SEEBECK ENVELOPE CALORIMETRY WITH A PD|D$_2$O+H$_2$SO$_4$ ELECTROLYTIC CELL[*]

WU-SHOU ZHANG[†,1,2], JOHN DASH[1], QIONGSHU WANG[1]

^{1}Low Energy Nuclear Laboratory, Portland State University, Portland, OR 97207-0751, USA

^{2} Institute of Chemistry, Chinese Academy of Sciences, P.O. Box 2709, Beijing 100080, China

Anomalous excess heat in Pd|D$_2$O+H$_2$SO$_4$ electrolytic cells was confirmed using an accurate method of heat measurement, Seebeck Envelope Calorimetry. A cell was placed in the calorimeter, which measures the output heat flux directly and avoids many of the problems other methods have. The maximum excess power thus far was 1.3 W (or 11 W cm^{-3}) with input power of 13 W at a current density of 0.4 A cm^{-2}. Calibrations were carried out before and after electrolysis experiments using a Pt|H$_2$O+H$_2$SO$_4$ electrolytic cell, a dummy cell with inner resistor, or a pure resistor. Different calibrations gave consistent device constants within experimental error. Pd cathodes were analyzed by scanning electron microscopy and energy dispersive spectrometry. Unexpected elements were observed on the sample surface after electrolysis.

1 Introduction

After the successful public demonstrations of excess heat in Pd|D$_2$O+H$_2$SO$_4$ electrolytic cells at Boston (ICCF10) in 2003 [1,2], we confirmed this anomalous effect using a more accurate calorimeter: a Seebeck Envelope Calorimeter (SEC). The SEC is a cube; the electrolysis cell is placed inside it. The SEC converts the heat flux through the six walls of the cube into a voltage signal using many thermocouples distributed uniformly in the walls. Many problems of isoperibolic calorimetry and mass flow calorimetry can be avoided by this method [3,4].

In this report we present the calorimetric results for the Pd|D$_2$O+H$_2$SO$_4$ electrolytic cell, results with Ti added to the D$_2$O+H$_2$SO$_4$ electrolyte, and the results of analysis of the Pd cathodes.

2 Experimental set-up

Closed cells are similar to that used before [1,2] except that the height is less in order to fit into the SEC as shown in Fig. 1(a) and described below. The electrolytic cell is a Pyrex cylinder (capacity is about 280 ml, ϕ_{in} = 50.7 mm and ϕ_{out} = 57.0 mm, wall thickness = 3.2 mm, h = 142 mm). A PTFE female top cap is ϕ 65 mm $\times$ 20 mm outside dimensions and ϕ 57 mm $\times$ 16 mm of inside. It has two holes, 0.5 mm diameter each, for the electrode lead wires. A PTFE plate (ϕ 50 mm $\times$ 8 mm) is used to suspend the recombination catalyst above the electrode. It has many holes of ϕ 0.8 mm, and also has two holes, 1 mm diameter each, for the electrode lead wires. A PTFE rod is fastened to

2

the perforated plate and the top cap ensures that the perforated plate is at a fixed distance above the electrolyte. A gasket (ϕ_{in} = 35 mm, ϕ_{out} = 57 mm, wall thickness = 2.5 mm) made of ethylene propylene (resistant to sulfuric acid) is used to seal the top cap against the top edge of Pyrex cylinder.

The Pd cathode is cut from a 99.9% palladium foil with $0.5 \times 10 \times 10$ mm^3 (Alfa Aesar, Stock #11514). It is then cold rolled to the desired thickness. The platinum anode is a foil $37.5 \times 23.8 \times 0.12$ mm^3. Pt leads are made of wire ($\phi 1$ mm $\times \sim 150$ mm) covered with heat-shrink Teflon tube.

