Research Article

Effects of D/Pd Ratio and Cathode Pretreatments on Excess Heat in Closed Pd|D_2O+D_2SO_4 Electrolytic Cells*

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Abstract

The resistance method was used in situ to determine the D/Pd ratio in the cathode of Pd|D_2O+D_2SO_4 electrolytic-calorimetric systems. Thirty-three experimental runs with excess heat production indicated that there is no clear correlation between the excess power and the D/Pd ratio. Most excess heat occurs when the ratio is $0.5 <$ D/Pd < 0.7. Three different cathode pretreatments were tested. It is found that the excess heat reproducibility rate is 2/11 (18%), 21/32 (66%) and 25/50 (50%), and maximum excess power of 45 ± 18 mW, 117 ± 24 mW and 128 ± 19 mW were achieved for samples etched in aqua regia, heated in D_2SO_4 and open electrolyzed in D_2SO_4, respectively, based on 93 runs of calorimetry with 25 Pd plates. This indicates that heating and open electrolyzing in D_2SO_4 are effective methods of pretreatment for excess heat production in subsequent electrolysis. Surface characterizations with 3D non-contact optical profiling, scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) were performed for Pd samples of cold rolled, pretreated and electrolyzed. The results showed that the surface roughness of palladium increases prominently after pretreatment. New element silver was detected on Pd surface after electrolysis.
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1. Introduction

In our previous studies, we observed anomalous heat in Pd|D_2O electrolytic cells by Seebeck Envelope Calorimetry (SEC) [1−5]. Two factors were found to be very important for experimental reproducibility. One is that the temperature increment (i.e. the difference between steady temperature and initial temperature) during electrolysis must be high
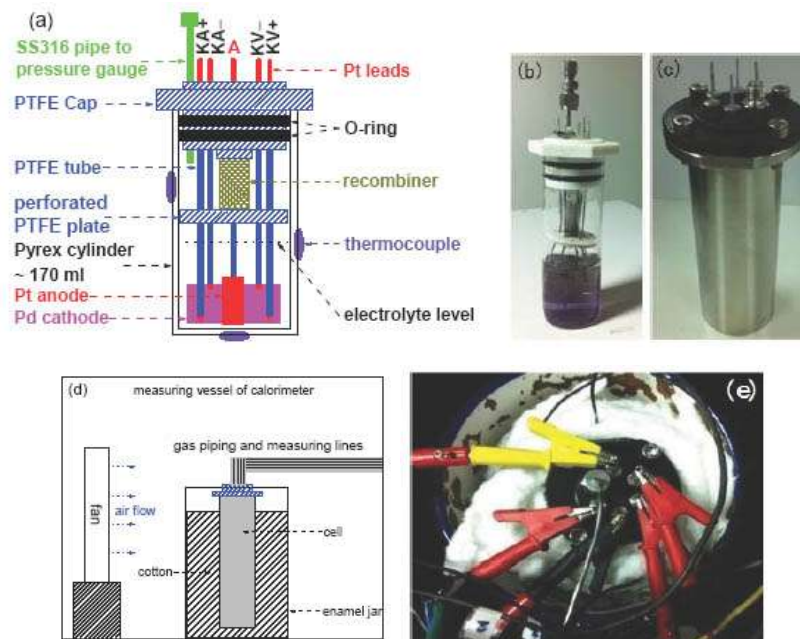

Figure 1. (a) Schematic of electrolytic cell (not in scale) used from January 2011 to October 2014. The symbol A represents anode; symbols KA+ (also the cathode), KA−, KV+ and KV− represent two source terminals and two sense terminals, respectively, in a 4-terminal AC resistance meter (HIOKI 3560); (b) photo of electrolytic cell of (a); (c) the cell since November 2014; (d) Schematic of different parts in the calorimeter (not in scale); (e) the cell of (c) with lead wires and thermocouples in calorimeter, the rust of porcelain enamel jar is a result of two explosions that happened before, due to failures of the catalyst.

enough; otherwise no excess heat will be observed [3]. Another is that the electrolysis of a Pd sample in an open cell is an effective way to activate the cathode for excess heat production in subsequent electrolysis in a closed cell [5]. In this paper, deep research on pretreatment methods will be reported.

