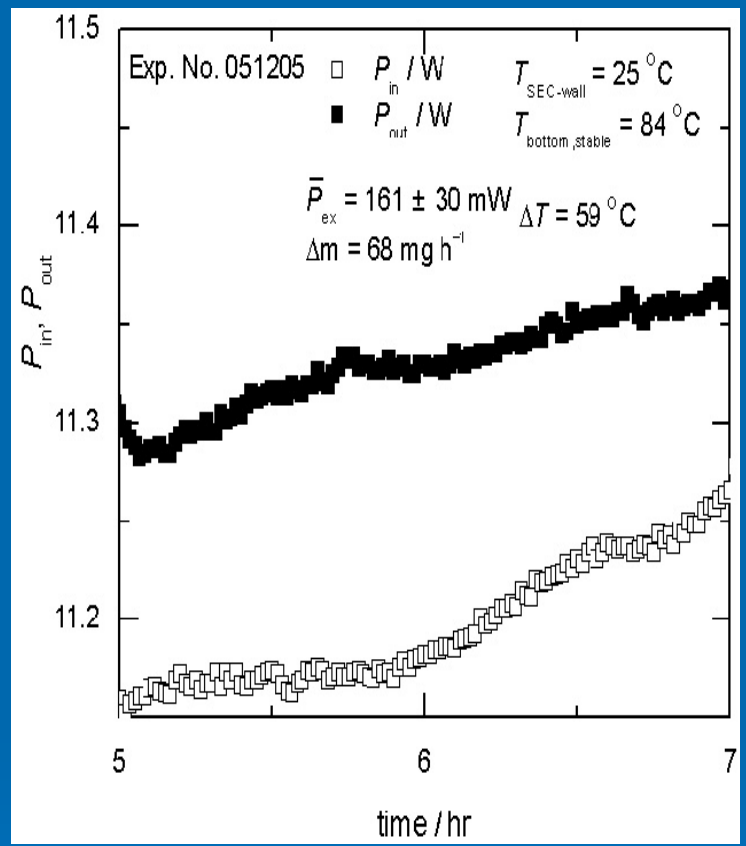
- 1. Introduction
- 2. Experimental setup
- 3. Calorimetric results
- 4. Conclusions

1. Introduction

- What are key factors for reproducibility of excess heat?
- (1) Temperature increment ΔT
- (2) Pre-electrolysis

(1) Temperature increment





Pd (0.25×25×25 mm^3). 3 A (0.24 A/cm^2).

Q_{ex} = 0.01 ± 0.03 kJ in 7.7 hr (Exp# 050925),

Q_{ex} = 4.44 ± 0.97 kJ in 7.5 hr (Exp# 051205).

Zhang & Dash, Proc. ICCF13, p. 202.

(2) Pre-electrolysis

2nd run gave more excess heat than that of 1st run:

Pd #	Run 1		Run 2	
	Exp. #	P_{ex}/mW	Exp. #	P_{ex}/mW
A	050101	33 ± 13	050103	198 ± 16
C	060209	0	060211	108 ± 29
E	051127	0	051129	215 ± 56
F1	051012	371 ± 60	051015	461 ± 20
F2	051021	247 ± 87	051024	386 ± 38
H	060404	50 ± 7	060406	129 ± 14
H	060412	81 ± 21	060413	119 ± 11

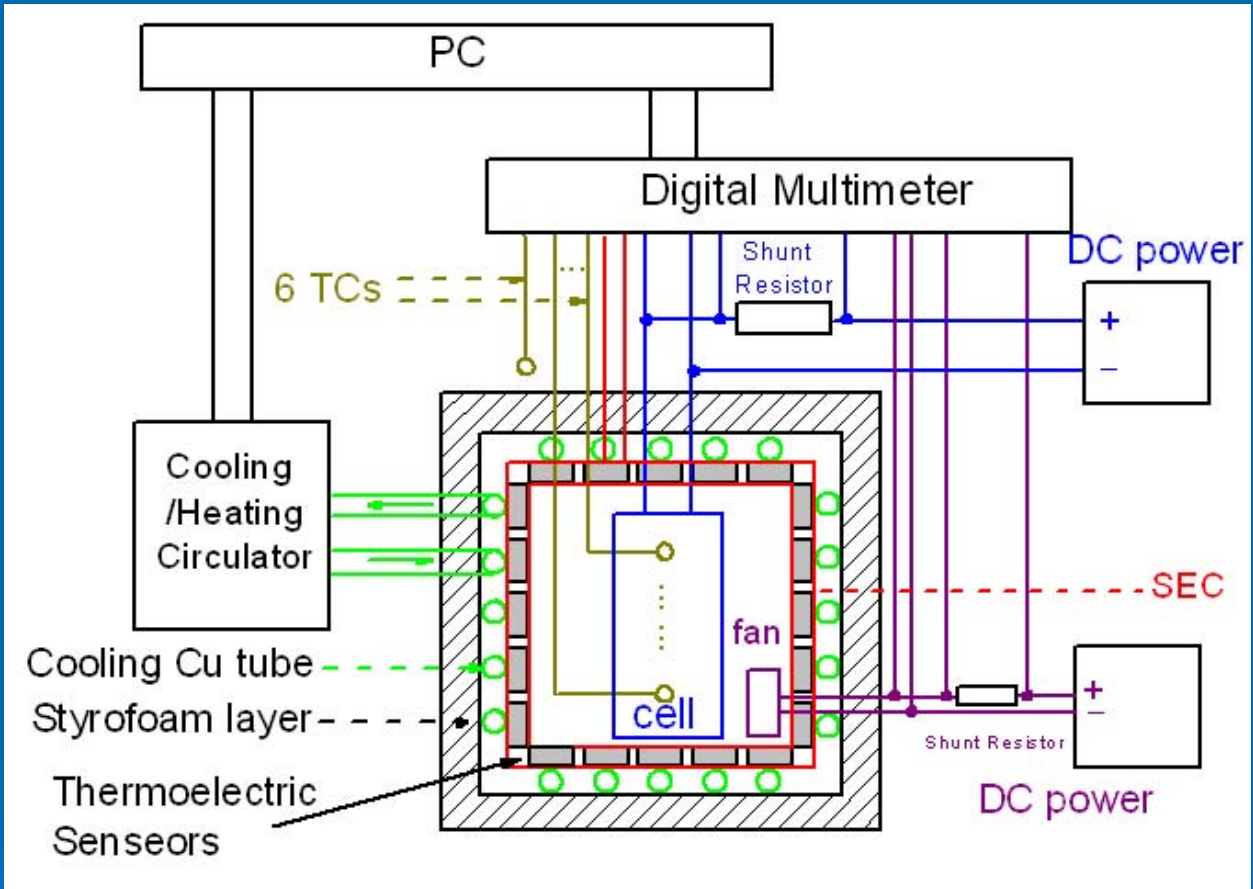
Zhang & Dash, Proc. ICCF13, p. 202.

First run should be the activation process.
This process is intended utilized in excess heat reproducibility.