The electrolyte is heavy water (99.9 at.%, Aldrich catalog #347167) mixed with 96.4% H_2SO_4 (J.T. Baker, Lot # K10030) by the volume ratio of 6.7:1.
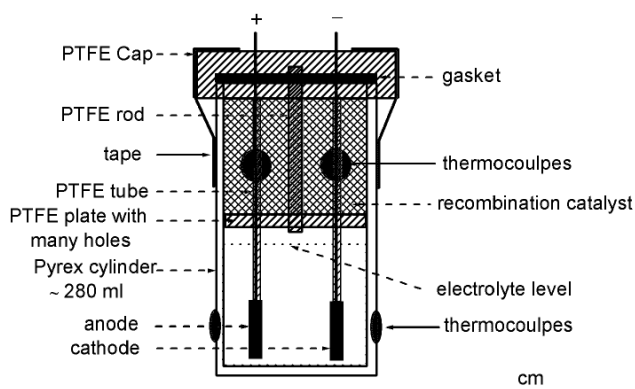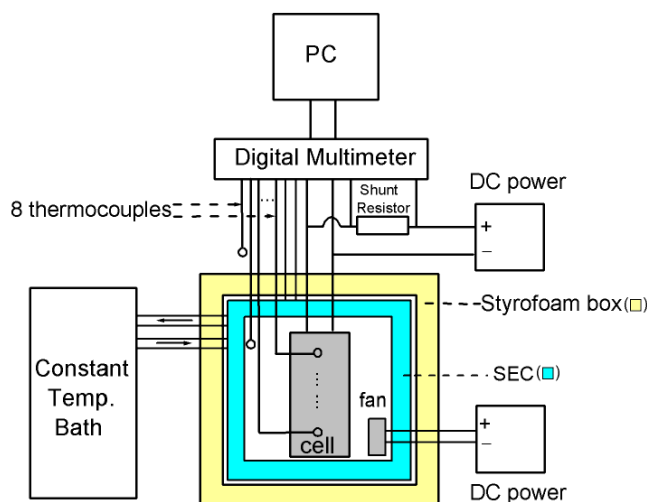

Figure 1(a). Schematic of electrolytic cell.

Figure 1(b). Schematic of calorimetric system.

Two types of catalyst were used in these experiments, one contains 0.5% Pd on coconut charcoal (United Catalysis); another contains 0.5% Pt on 1/8 inch diameter

alumina pellets (Alfa Aesar). Before each experiment, the catalyst was thoroughly dried in an oven at 88°C in order to drive out the liquid adsorbed during previous electrolysis.

A schematic of the calorimetry system is shown in Fig. 1(b). The SEC (Thermonetics Corp.) has inner dimensions of $18.3 \times 18.3 \times 18$ cm^3 (W $\times$ D $\times$ H). A fan (Panaflo®, Model FBA08A12H1A, $80 \times 80 \times 25.5$ mm^3, DC12 V, 173 mA, 2.08 W) is used to eliminate temperature gradients in the SEC [3]. The temperature of the SEC wall ($T_{SEC\ wall}$) is controlled by a constant temperature bath (NESLAB, RTE-111); the temperature stability is ± 0.1°C. The SEC is covered with Styrofoam to avoid the influences of room temperature fluctuations on calorimetry.

An HP 6267B DC power supply (0 to 40 V, 0 to 10 A) is used for galvanostatic electrolysis. The electrolysis current is measured with a shunt resistor, which is a standard resistor of 0.1 Ω with 0.04% precision (Leed & Northrup 4360). The electrolytic cell is placed in the center of the SEC. Eight K-type thermocouples are used to monitor temperatures: one is for ambient temperature outside the SEC; one is for air temperature in the SEC; two are attached on the outside of the cell wall at the middle height of electrolyte; four are attached on the wall at the middle height of catalyst. All data are monitored by a Keithley 2000-20+scan digital multimeter. The data are automatically logged every minute using TestPoint 3.3 software.

The mass of the cell was measured before and after electrolysis using a My Weigh i500 balance (max. 500 g, d = 0.1 g). After Jan 1, 2005 this was replaced with an Ohaus D54 balance (max. 2000 g, d = 0.01 g). The Pd sample is weighed with a Mettler H70 (max. 160 g, d = 0.01 mg).

Calibration experiments are conducted using a Pt|H_2O+H_2SO_4 electrolysis cell, a pure resistor, or a dummy cell with a resistor in it. Calibrations are carried out before and after every electrolysis experiments.

Surface topography and element analysis of the palladium cathode surface is performed using an ISI-SS40 scanning electron microscope (SEM) with an attached Oxford model 5565 energy dispersive spectrometer (EDS).