McKubre et al. [6] and Kunimatsu et al. [7] reported that D/Pd > 0.8–0.9 is a necessary condition to obtain excess heat in Pd|D_2O electrolytic systems around room temperature. This requirement is in conflict with our experiences [1−5]. From April 2011, we have been measuring in situ the D/Pd ratio in electrolysis and calorimetry. The results showed that high loadings of D into Pd are unnecessary for excess heat production.

In recent years Violante's group found that the surface morphology of the cathode plays a key role in excess heat production in Pd|D_2O electrolytic cells [8,9]. This conclusion is similar to our discovery on pretreatment because both of them are surface effects. In this paper, we will report the characteristics of effective Pd surfaces.

2. Experimental Set-up

The electrolytic cell used from January 2011 to October 2014 was an advanced model compared to the previous design [5]. Its schematic and photo are shown in Figs. 1(a) and (b), respectively. The cell is made of borosilicate glass (φ_{in} 41 × φ_{out} 45 × 130 mm³) and it has a PTFE cap with a SS316 pipe connected to a deuterium gas cylinder and a pressure gauge. The bottom part of the male cap has two grooves of 4 mm width and 2.5 mm depth for O-rings (φ_{in} = 31.5 mm, width = 3.55 mm, made of nitrile butadiene rubber) to seal the cell. In addition, the cap has five

holes for electrode leads as shown in Fig. 1(a). High-temperature sealant (Thomas Technologies Co. Ltd, Chengdu, China), which solidifies at 120°C, is filled into the gaps between the leads and the cap to prevent escape of the off gases from the cell. A Pt cylindrical mesh filled with recombination catalyst (Alfa Aesar, Stock #89106, Lot #C24R036) to recombine excess D_2 and O_2 is suspended under the PTFE cap as shown in Fig. 1(b). The quantity of catalyst generally varies from 35 to 45 pellets (weight ~ 0.05 g /pellet).

From November 2014 to now, a SS316 flange was used outside the borosilicate cylinder to prevent an explosion, as shown in Fig. 1(c). The cap is also made of SS316, and is covered with Teflon coating to prevent corrosion. Cored screws and small O-rings are used to seal gaps between the leads and cap as partly shown in Fig. 1(c). Four screws are used to fix the cap and the flange. This cell gives better pressure tightness than the prior one. However, the Teflon coating is not so stable and has to be replaced after some runs.

The electrolyte is $D_2O + D_2SO_4$ mixed solution, to which we always added 0.2–0.4 g of titanium powder. Both deuterated reagents are from Beijing Chemical Reagent Company (>99.9 atom % D) with the mass ratio of $D_2O:D_2SO_4$ about 5:1. The platinum foil (normally $0.02 \times 31 \times 43$ mm^3) anode and leads are from General Research Institute for Nonferrous Metals (GRINM) as before [3].

Palladium samples from four different sources were used during the experiments. The physical properties, pretreatment methods and maximum excess power produced during electrolysis in closed Pd|D$_2$O cells are listed in Table 1 for Pd #4 to 33 in total of 157 runs from July 27, 2011 to May 26, 2016. Most of samples are from Alfa Aesar, Stock #11514, 99.9% purity. Pd #6, provided by John Dash, is also from Alfa Aesar. Pd #4, 5 and 17, provided by Da-Lun Wang, are from Kunming Institute of Precious Metals (KIPM). Pd #7, 18 and 27 are from GRINM, 99.95% purity. Pd #20 and 21 are from AVIC Beijing Institute of Aeronautical Materials (BIAM). Before the first electrolysis run, a Pd sample from Alfa or KIPM is cold rolled to the desired thickness and then washed with pure alcohol and de-ionized water to remove surface contamination. A scanning electron microscope in combination with an energy dispersive spectrometer (SEM-EDS; HITACHI, S-4300) is used to characterize the Pd surface morphology and elemental composition. A 3D Noncontact Optical Profiler (BRUKER ContourGT) and an Atomic Force Microscope (BRUKER Dimension FastScan AFM) are used to measure the surface roughness.

Five Pt leads ($\varphi 0.8$ mm), covered with heat-shrink Teflon tubing for protection, are welded to the Pt anode and a Pd cathode by a spot-welder. The loading ratios of D/Pd are determined by the resistance method using HIOKI 3560 AC mΩ HiTESTER to avoid DC voltage shifts during electrolysis, as discussed [10].