2. Experimental setup

- 2.1. Calorimetric system
- 2.2. Electrolytic Cell

2.1. Calorimetric system



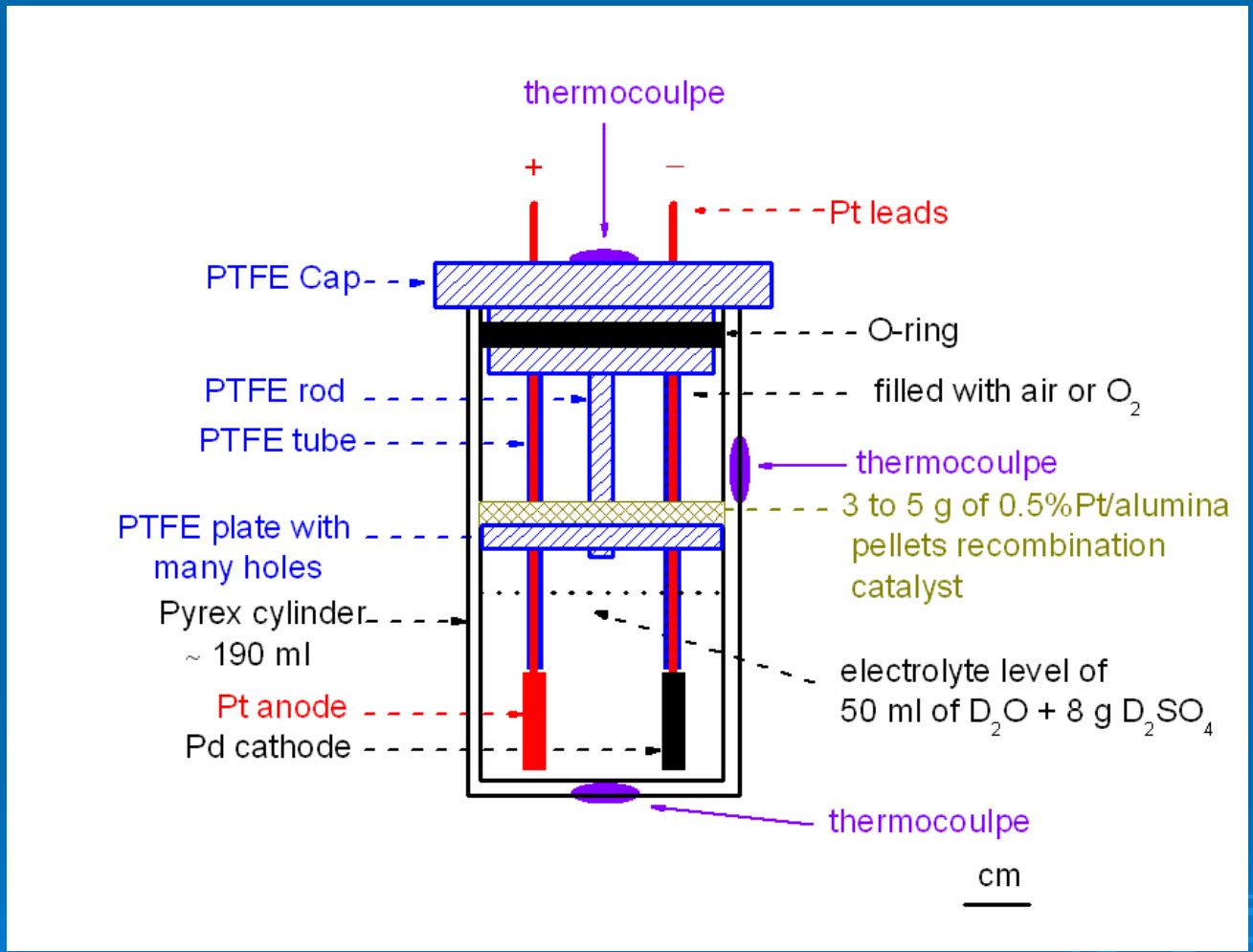
Schematic of calorimetry system

Zhang, Dash & Zhang, Proc. ICCF14;
Zhang, Acta Thermochim. (submitted);
Zhang, China Patent. 200910085862

Photo of Seebeck Envelope Calorimeter (SEC)

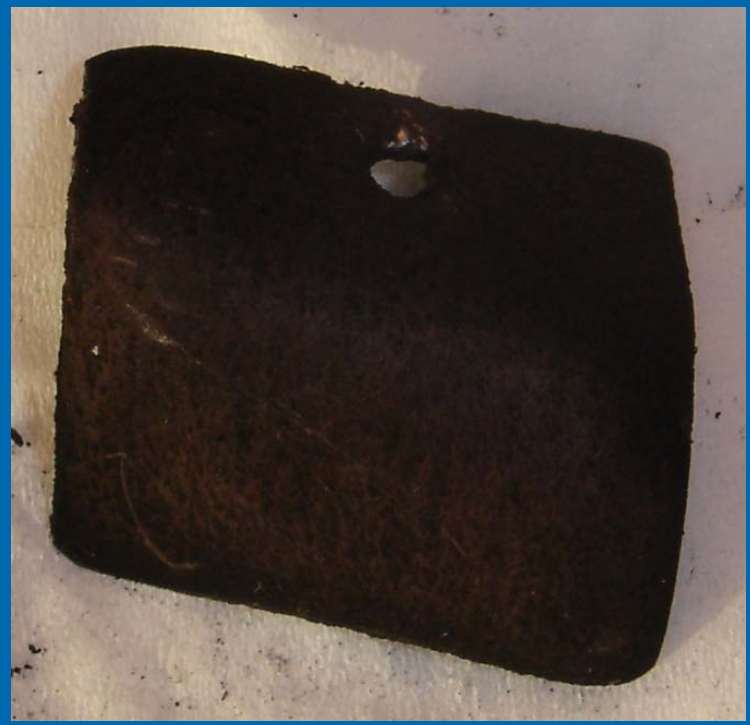
Photo of system

2.2. Electrolytic Cell



Schematic of Pd|D_2O+D_2SO_4 electrolytic cell (ϕ_{in} 4.2 ×14 cm^2)

Photo of cell (ϕ_{in}4.2 $\times$14 cm^2)



Photos of Pd #1 ($0.25 \times 25 \times 25$ mm^2) before (left) and after (right) electrolysis.