3   Results

3.1. *Calorimetric results*

Firstly, we present calibration results. A resistor provided by the SEC manufacturer was placed at the center of the SEC. $T_{SEC\ wall}$ was the same as that used for the experimental Pd|D_2O electrochemical cell calorimetry. After the calorimeter reached steady state with the fan turned on, the background signal was stable. Then, power was applied to the resistor. After the output signal reached steady state, the power was turned off. The output signal was monitored during the cool down. The device constant is the quotient of average stable input power to the average net output signal at steady state. The net output signal is the gross output signal minus the signal produced by the power supplied to the fan. For input power of 11 W, the fan power decreases by 23 ± 3 mW (1.4 %) during calibration or calorimetry. The decrease in fan power during calibration is the same magnitude as the decrease during calorimetry, so there should be no net effect on the calculated excess power. One calibration requires about 12 hours.

Figure 2(a) shows the results of one of the calibration experiments. It gave the device constant of 182.34 ± 0.20 W/V. The time constant is 15 minutes here. Due to the large inner volume (6 liter), the time constant of the SEC is mostly determined by the heat capacity and conductivity of the sample under test, rather than the SEC itself.
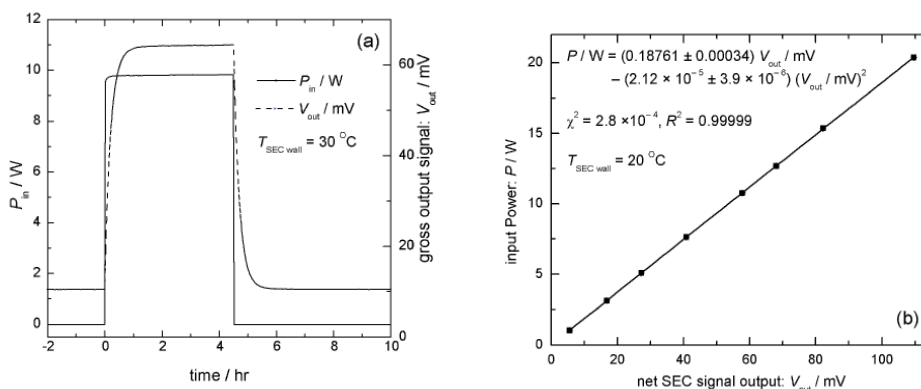

Figure 2. (a) An example of calibration (Exp. No. 051005); (b) calibrations at different input power, where χ^2 is the sum of squared residuals; R^2 is the coefficient of determination (Exp. No. 041228).

Calibrations were performed at input power ranging from about 1 to 20 W. In this range, the device constant changes only slightly, as shown by the equations in Fig. 2(b). This means that the SEC behaves as an ideal calorimeter. The slight non-linear term of the device constant with increasing power is caused by the nonlinear increase in electromotive force produced by the SEC thermocouples. However the device constant varies. For example, there were 11 calibration runs during December 2005. The device constant ranged from 180.6 to 181.8 W/V, a variation of less than 1%. The before-and-after calibrations for an experiment typically give device constants which differ by less than 0.5%. The actual device constant used for calculating the excess power and energy is the average value of those obtained before and after the electrolysis with the same power input as that used in electrolysis.

Besides the resistor, a $Pt|H_2O+H_2SO_4$ electrolytic cell or a dummy cell with a resistor in it was also used to calibrate the SEC. Both of these cells have the same dimensions as that used for $Pd|D_2O+H_2SO_4$ electrolysis; this arrangement could exclude the errors induced by the difference between temperature distributions of working cell and calibration resistor. The results showed that those three different calibrations gave the same device constant within experimental error.

Seven Pd samples have been tested in experiments; four of them gave reproducible excess heat. The calorimetric results for the best sample, Pd-A, are presented here in detail. The sample Pd-A ($9.0 \times 37.2 \times 0.35$ mm^3, total area of 7.08 cm^2, weight 1.3418 g) was cold rolled from 0.5 mm to 0.35 mm thickness. One example of excess heat production and related parameters are shown in Fig. 3.

Fig. 3(a) shows that the power input decreases rapidly in the first two hours because the input power heats the cell, as shown in Fig. 3(b); therefore the electrolyte conductivity

increases and overvoltages on the two electrodes decrease with time. These factors make the cell voltage decrease correspondingly.