Before and after each electrolysis, the cell is weighed with a Mettler balance (PM1200, 1 mg readability) to monitor the weight loss. If the catalyst is working well, electrolysis at 3 A for 10 h will induce mass loss $\Delta m < 0.2$ g and the corresponding decomposition energy of heavy water will be less than 3 kJ; otherwise, the calorimetry may be complicated because excess heat is not prominent in these tests.

Three K-type thermocouples are attached outside the cell for temperature measurements, as shown in Fig. 1(a). The first is at the height of the recombination catalyst to monitor the recombining process of deuterium and oxygen gases. The second thermocouple is at the height of electrolyte level, and the third is on the bottom of the cell. The average value of the second and third temperatures is considered to be the electrolyte temperature in this paper. Generally, the temperature around the electrolyte level was greater than that of bottom by 5–10°C during experiments.

The power supply and data logging system are similar to that [5] with some modifications. All parameters are measured every 10 s. The input energy is the integration of input power (electrolytic current × cell voltage) with electrolysis time. The output energy is the integration of output power with electrolysis time and cooling time (around 10 h) of a heated cell.

Measurement of excess power is made by a decimeter-size heat-flow calorimeter which was fully demonstrated to have stability and accuracy in [4,5,11]. The electrolytic cell is placed in an enamel jar filled with cotton for heat insulation as shown in Figs. 1(d) and (e). The jar is located in the center of the measuring vessel with inner sizes of 26 cm × 26 cm × 26 cm and the air in the vessel is mixed with a fan to ensure temperature homogeneity. The

Table 1. Summary of excess power for various samples from July 27, 2011 to May 26, 2016.