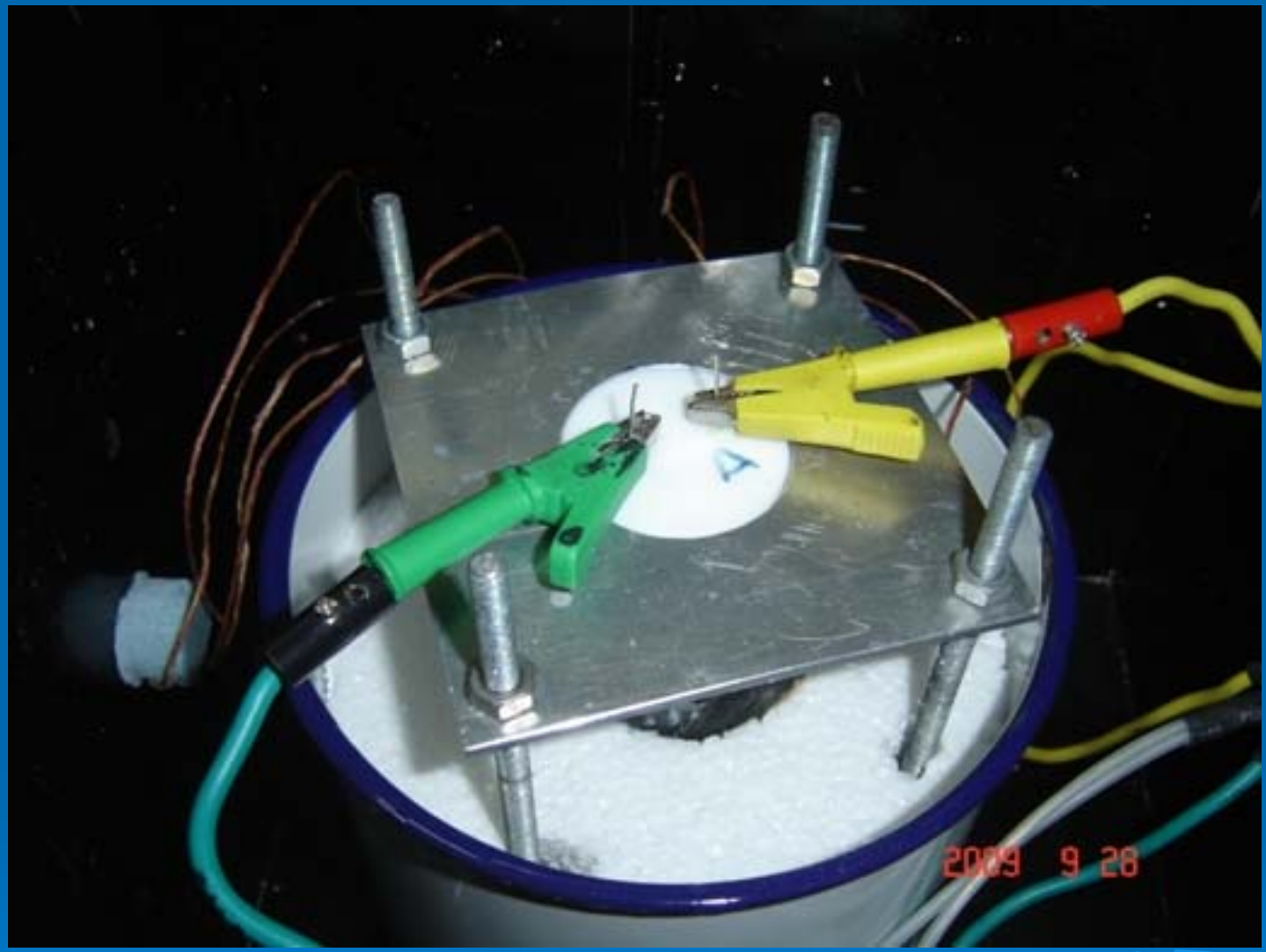


Photo of Pd|D_2O cell in SEC

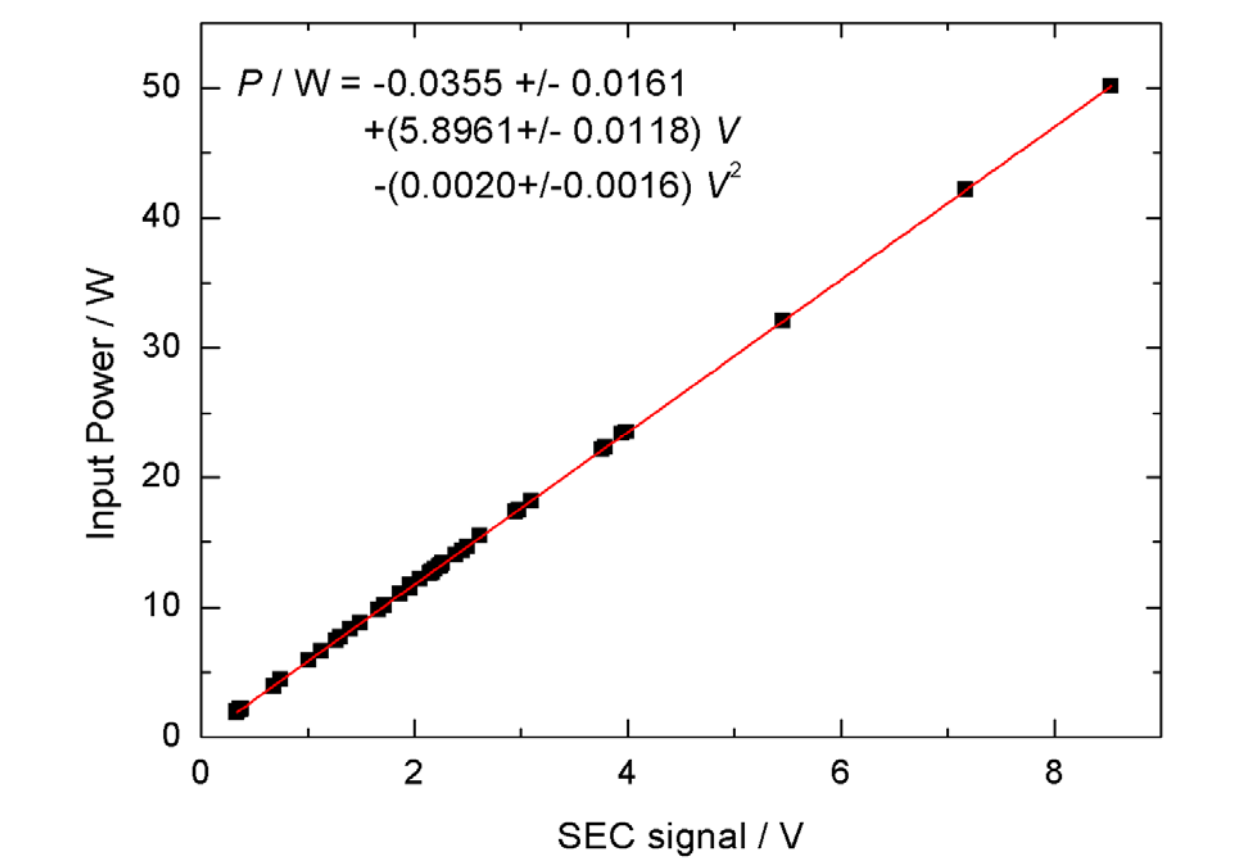
3. Calorimetric Results

- 3.1. Calibration
- 3.2. Excess heat from Pd plate

3.1. Calibration and contrast experiments

3.1.1. Calibration using resistance heater
3.1.2. Pt|D_2O electrolysis
3.1.3. dead Pd|D_2O electrolysis
3.1.4. Pd|H_2O electrolysis

3.1.1. Calibration using resistance heater

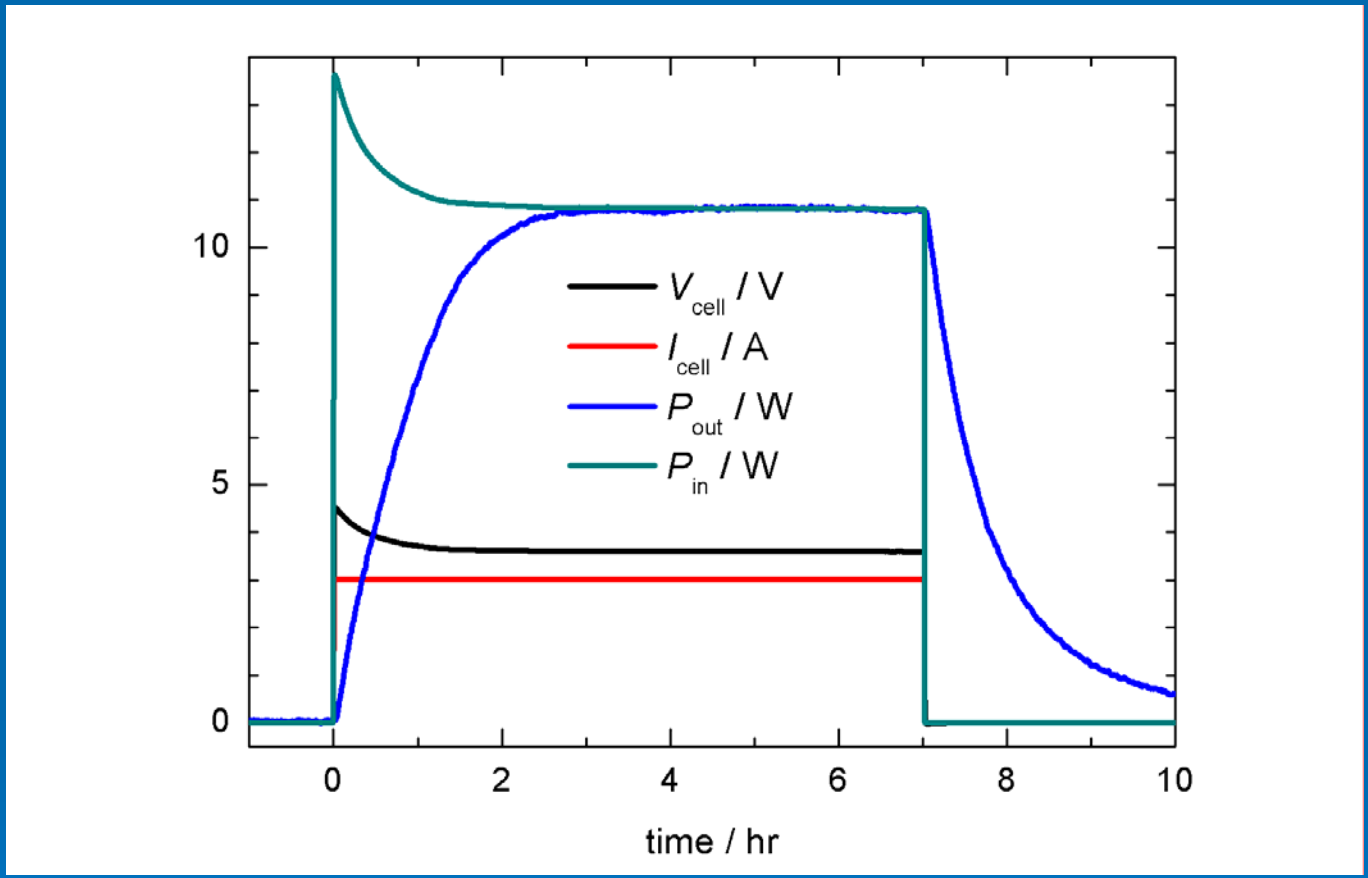


Input powers: 2 to 50 W (55 data)