Another phenomenon is that the catalyst temperature (indirectly measured on the outer wall of the cell) has some fluctuation possibly because of the coarse grains of charcoal (about $2 \times 3 \times 6$ mm^3) and the inhomogeneous properties of the solid/gas reaction. Fine particles of catalyst produced by pulverizing the large grains can improve the stability and uniformity of temperature. However this method does not improve the catalysis and it makes the catalyst more difficult to handle.
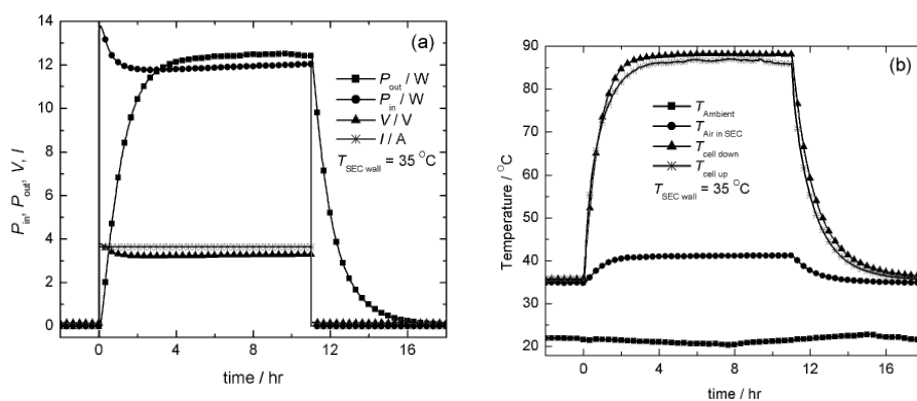

Figure 3. An example of electrochemical calorimetry on the Pd|D$_2$O+H$_2$SO$_4$ cell for sample Pd-A (Exp. No. 050110), (a) power signals and (b) temperatures. Parameters: total current is 3.65 A, average current density is 0.52 A cm^{-2}, total input heat is 474.40 kJ, excess heat is 19.46 kJ, average input power is 11.980 W, average excess power is 0.492 ± 0.015 W (without including mass loss) to 0.753 ± 0.053 W (including mass loss of 0.7 g).
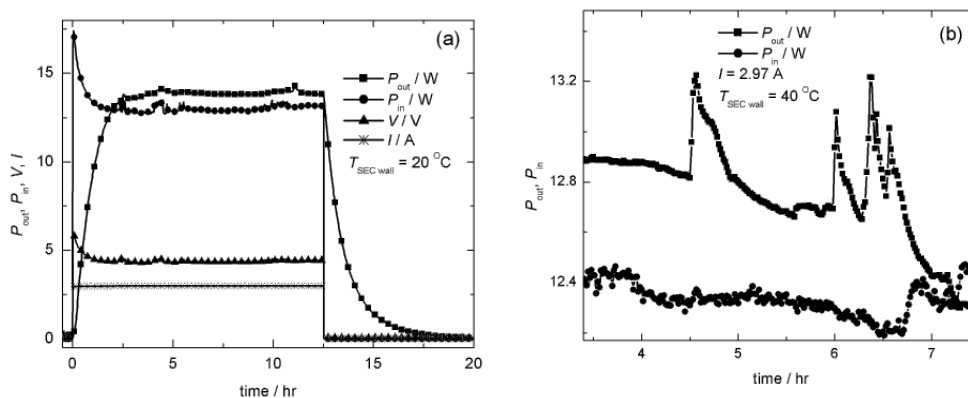

Figure 4. Other examples of excess heat produced in the Pd|D$_2$O+H$_2$SO$_4$ cell for sample Pd-A. (a) The maximum excess power in Exp. No. 041125. Parameters: average current density is 0.42 A cm^{-2}, total input heat is 592.24 kJ, excess heat is 44.05 kJ, average input power is 13.143 W, average excess power is 0.978 ± 0.032 W (without including mass loss) to 1.273 ± 0.065 W (including mass loss of 0.9 g). (b) An example of heat bursts during excess power production in Exp. No. 041122.

Part of the water produced by the recombination of oxygen and deuterium gases is adsorbed by the catalyst. The fraction of the water adsorbed depends on electrolysis

current and time, and the temperature and activity of the catalyst. It is from 40% to 80% in our experiments.

Heat bursts have been observed from sample Pd-A, in addition to the stable excess heat, in three different experiments. One example is shown in Fig. 4(b).