Pd #	size mm^3	mass g	area cm^2	$P_{ex,max}$* mW	Rp#	source (Lot #) purity	Exp. #	pretreatment methods
4	$0.5 \times 10 \times 30$	1.7836	6.28	117 ± 15	4/10	KIPM, unknown	110727-110907	open electrolyzing
5A	$0.5 \times 11 \times 31$	1.8854	7.24	73 ± 17	2/18	KIPM, unknown	120508-121009	open electrolyzing
5B$^\&$	$0.33 \times 18 \times 31$	1.7682	11	59 ± 32	2/12	KIPM, unknown	121218-130524	open electrolyzing
6	$0.25 \times 12 \times 34$	1.0767	8.1	61 ± 23	5/13	Alfa Aesar, 99.9%	121013-121129	treated in flame for 40 min, open electrolyzing
7	$0.05 \times 14 \times 31$	0.3043	8.41	28 ± 26	1/5	GRINM (03-120) 99.95%	130824-130906	open electrolyzing
8	$0.26 \times 14 \times 31$	1.2798	8.60	45 ± 18	1/8	Alfa Aesar (E17Y001) 99.9%	130912-130925	etching in hot H_2SO_4 and aqua regia
9	$0.2 \times 14 \times 33$	1.3969	9.86	-14 ± 18	0/2	Alfa Aesar (E17Y001) 99.9%	130927-130929	etching in aqua regia
10	$0.26 \times 10 \times 32$	0.9886	6.62	$-34 \pm 18^\$$	0/2	Alfa Aesar (E17Y001) 99.9%	130930-131011	etching in aqua regia
11	$0.30 \times 11 \times 33$	1.3863	7.56	16 ± 19	0/3	Alfa Aesar (E17Y001) 99.9%	131013-131023	etching in aqua regia, open electrolyzing
12	$0.26 \times 11 \times 31$	1.1296	6.97	42 ± 19	2/5	Alfa Aesar (E17Y001) 99.9%	131028-131105	open electrolyzing
13	$0.24 \times 11 \times 31$	1.0686	7.08	66 ± 16	3/4	Alfa Aesar (E17Y001) 99.9%	131109-131115	open electrolyzing
14	$0.22 \times 10 \times 33$	1.1226	6.29	101 ± 22	1/4	Alfa Aesar (E17Y001) 99.9%	131120-131126	open electrolyzing
15	$0.26 \times 10 \times 30$	1.0890	6.39	87 ± 24	4/4	Alfa Aesar (E17Y001) 99.9%	131129-131226	heating in D_2SO_4
16	$0.34 \times 10 \times 31$	1.3704	6.80	117 ± 24	6/7	Alfa Aesar (E17Y001) 99.9%	131231-140123	heating in D_2SO_4
17	$0.26 \times 10 \times 31$	1.1317	6.44	27 ± 16	1/3	KIPM, unknown	140112-140116	heating in D_2SO_4
18	$0.05 \times 10 \times 32$	0.2280	6.56	48 ± 16	1/2	GRINM (03-120) 99.95%	140118-140120	heating in D_2SO_4
19	$0.34 \times 11 \times 31$	1.5105	6.95	30 ± 16	1/2	Alfa Aesar (E17Y001) 99.9%	140211-140214	heating in D_2SO_4
20	$0.8 \times 1.4 \times 31$	0.2875	1.39	45 ± 33	2/3	BIAM, unknown	140217-140222	annealing, heating in D_2SO_4
21	φ2.4×20	1.1158	1.54	23 ± 33	0/2	BIAM, unknown	140224-140226	mercerizing, heating in D_2SO_4
22	$0.36 \times 10 \times 34$	1.5710	7.37	70 ± 33	3/3	Alfa Aesar (E17Y001) 99.9%	140301-140315	heating in D_2SO_4, electro-deposited Cu or Au
23	$0.34 \times 11 \times 31$	1.4627	7.07	40 ± 14	3/3	Alfa Aesar (E17Y001) 99.9%	140319-140325	heating in D_2SO_4, electro-deposited Cu
24	$0.26 \times 11 \times 31$	1.0146	6.38	26 ± 14	1/2	Alfa Aesar (E26W014) 99.9%	140327-140410	heating in D_2SO_4
25	$0.30 \times 11 \times 31$	1.2388	6.85	31 ± 19	1/2	Alfa Aesar (E26W014) 99.9%	140412-140528	open electrolyzing
26	$0.26 \times 10 \times 30$	1.0972	6.51	70 ± 19	1/1	Alfa Aesar (E26W014) 99.9%	140605	open electrolyzing
27	$0.05 \times 15 \times 32$	0.3351	9.65	$-29 \pm 19^\$$	0/1	GRINM (03-120) 99.95%	141012	none
28	$0.26 \times 11 \times 31$	1.0604	7.14	61 ± 19	3/4	Alfa Aesar (J30Z002) 99.9%	141121-141202	open electrolyzing
29A	$0.3 \times 11 \times 31$	1.0570	7.28	128 ± 19	4/4	Alfa Aesar (J30Z002) 99.9%	141204-141214	open electrolyzing
29B$^\&$	$0.12 \times 26 \times 32$	0.9496	16.73	24 ± 14	1/4	Alfa Aesar (J30Z002) 99.9%	150705-160526	etching in aqua regia
30	$0.26 \times 10 \times 31$	1.0511	6.64	47 ± 32	1/3	Alfa Aesar (J30Z002) 99.9%	141218-141224	open electrolyzing
31	$0.22 \times 14 \times 30$	1.1995	8.39	108 ± 32	3/3	Alfa Aesar (J30Z002) 99.9%	141226-141231	open electrolyzing
32	$0.27 \times 22 \times 30$	2.1150	14.04	100 ± 32	5/10	Alfa Aesar (J30Z002) 99.9%	150107-150316	open electrolyzing
33	$0.26 \times 12 \times 31$	1.1428	7.98	61 ± 45	1/8	Alfa Aesar (J30Z002) 99.9%	150328-150531	open electrolyzing

* $P_{ex,max}$ is the maximum stable (always > 1 hr) excess power; # Rp is reproducibility; $^\$$Although the excess power is a negative value beyond one standard deviation, it should be positive after including mass loss; $^\&$ Pd #5B and 29B were cold rolled from Pd #5A and 29A, respectively.