Duration: Jul 2008 to Sep 2009

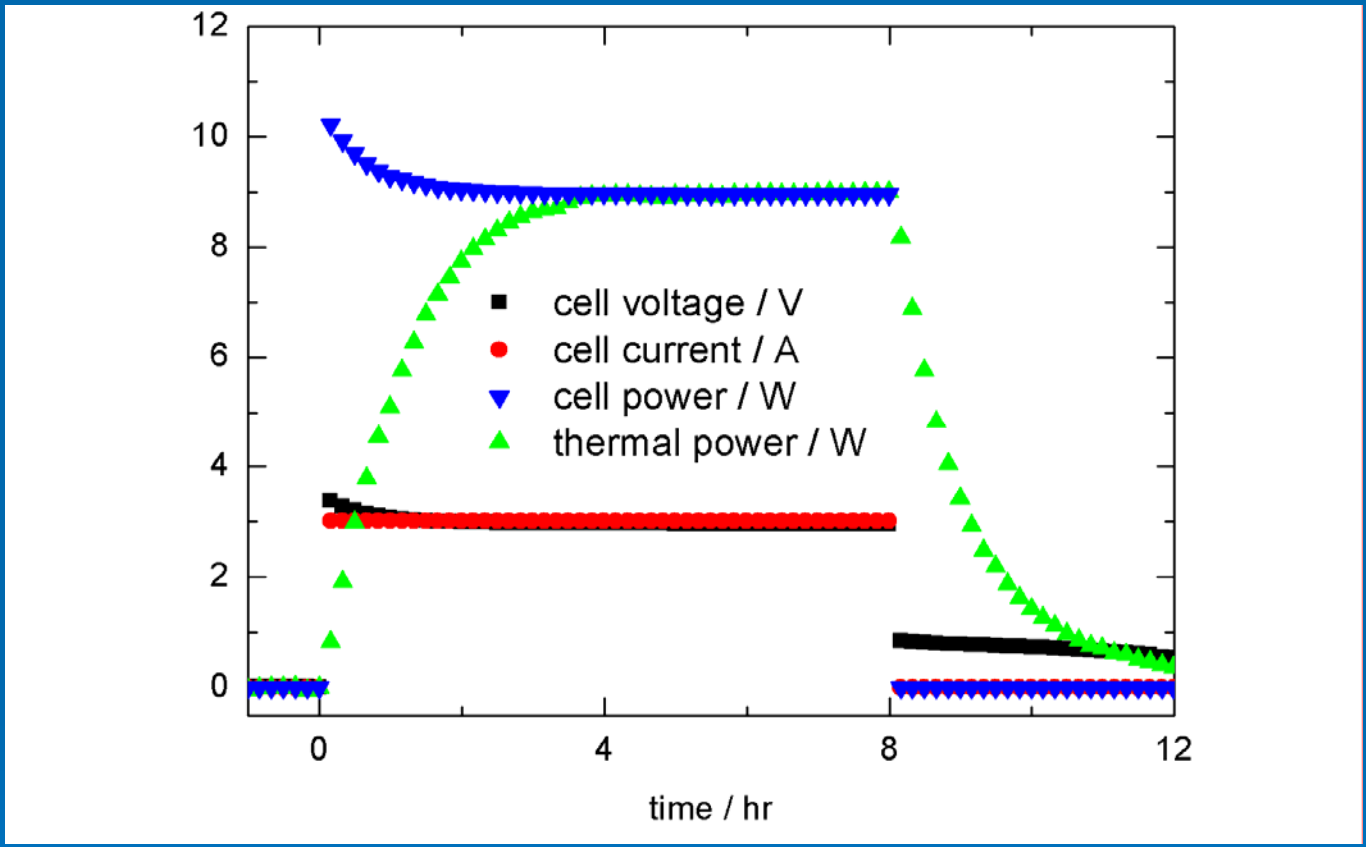
R^2 = 0.99997, Residual Sum of Squares = 0.1661, mean square = 0.0031.

3.1.2. Pt|D_2O electrolysis



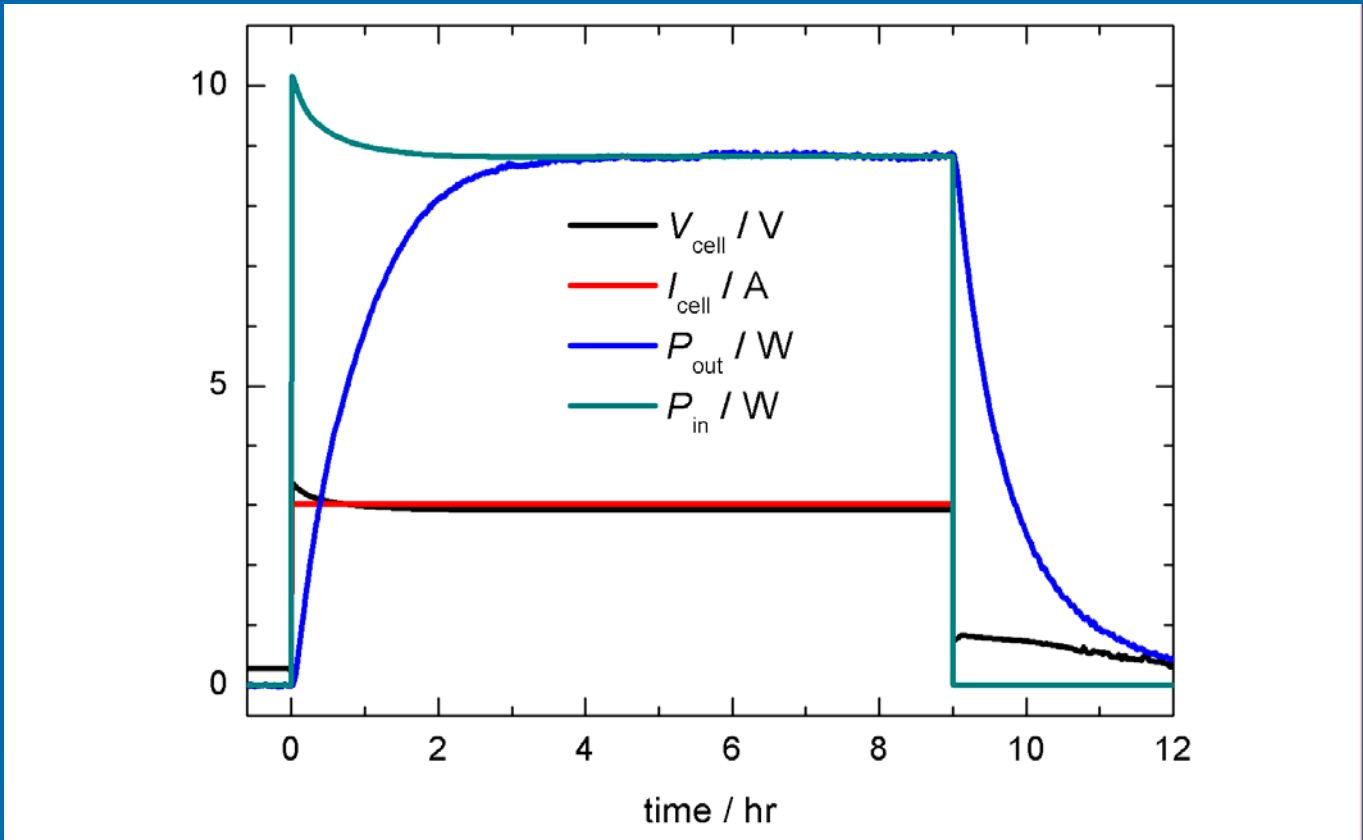
Calorimetry of Pt|D_2O system (Exp. #090824).
P_{in} = 10.819±0.007 W, P_{ex} = 1±24 mW, 0.01% (4.5 to 7 hr);
Q_{in} = 278.20±0.06 kJ, Q_{ex} = –0.29 ± 1.25 kJ, –0.10%;
Including 84 mg of mass loss: Q_{ex} = 0.95 ± 1.26 kJ, 0.34%.