The excess heat was measured at different SEC wall temperatures; one set of results is shown in Table 1 and Fig. 5. We have conducted calorimetry with $T_{SEC\ wall}$ at 40°C, which causes the electrolyte temperatures to approach boiling. Therefore the mass loss is great due to the evaporation increase at higher temperature, and the excess power calculation is not accurate. Therefore, the highest temperature listed here is 35°C.

Table 1. Excess heats at different temperatures for sample Pd-A, with ~ 0.02 g/ml Ti added to the electrolyte.

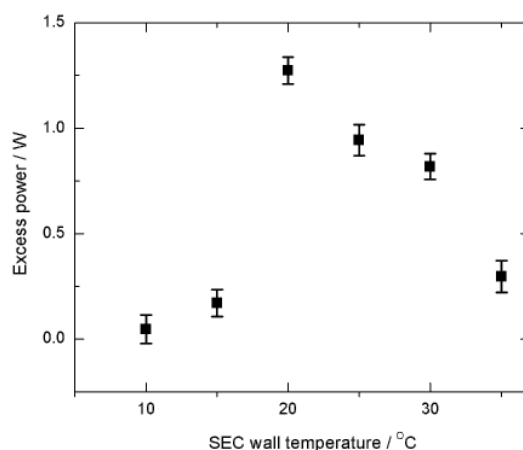| Exp. No.	$T_{SEC\ wall}$ / °C	Electrolysis time / hr	Average input power / W	Average excess power including mass loss / W
041126	10	11.5	12.922	0.046 ± 0.067
041128	15	9	12.000	0.171 ± 0.065
041125	20	12.5	13.143	1.273 ± 0.065
041130	25	9	11.640	0.944 ± 0.074
041120	30	13.5	12.763	0.819 ± 0.061
041204	35	8.5	11.149	0.296 ± 0.075

Figure 5. Dependence of excess power on temperature of SEC wall for Sample Pd-A, the current is 3 A (the corresponding current density is 0.42 A cm^{-2}); the input power is 11 to 13 W.

Beside the dependence of excess power on temperature, the excess power is proportional to the current density up to at least 0.5 A cm^{-2} as illustrated in Table 2 and Fig. 6. Our set-up now cannot identify the excess power at higher current more than 4 A because the catalyst cannot recombine all of the off gases produced by higher currents. These results also agree with the reported behavior of excess power found as early as 1989 [5].

Table 2. Excess heat at different current densities for sample Pd-A.

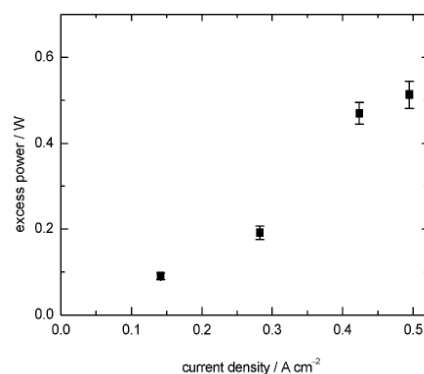| Electrolysis current density / A cm^{-2}	Excess power including mass loss / W
0.14	0.090 ± 0.007
0.28	0.191 ± 0.016
0.42	0.470 ± 0.025
0.49	0.513 ± 0.032

Figure 6. Dependences of excess power on current density for sample Pd-A (Exp. No. 041115).

From October 2004 to November 2005, we have conducted electrochemical calorimetry on Pd|D$_2$O+H$_2$SO$_4$ systems for 7 Pd samples; the results are summarized in Table 3. In the 7 samples, sample Pd-A, Pd-E and Pd-F gave excess heat in 70% of the experiments with Ti in the electrolyte. Pd-F uses two almost identical cells with Pd cathodes connected in series. Sample Pd-B produced excess heat in the first experiment only. Samples Pd-C and Pd-D have never given any excess heat.

The electrolyte used for samples Pd-A and Pd-B was electrolyte previously used for Ti|D$_2$O+H$_2$SO$_4$ electrolysis. Therefore, some titanium was dissolved in the electrolyte [7]. To identify the effects of titanium additive on the excess heat, we dissolved titanium in electrolyte from experiments involving sample Pd-D. Its effects on excess heat are also shown in Table 3. The concentration of titanium is expressed by the mass of titanium per unit volume of electrolyte. The data in Table 3 indicate that titanium in the electrolyte enhances excess heat production [7].