calorimeter is calibrated with an electric heater in 2-W steps, up to a power level greater than the electrolysis power, e.g. the maximum calibration power is 12 W if the electrolysis power is planned to be around 10 W. The input power P and output signal E can be simulated by a linear equation. For accuracy, we fit their relationship with a quadratic form:

$$P = D_1 E + D_2 E^2, \tag{1}$$

where P is the input power in Watts and E is the output electromotive force in Volts; D_1 is the device constant in W V^{-1}; D_2 is the coefficient of the quadratic term. The intercept term in Eq. (??) is forced to zero to ensure no signal without input power. The device constant D_1 and the uncertainty over more than 41 months are shown in Fig. 2. Fluctuations of room temperature in different seasons affect the long-term precision; however, this calorimeter is calibrated every 2–4 weeks when it is used in experiments, and this is accurate enough to give a true signal of excess power with the uncertainty around 30 mW for many experiments. At the same time, we consider a result to be assured production of excess heat only when both of the excess power and the excess energy (output energy minus

input energy) are positive values, to avoid misjudgments. If both of them are negative and the mass loss rate of the cell in electrolysis is greater than 20 mg h^{-1}, the result has to be considered a failed experiment.

On Oct. 10, 2014 (Exp. #141010), a control experiment was conducted with a Pt foil (0.02 $\times$ 17 $\times$ 29 mm^3) in place of Pd cathodes. Electrolysis current of 3 A was applied for 12 h, the input and excess power were 8.462 $\pm$ 0.003 W and $-$ 0.014 $\pm$ 0.019 W, respectively, under steady state. Another control experiment (Exp. #141012) was done using Pd #27. (We had difficulty producing excess heat with this batch of samples.) The stable excess power was $-$ 0.029 $\pm$ 0.019 W while the input power was 8.721 $\pm$ 0.004 W at 3 A. These two results and other negative results with Pd|D$_2$O all confirmed that our calorimetry is credible.

3. Results

3.1. Effects of D/Pd ratio and other parameters on excess power

The relationship between the resistance ratio and the D/Pd ratio at room temperature has been well known for many years [10,12,13]; however, the temperature coefficient of resistance of Pd–D, α_D, in the miscibility gap has not been determined up to now, so the similar parameter of Pd–H, α_H, had to be used by various groups in the past. We found that the application of α_H to the Pd–D system will induce what appears to be a physically impossible result, i.e. the D/Pd ratio will increase with time but not decrease as expected in a short period just after electrolysis is stopped. Therefore, we had to determine α_D by ourselves. We calculated it using the resistance data during the cooling process after the electrolysis is stopped, as shown in Fig. 3(a). Of course, we had to ensure resistance only decreases linearly
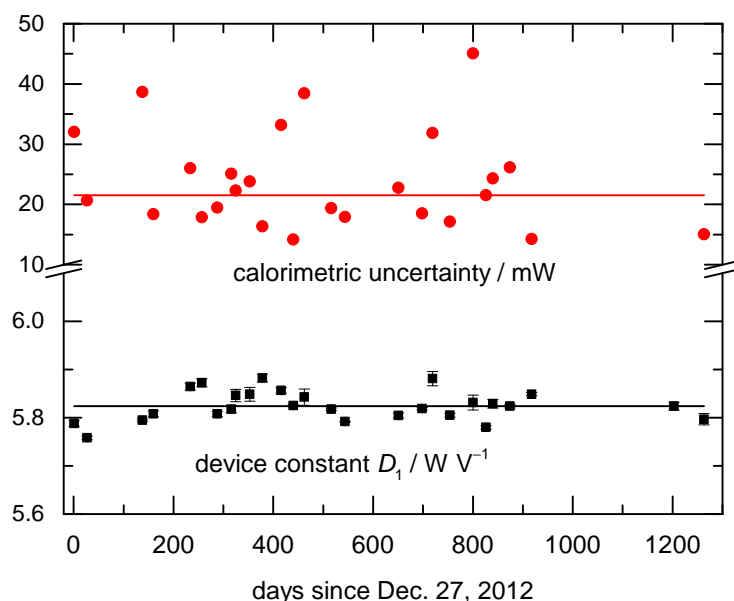