3.1.3. dead Pd|D_2O electrolysis



Calorimetry of dead Pd|D_2O system (#090622).
P_{in} = 8.9556±0.0029 W, P_{ex} = –0.4±22 mW, –0.004% (5 to 8 hr);
Q_{in} = 262.38±0.05 kJ, Q_{ex} = –0.55 ± 0.90 kJ, –0.21%;
Including 22 mg of mass loss: Q_{ex} = –0.22 ± 0.90 kJ, –0.08%.

3.1.4. Pd|H_2O electrolysis



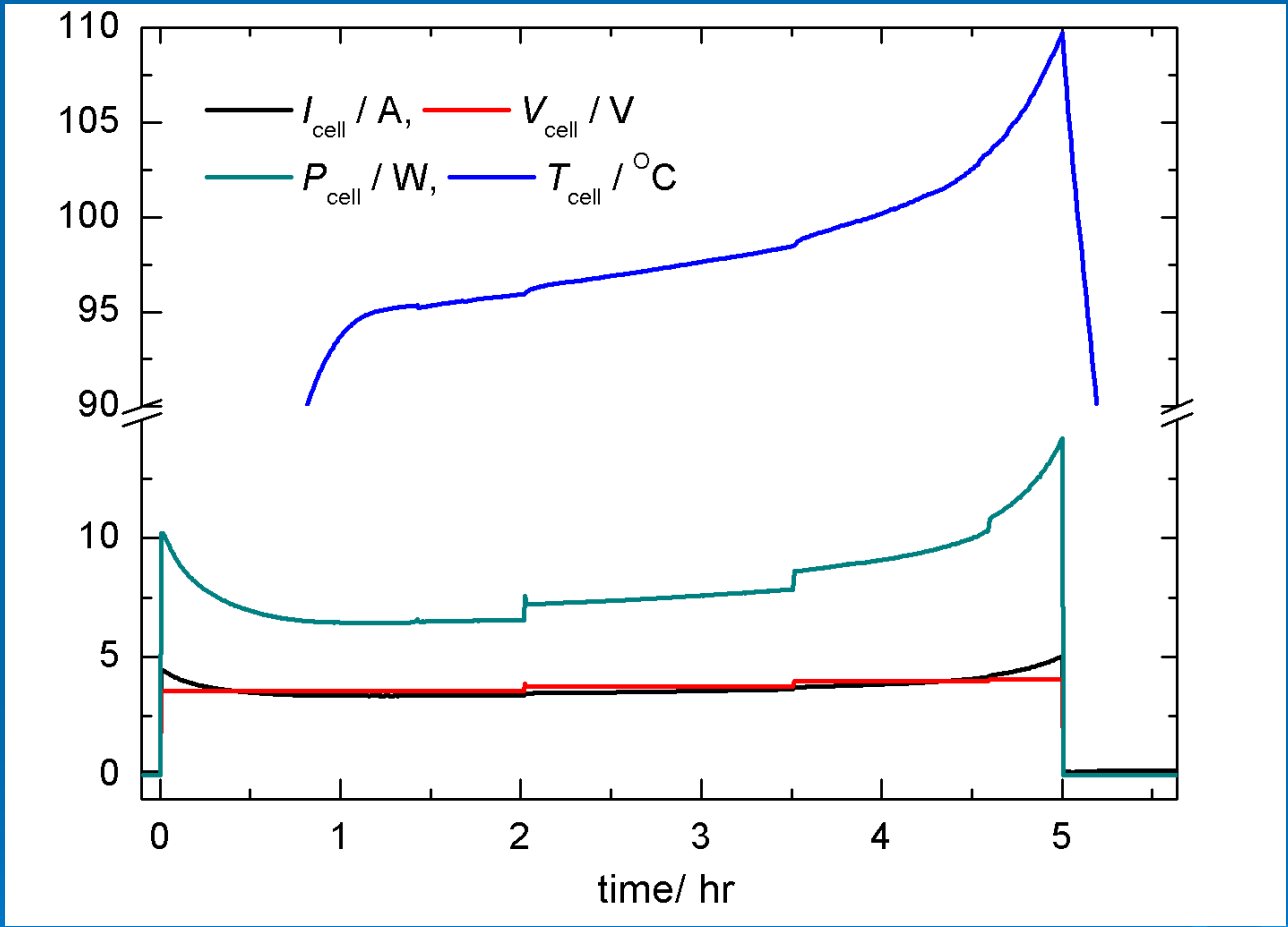
Calorimetry of Pd|H_2O system (#091002).
P_{in} = 8.824±0.004 W, P_{ex} = 6±29 mW, 0.07% (4 to 9 hr);
Q_{in} = 287.98±0.06 kJ, Q_{ex} = –0.51 ± 1.16 kJ, –0.18%;

Including 38 mg of mass loss: Q_{ex} = 0.06 ± 1.17 kJ, 0.02%.