Table 3. Summary of excess powers for different samples from Oct 2004 to Nov 2005

Pd No.	sizes / mm^3	Exp. No.	$P_{ex,max}$ / W*	Rp** without Ti	Rp** with Ti	C_{Ti}
A	$0.35 \times 9 \times 37$	041012-050714	0.978 ± 0.032	2/9	10/17	~0.02 g/ml
B	$0.25 \times 10 \times 61$	050120-050227	0.226 ± 0.016		1/12	~0.02 g/ml
C	$0.4 \times 25 \times 25$	050316-050503	0.010 ± 0.003	0/6		
D	$0.05 \times 11 \times 34$	050720-050805	0.019 ± 0.017	0/4	0/1	~0.03 g/ml
E	$0.25 \times 25 \times 25$	050811-051006	0.759 ± 0.161	0/2	4/4	~0.03 g/ml
F1	$0.3 \times 9 \times 25$	051006-051109	0.461 ± 0.020		9/11	~0.03 g/ml
F2	$0.3 \times 9 \times 23$					
Total				10%	53%	

* Maximum average excess powers do not include the mass losses

** Rp = Reproducibility

3.2. Scanning electron microscopy measurements

We analyzed Pd sample surfaces before and after electrolysis, and we found changes in the characteristic X-ray spectra. In particular Pd $L\beta/L\alpha$ ratio is higher on the Pd cathode after electrolysis. As noted previously this may be due to the occurrence of silver after electrolysis [2], because Ag $L\alpha$ overlaps with Pd $L\beta$. For comparison, we present the blank results firstly. Fig. 7 shows the SEM and corresponding characteristic X-ray spectrum with an EDS for a Pd sample before electrolysis. We find the surface is very smooth and the Pd $L\beta/L\alpha$ ratio is 0.41, compared with 0.42, the ratio expected for pure Pd.
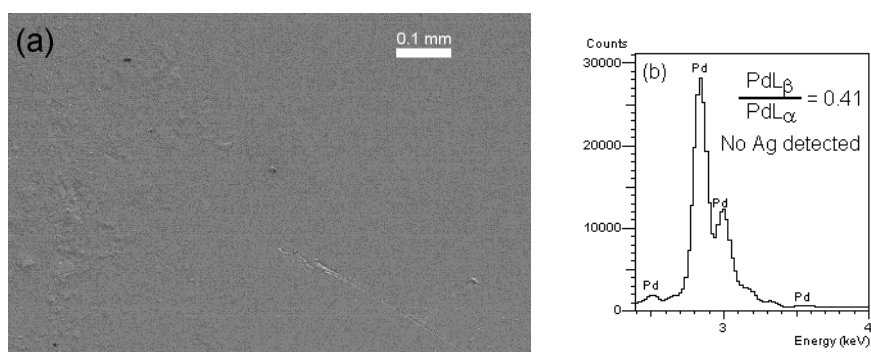

Figure 7. (a) SEM image of a Pd sample before electrolysis, (b) X-ray spectrum on the total area of (a) measured by EDS.
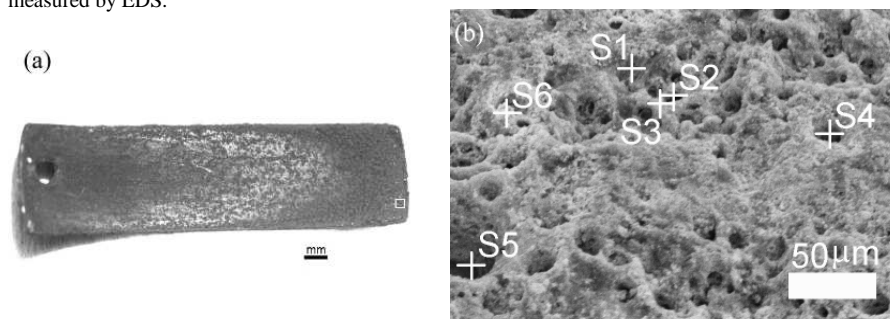

Figure 8. (a) Light microscope photo of sample Pd-A after electrolysis for 429 hours, (b) SEM picture of square region shown in bottom right corner of sample Pd-A in (a).

