We have focused on the reproducibility of excess heat in Pd|D_2O electrolytic cells for some years [1–3]. It was found that excess heats can be reproduced under proper procedure and excess heats occur instantly after electrolyzing for a few hours rather than several days or months. The most important characteristics of excess heat production are following points:

(1) The pretreatment of palladium sample at high temperature is necessary.

(2) Temperature increment during electrolysis is a key factor [2].

(3) Noises of cell voltage decrease when excess heats occur during galvanostatic electrolysis at some time.

Experimental details will be reported in the conference.

References:
Characteristics of excess heat in Pd|D$_2$O+D$_2$SO$_4$ 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 $\Delta T$
- (2) Pre-electrolysis
Pd (0.25×25×25 mm³). 3 A (0.24 A/cm²).

\[ Q_{ex} = 0.01 \pm 0.03 \text{ kJ in 7.7 hr (Exp# 050925),} \]

\[ Q_{ex} = 4.44 \pm 0.97 \text{ kJ in 7.5 hr (Exp# 051205).} \]

(2) Pre-electrolysis

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

<table>
<thead>
<tr>
<th>Pd #</th>
<th>Run 1</th>
<th>Run 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exp. #</td>
<td>$P_{ex}/\text{mW}$</td>
</tr>
<tr>
<td>A</td>
<td>050101</td>
<td>$33 \pm 13$</td>
</tr>
<tr>
<td>C</td>
<td>060209</td>
<td>$0$</td>
</tr>
<tr>
<td>E</td>
<td>051127</td>
<td>$0$</td>
</tr>
<tr>
<td>F1</td>
<td>051012</td>
<td>$371 \pm 60$</td>
</tr>
<tr>
<td>F2</td>
<td>051021</td>
<td>$247 \pm 87$</td>
</tr>
<tr>
<td>H</td>
<td>060404</td>
<td>$50 \pm 7$</td>
</tr>
<tr>
<td>H</td>
<td>060412</td>
<td>$81 \pm 21$</td>
</tr>
</tbody>
</table>

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
2.2. Electrolytic Cell

Schematic of Pd|D$_2$O+D$_2$SO$_4$ electrolytic cell ($\phi$ in 4.2 × 14 cm$^2$)
Photo of cell ($\phi_{in} 4.2 \times 14 \text{ cm}^2$)
Photos of Pd #1 (0.25 × 25 × 25 mm²) before (left) and after (right) electrolysis.
Photo of Pd|D$_2$O 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|D₂O electrolysis
3.1.3. dead Pd|D₂O electrolysis
3.1.4. Pd|H₂O electrolysis
3.1.1. Calibration using resistance heater

Input powers: 2 to 50 W (55 data)
Duration: Jul 2008 to Sep 2009

\[ P / W = -0.0355 \pm 0.0161 \\
\pm (5.8961 \pm 0.0118) V \\
\pm (0.0020 \pm 0.0016) V^2 \]

\[ R^2 = 0.99997, \text{ Residual Sum of Squares} = 0.1661, \]
mean square = 0.0031.
3.1.2. Pt|D$_2$O electrolysis

Calorimetry of Pt|D$_2$O system (Exp. #090824).

$P_{\text{in}} = 10.819 \pm 0.007$ W, $P_{\text{ex}} = 1 \pm 24$ mW, 0.01% (4.5 to 7 hr);

$Q_{\text{in}} = 278.20 \pm 0.06$ kJ, $Q_{\text{ex}} = -0.29 \pm 1.25$ kJ, −0.10%;

Including 84 mg of mass loss: $Q_{\text{ex}} = 0.95 \pm 1.26$ kJ, 0.34%.
Calorimetry of dead Pd|D$_2$O system (#090622).

$P_{\text{in}} = 8.9556 \pm 0.0029$ W, $P_{\text{ex}} = -0.4 \pm 22$ mW, $-0.004\%$ (5 to 8 hr);

$Q_{\text{in}} = 262.38 \pm 0.05$ kJ, $Q_{\text{ex}} = -0.55 \pm 0.90$ kJ, $-0.21\%$;

Including 22 mg of mass loss: $Q_{\text{ex}} = -0.22 \pm 0.90$ kJ, $-0.08\%$. 
3.1.4. Pd|H₂O electrolysis

Calorimetry of Pd|H₂O system (#091002).

\[ P_{\text{in}} = 8.824 \pm 0.004 \, \text{W}, \quad P_{\text{ex}} = 6 \pm 29 \, \text{mW}, \quad 0.07\% \ (4 \text{ to } 9 \text{ hr}); \]
\[ Q_{\text{in}} = 287.98 \pm 0.06 \, \text{kJ}, \quad Q_{\text{ex}} = -0.51 \pm 1.16 \, \text{kJ}, \quad -0.18\%; \]

Including 38 mg of mass loss: \[ Q_{\text{ex}} = 0.06 \pm 1.17 \, \text{kJ}, \quad 0.02\%. \]
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. $T_{\text{max}} = 110 \, ^\circ\text{C}$. 
Excess power after activation (Exp. # 081223).
Pd#1, 3 A (0.24 A/cm$^2$) $\times$ 8 hr, $T_{SEC} = 25.00$ °C

$P_{ex,max} = 0.220 \pm 0.016$ W (4.5 to 5 hr);
$P_{ex,stable} = 0.120 \pm 0.018$ W (7 to 8 hr).

$Q_{ex} = 2.46 \pm 0.33$ 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. $T_{\text{max}} = 99 \, ^{\circ}\text{C}$.

Right: Excess power after activation (Exp. #090525). Pd#2, 3 A (0.24 A/cm²) × 8 hr, $T_{\text{SEC}} = 25.00 \, ^{\circ}\text{C}$, $P_{\text{ex}} = 0.120 \pm 0.020$ W (5 to 6 hr).
### 3.2.2. Excess powers for different samples

#### Summary of different Pd samples

<table>
<thead>
<tr>
<th>Pd #</th>
<th>size/mm³</th>
<th>$P_{\text{ex, max}}$/mW</th>
<th>Reproducibility</th>
<th>Sample source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.25 × 25 × 25</td>
<td>220 ± 16</td>
<td>21/35</td>
<td>Alfa Aesar, cold rolled, Provided by John Dash</td>
</tr>
<tr>
<td>2</td>
<td>0.25 × 25 × 25</td>
<td>120 ± 20</td>
<td>6/7</td>
<td>GRINM, Beijing, cold rolled</td>
</tr>
<tr>
<td>3</td>
<td>0.05 × 11 × 31</td>
<td>0</td>
<td>0/3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.50 × 10 × 30</td>
<td>0</td>
<td>0/5</td>
<td>Provided by D.L. Wang</td>
</tr>
</tbody>
</table>
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, $P_{\text{ex}} = -15 \pm 25$ mW).
(1b) $R$ vs. $T$ without excess power produced (Pt cathode, $P_{\text{ex}} = 1\pm24$ 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, $P_{\text{ex}} = 0.120 \pm 0.020$ W).
4. Conclusions

- (1) Clear evidence of excess heat in Pd|D₂O + D₂SO₄ 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.
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Thank you