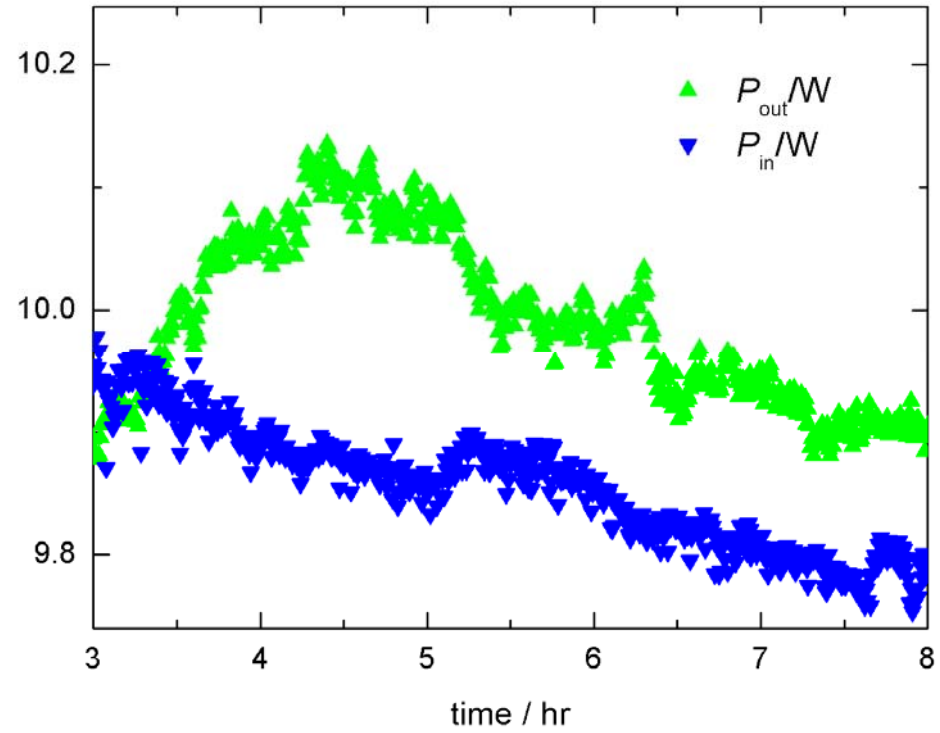
3.2. Excess heat from Pd plate

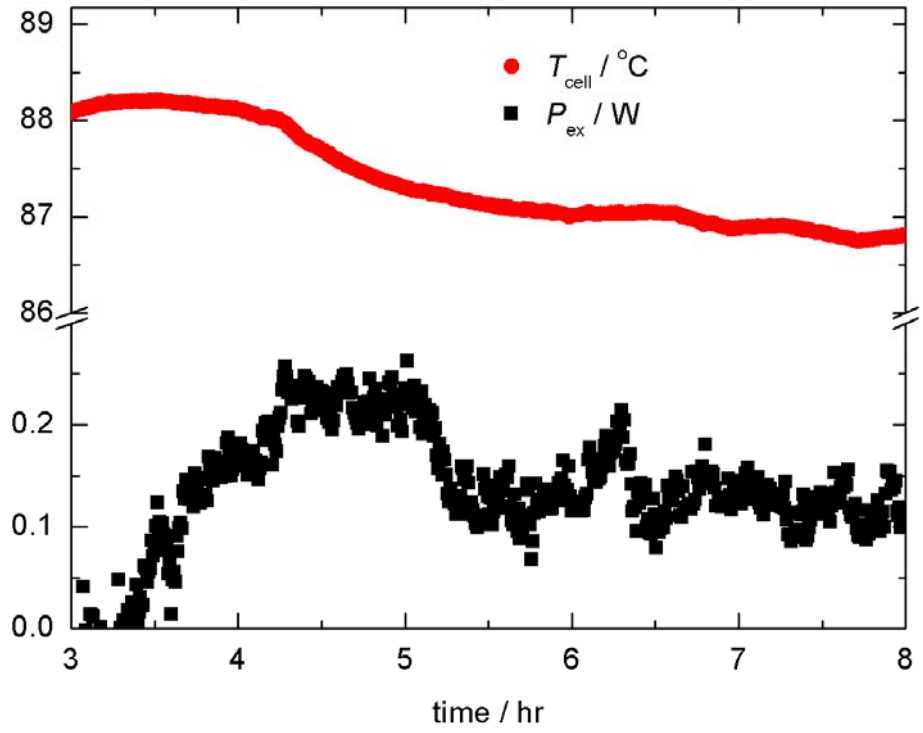
3.2.1. Excess powers on pretreatments
3.2.2. Excess powers for different samples
3.2.3. Excess powers and cell’s resistance

3.2.1. Effects of pre-electrolysis on excess powers

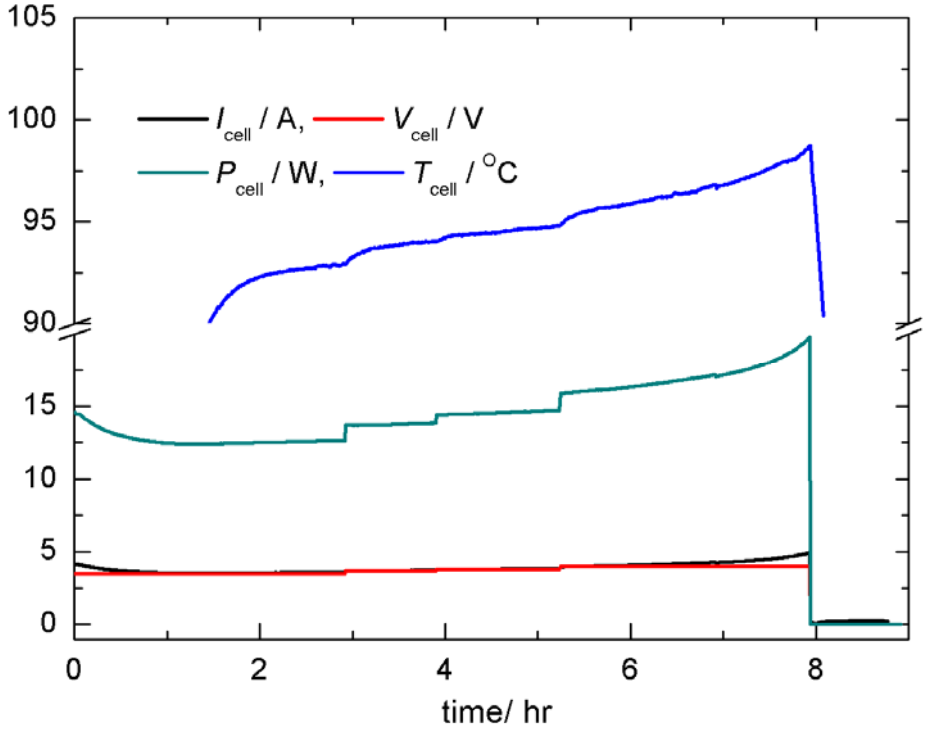


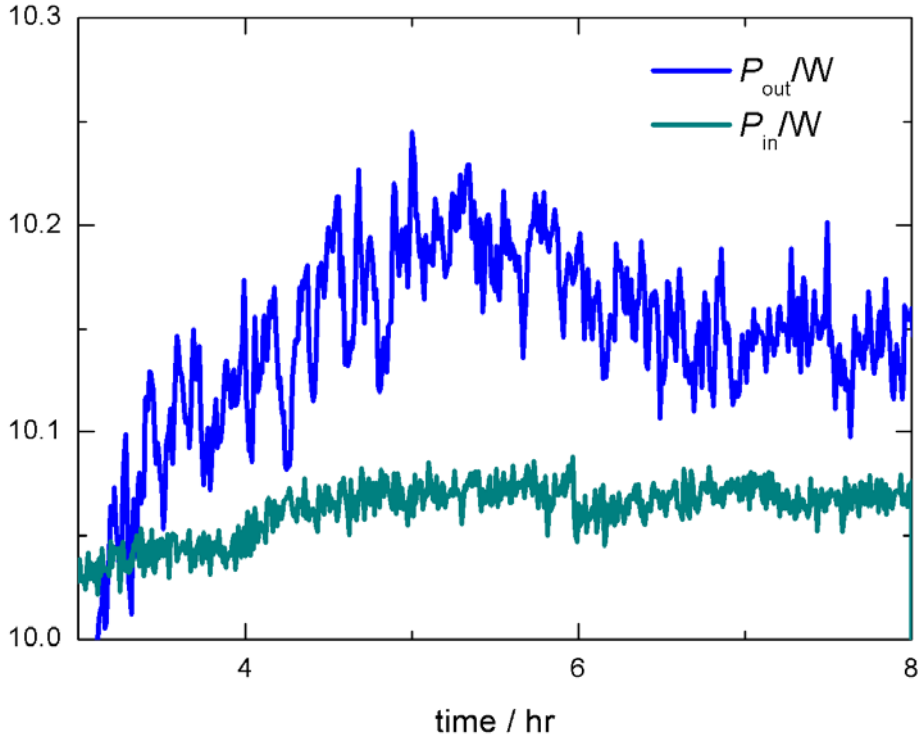
Sample activation, pre-electrolysis in an open cell (Exp. # 081220). 3.5 A × 2 hr + 3.7 A × 1.5 hr + 3.9 A × 1 hr + 4 A × 0.5 hr. T_{max} = 110 °C.





Excess power after activation (Exp. # 081223).
Pd#1, 3 A (0.24 A/cm^2)× 8 hr, T_{SEC} = 25.00 °C
$P_{ex,max}$ = 0.220 ± 0.016 W (4.5 to 5 hr);
$P_{ex,stable}$ = 0.120 ± 0.018 W (7 to 8 hr).
Q_{ex} = 2.46 ± 0.33 kJ.





Left: Sample activation, pre-electrolysis in an open cell (Exp. # 090521). Pd#2, 3.5 A × 3 hr + 3.7 A × 1 hr + 3.9 A × 1.3 hr + 4 A × 2.7 hr. T_{max} = 99 °C. Right: Excess power after activation (Exp. #090525). Pd#2, 3 A (0.24 A/cm2) × 8 hr, T_{SEC} = 25.00 °C, P_{ex} = 0.120 ± 0.020 W (5 to 6 hr).