Figure 2. Changes of device constant (average value $\langle D_1 \rangle = 5.8246 \pm 0.0312 \, (0.54\%) \, \text{W V}^{-1}$) and uncertainty (average value $\langle \sigma \rangle = 24.3 \pm 8.6$ mW) of the calorimeter at 25°C (the set temperature for all results listed in this paper) over 41 months (Dec. 27, 2012 to June 11, 2016).
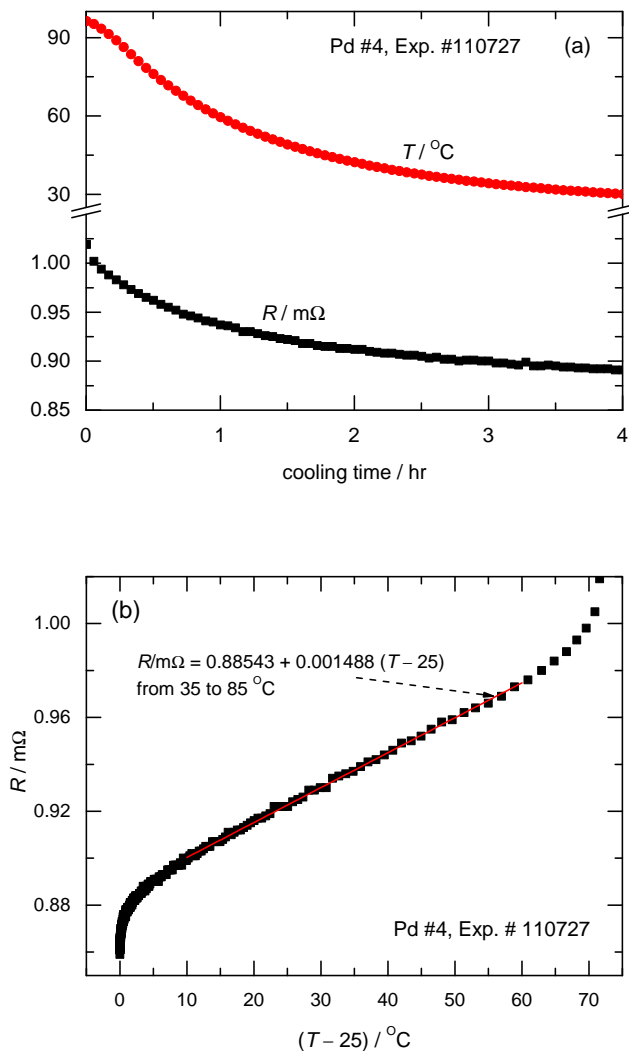
Figure 3. (a) Changes in resistance and temperature of a Pd cathode with time during cooling after stopping deuterium absorption by electrolysis; (b) Resistance vs. temperature in (a), only middle part has linear relationship between these two variables as shown by the fitting line and formula (Pd #4, Exp. #110727).

with temperature, and this means only part of data from cooling is chosen, as shown in Fig. 3(b). α_D with $0 < D/Pd < 0.7$ is obtained by collecting some runs of experiments as shown in Fig. 4 and simulated by a linear equation, the resulted resistance coefficient is

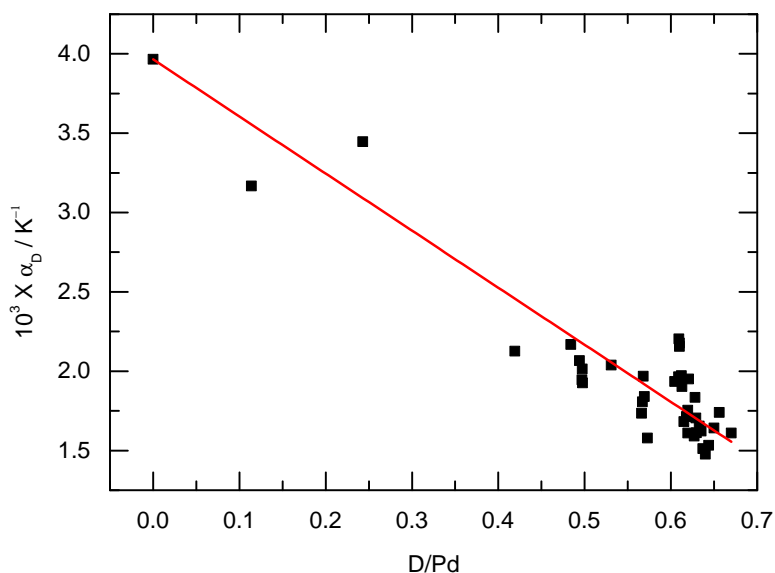$$\alpha_D/\text{K}^{-1} = 0.003965 - 0.003597x. \tag{2}$$

Figure 4. Collections of temperature coefficients of resistance of Pd–D in 39 runs of experiment for Pd #1, 4, 5 and 6 from May 10, 2011 to Oct. 24, 2012. The corresponding fitting formula is Eq. (**??**).