Figure 8 shows the surface pictures of sample Pd-A after electrolysis for 429 hours. The cathode bends towards the anode during electrolysis as observed previously [6]. The photo and SEM picture both indicate that the Pd electrode is covered with a deposit. The EDS results of Table 4 show that this deposit is mostly Pt, which dissolves from the anode.

Figure 9 shows part of the characteristic X-ray spectrum from the dark spot S2 in Fig. 8(b). Spot S2 is from a hole in the surface. It should be the bare Pd surface. Bright spot S3 is at the edge of the hole, where the Pt is deposited. It seems likely that the holey

regions are places where palladium-deuterium electrode reactions occur after some time electrolysis. Fig. 9 shows an increase in Pd Lβ/Lα. Using deconvolution software, it is found that S2 has 6.5 atomic% Ag and S3 has no Ag. Other results in our group show that Pd Lβ/Lα may be 1 or greater on the Pd cathode after electrolysis in heavy water. This is convincing evidence of the presence of localized concentrations of Ag [7].
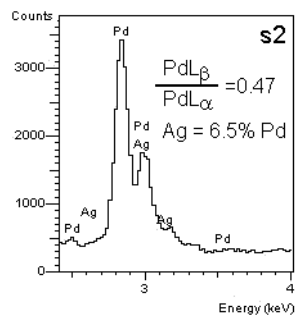

Figure 9. X-ray spectrum at spot 2 shown in Fig. 8(b).

Table 4. Element compositions at spots shown in Fig. 8(b).

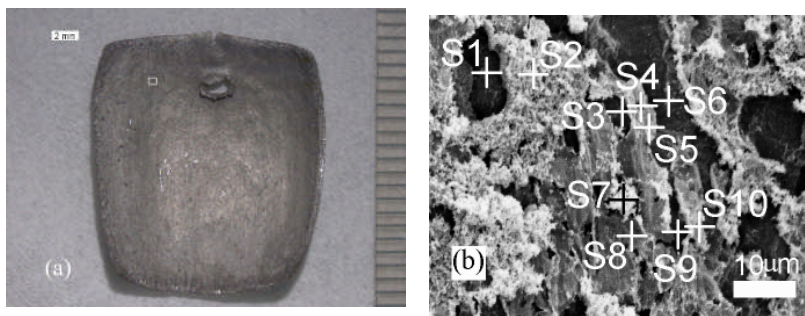| No.	Pd / at.%	Ag / at.%	Pt / at.%	Ag/Pd
1	34.2	0	65.8	0.000
2	54.8	3.6	41.7	0.065
3	56.3	0	43.7	0.000
4	35.5	4.5	60.0	0.126
5	52.0	0	48.0	0.000
6	38.2	0	61.8	0.000

Figure 10. (a) Light microscope photo of sample Pd-E after electrolysis for 93 hours, (b) SEM picture of square area shown around the top left corner of sample Pd-E in (a).

Table 5. Element compositions at spots shown in Fig. 10(b).

No.	Ti / at.%	Pd / at.%	Ag / at.%	Pt / at.%	Ag/Pd
1	0	52.3	4.8	43.0	0.092
2	0	77.9	3.2	19.0	0.041
3	0	80.1	5.3	14.7	0.066
4	0	73.5	3.4	23.2	0.046
5	0.3	71.0	2.1	26.6	0.030
6	0	79.8	5.7	14.5	0.072
7	0.9	29.9	1.1	68.2	0.035
8	0	61.6	3.8	34.6	0.061
9	0.4	86.7	3.5	9.5	0.040
10	0	67.9	2.5	29.5	0.037

Besides sample Pd-A, we also measured silver on other Pd samples after electrolysis. Another example is shown in Figure 10 and Table 5; this sample also produced excess heat. Because the results are qualitatively the same as those of sample Pd-A, we will not discuss them in detail.

4   Discussion and Conclusion

Our SEC calorimetric results showed that excess heat is produced in a $Pd|D_2O+H_2SO_4$ electrolytic cell, thus confirming the positive results obtained by isoperibolic calorimetry. The excess heat was qualitatively reproducible for some samples. Ti additions to the electrolyte improved reproducibility of excess heat, possibly by depositing on the cathode and catalyzing reactions which produce excess heat. Localized changes in the surface topography of the Pd cathodes correlate with changes in the characteristic X-ray peaks of Pd. As before, these are interpreted in terms of localized concentrations of Ag, which is thought to be produced during electrolysis.

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