3.2.2. Excess powers for different samples

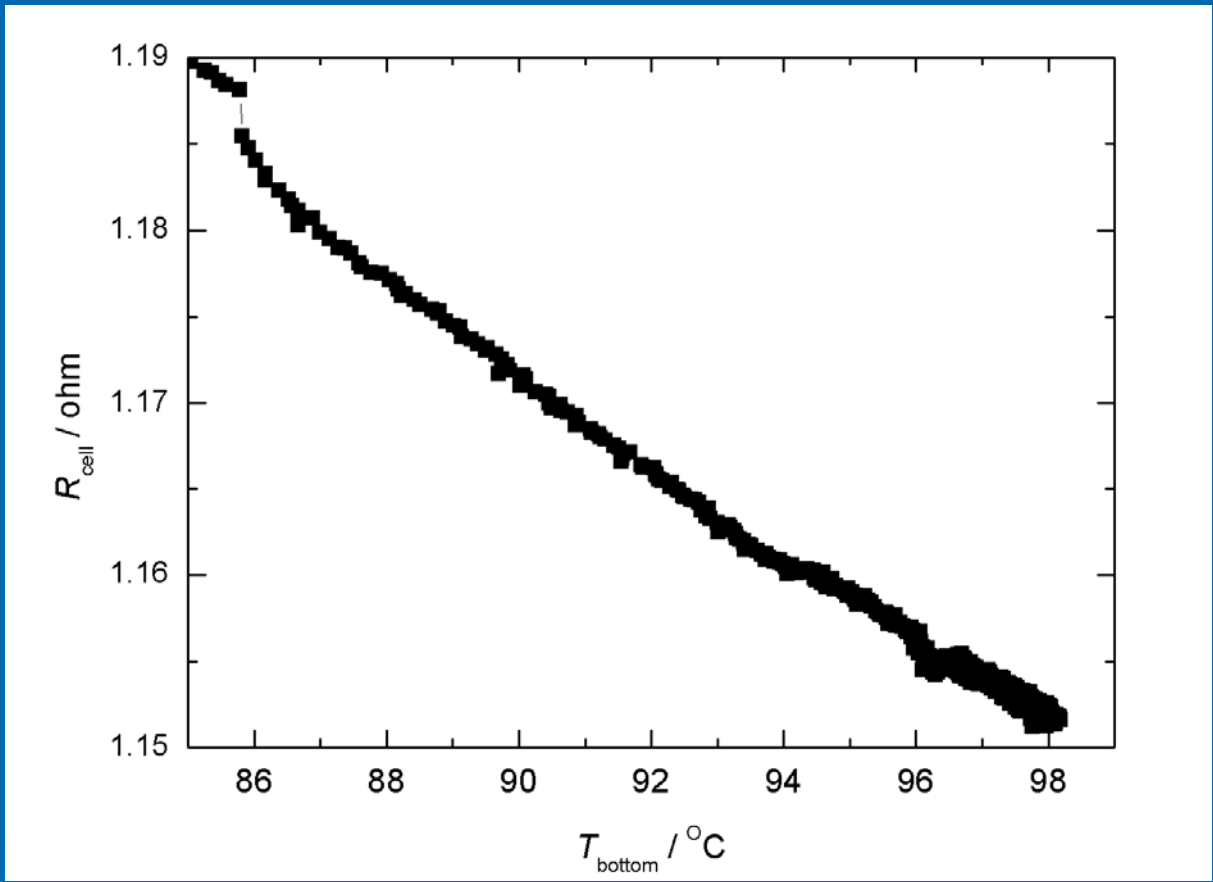
Summary of different Pd samples

Pd #	size/mm^3	$P_{ex,max}$ /mW	Reproducibility	Sample source
1	$0.25 \times 25 \times 25$	220 ± 16	21/35	Alfa Aesar, cold rolled, Provided by John Dash
2	$0.25 \times 25 \times 25$	120 ± 20	6/7	
3	$0.05 \times 11 \times 31$	0	0/3	GRINM, Beijing, cold rolled
4	$0.50 \times 10 \times 30$	0	0/5	Provided by D.L. Wang

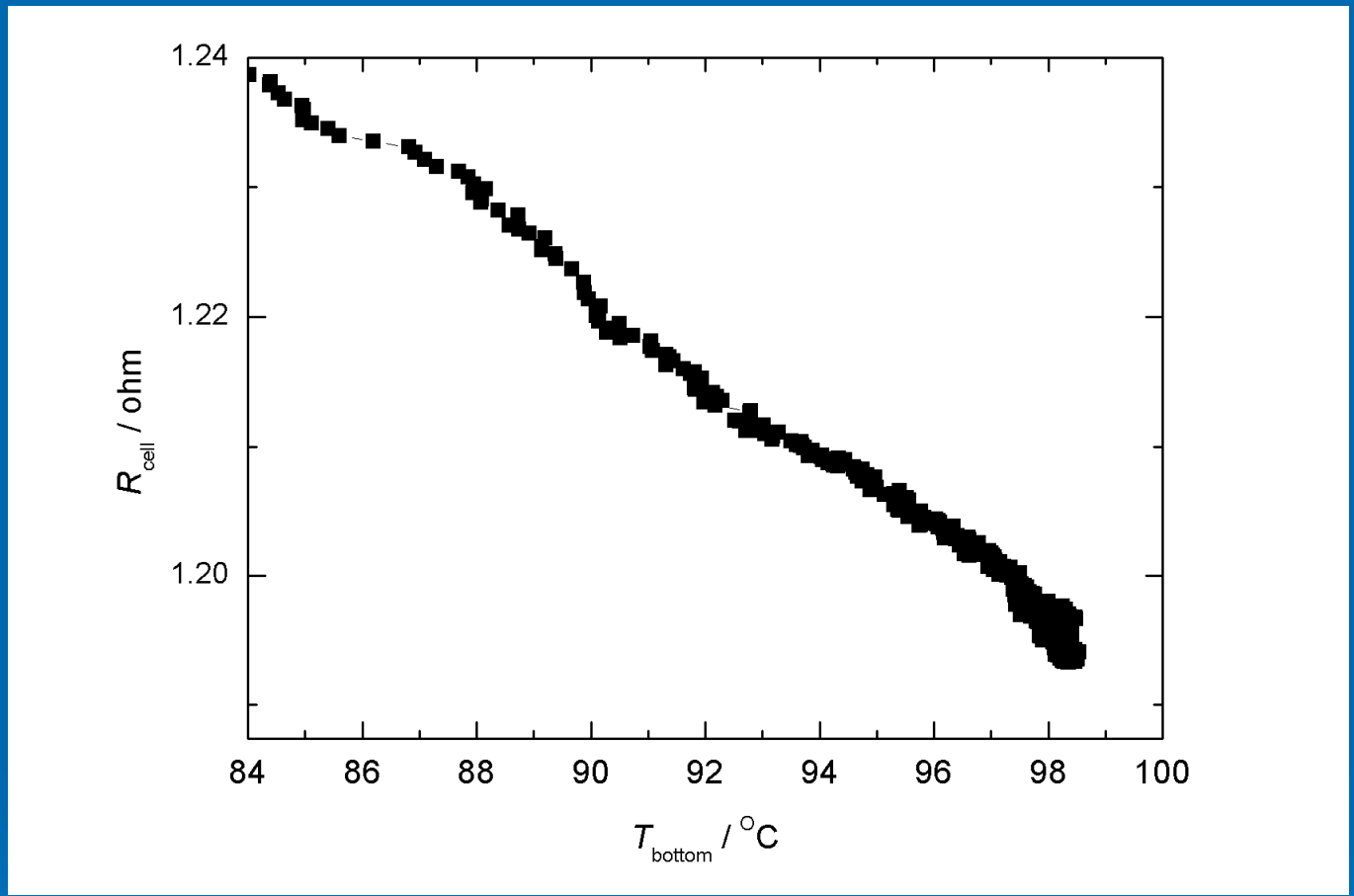
3.2.3. Excess powers and cell's resistance

(1) *R* vs. *T* (no excess heat)
(2) *R* vs. *T* (excess heat)