In our experiments, the D/Pd ratio at different temperatures was determined in situ by combining this factor and Eqs. (**??**) and (13) in [10]. Of course, α_D here must also be considered as a qualitatively and acceptable substitute of α_H, it needs to be measured in carefully designed experiments in future.

Figure 5 shows an example of in situ D/Pd ratio measurement during excess heat production in electrolysis. We find that the cathode resistance and the cell temperature increase with time as shown in Figs. 5(a) and (b), respectively. The D/Pd ratio increases with time due to deuterium absorption at the beginning of electrolysis; however, the cathode begins to desorb deuterium after 12 min of electrolysis, because the temperature is too high as we discussed previously [14]. It is found that the average D/Pd ratio is only 0.60 when excess power is 0.103 W as shown clearly in Fig. 5(c). This is in direct conflict with the previous conclusion that high loading ratios of D/Pd are needed for excess power production [6,7].

Figure 6 is a collection of data from 75 runs of positive results with excess power, with 21 samples. It illustrates how excess power is dependent on different parameters. Because the D/Pd ratio was not measured before July 2011, and it was not successfully measured in every run after that, the data points in Fig. 6(a) are from only 33 runs with 16 samples. We find that there is no clear correlation between the excess power and the D/Pd ratio. Most excess heat occurs when D/Pd is 0.5–0.7 below the threshold value of 0.8–0.9 cited [6,7]. This means that high loading ratios of D/Pd are not necessary for excess heat production. Another effect is the initial D/Pd ratio; we obtained excess heat for Pd samples both with deuterium already absorbed (e.g. Fig. 5(a)) and without any deuterium at the beginning of electrolysis. Therefore, the initial D/Pd ratio has no clear influence on excess heat production. In our experiments, the closed cell was only filled with deuterium gas to increase the D/Pd ratio in some runs; however, we did not find effects of atmospheres on the deuterium absorption during electrolysis. Therefore, we always carried out experiments with
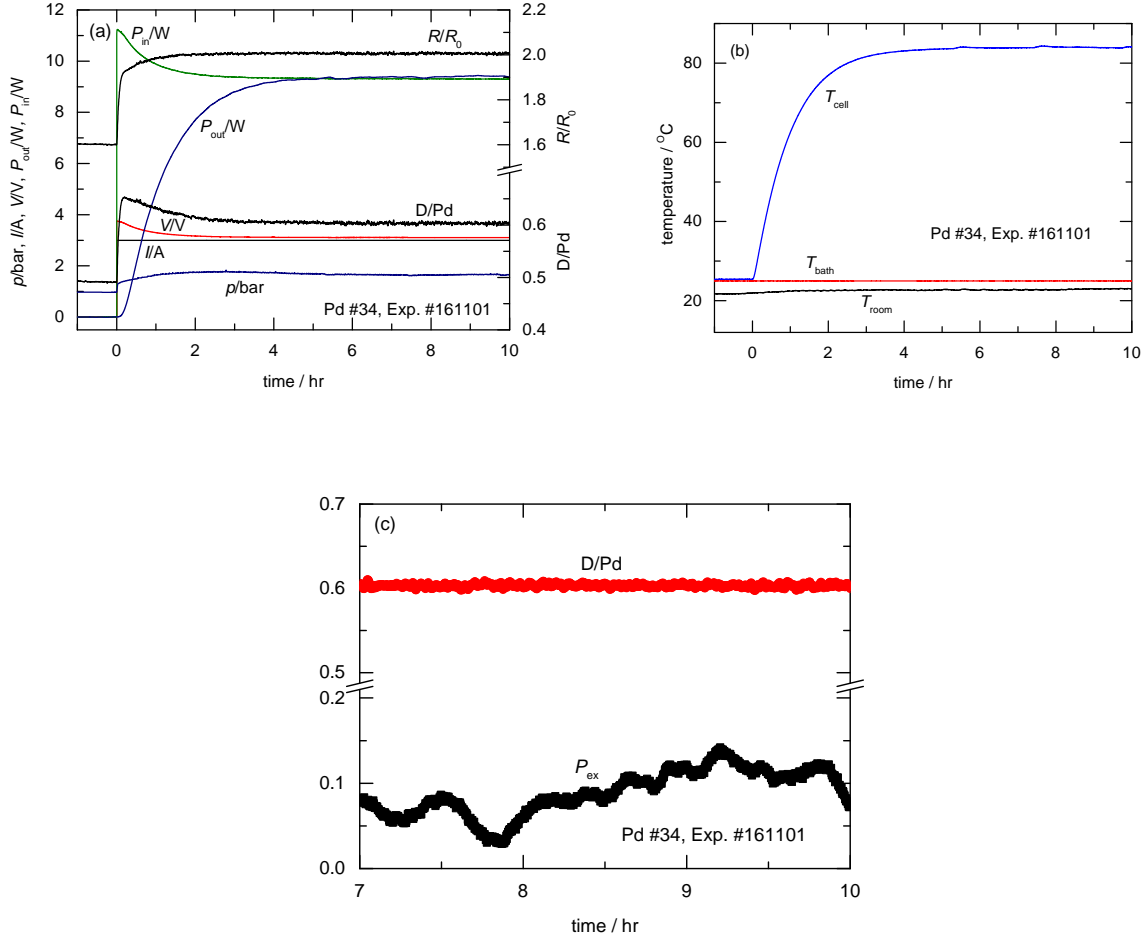
Figure 5. Applied current I, cell voltage V, input power P_{in}, output power P_{out}, gas pressure p, cathode resistance ratio R/R_0 (instantaneous resistance to the initial value of the free deuterium at 25°C), D/Pd ratio, cell temperature T_{cell}, room temperature T_{room}, bath temperature T_{bath} (= temperature of outer wall of calorimeter) and excess power P_{ex} in electrolysis of Exp. #161101 with Pd #34 (0.25 × 12 × 33 mm ^{3}, Alfa Aesar, Lot #J30Z002). Average values $\langle P_{\mathrm{ex}} \rangle = 103 \pm 17$ mW and $\langle \mathrm{D/Pd} \rangle = 0.60 \pm 0.02$ in 8–10 h.