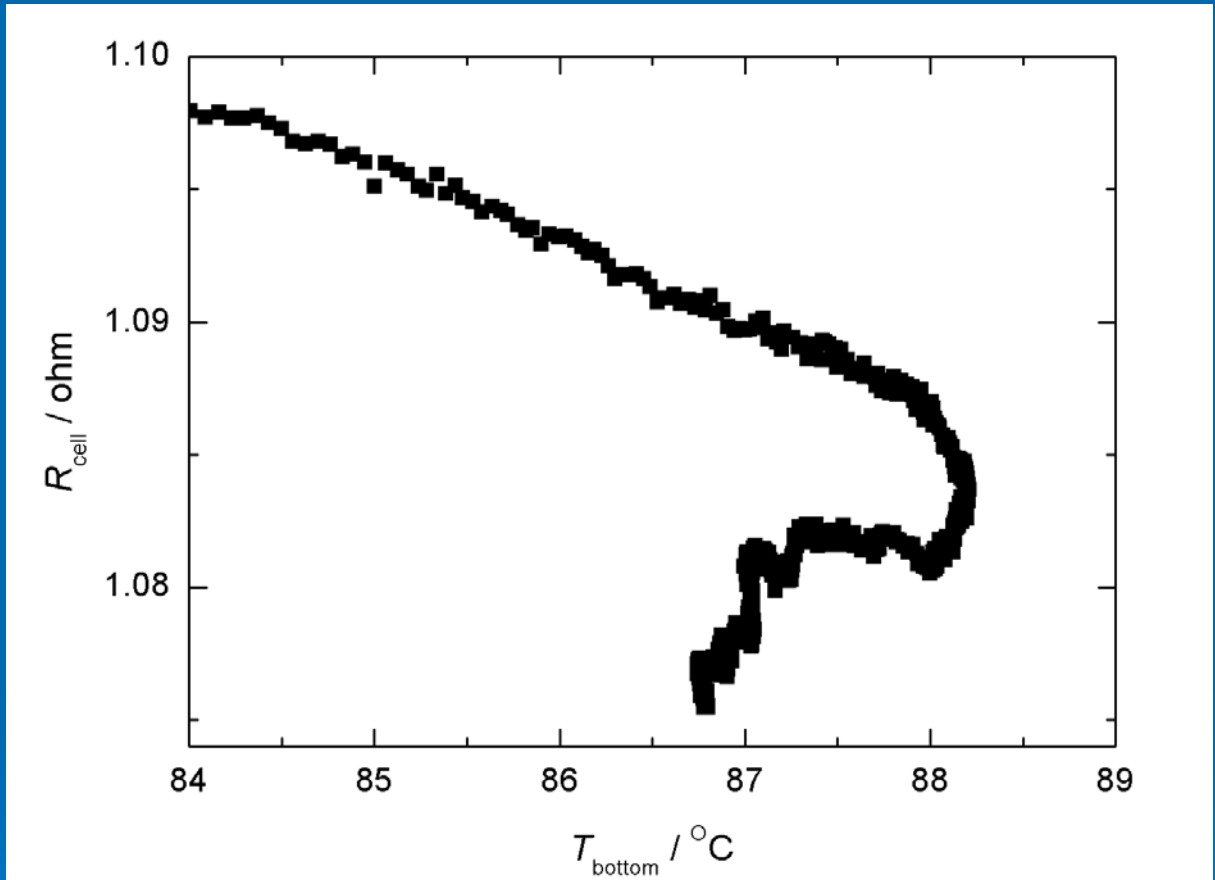
R **=** cell's resistance
T = cell's temperature



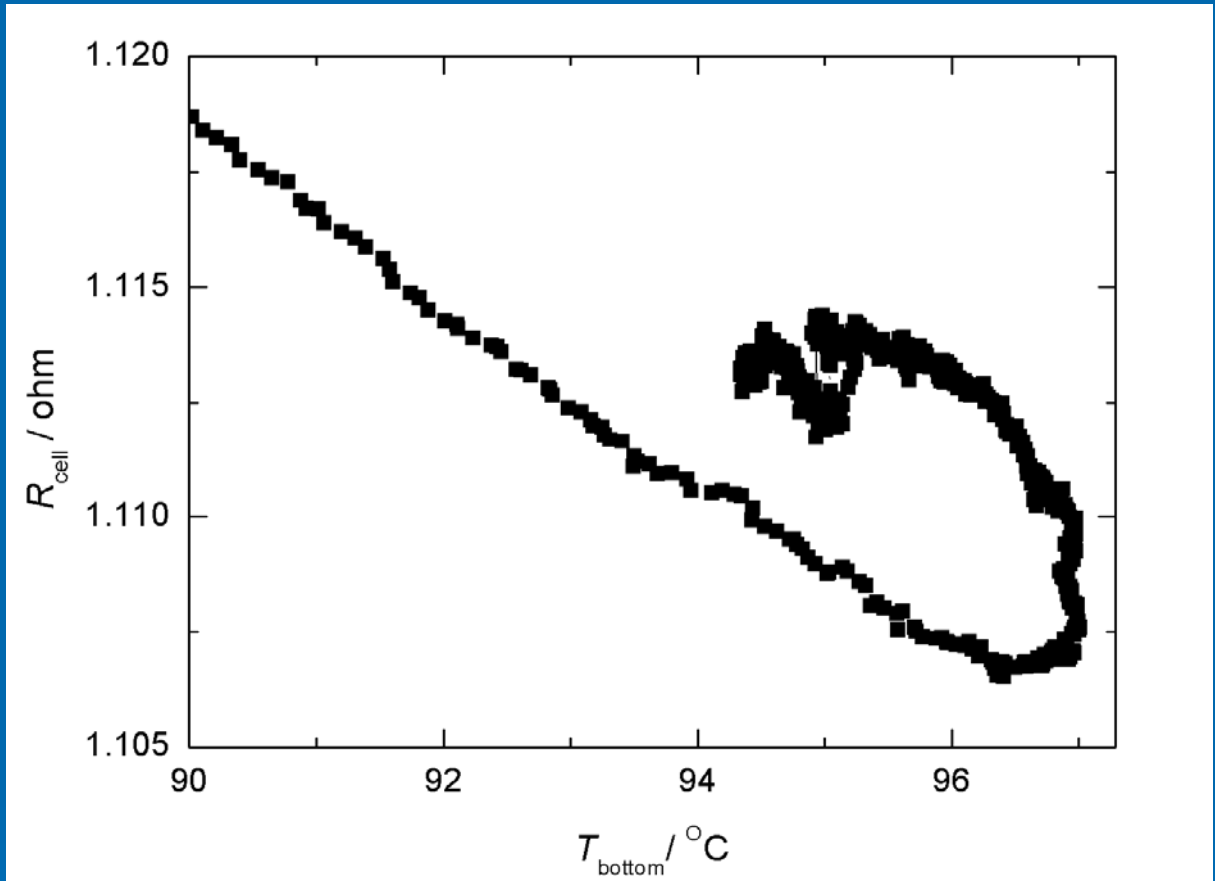
- (1a) *R* vs. *T* without excess power produced (Pd#1, Exp. #090902, $P_{ex} = -15 \pm 25$ mW).



- (1b) *R* vs. *T* without excess power produced (Pt cathode, P_{ex} = 1±24 mW, Exp. #090824).



- (2b) *R* vs. *T* with excess power produced (Pd#1, Exp. #081223, $P_{ex} = 0.220 \pm 0.016$ W).



(2b) *R* vs. *T* with excess power produced (Pd#2, Exp. #090525, P_{ex} = 0.120 ± 0.020 W).

4. Conclusions

- (1) Clear evidence of excess heat in Pd|D_2O + D_2SO_4 electrolytic system.
- (2) Pre-electrolysis in open cells is an easy way to reproduce excess heat in subsequent electrolysis in closed cells.
- (3) Cell's resistances change irreversible with cell's temperature when excess heats appear.

Acknowledgments

- Prof. J. Dash, Z.-L. Zhang
- NSFC 20673129 & 20973185
- 973 Program 2009CB226113

Thank you