the closed systems with only air in the cell.

On the other hand, from Fig. 6(c), we find there is clear correlation between the excess power and the cell temperature as observed by us previously [3] and also reported by Storms recently [15].

In our experiments, we intentionally increase the cell temperature by using more cotton in the jar, although the applied current heat the cell at the same time. This is the reason why there is correlation between the excess power and the current density as shown in Fig. 6(b) but Figs. 6(b) and (c) are unlike each other.

3.2. The effects of different pretreatments on excess heat reproducibility

In a previous paper [5], we reported that open electrolyzing of Pd cathode in D_2SO_4 heavy water solution until the electrolyte is used up is an effective way to stimulate excess heat in subsequent runs of electrolysis, and Pd #1 maintained its activity after lying in a sample box for more than 6 months. Since then, we used this sample as a cathode in a H_2O cell in two runs (Exp. #091001 and 091002) for blank calorimetry [5]. After that, this sample was dead; it produced no excess heat in subsequent 13 runs of calorimetry with three runs of open electrolyzing for activation. It
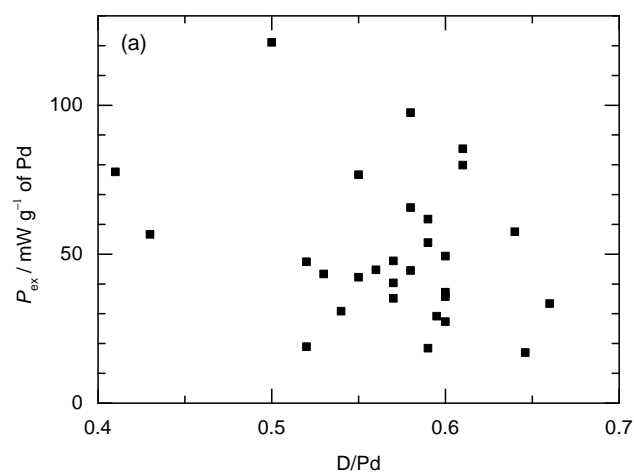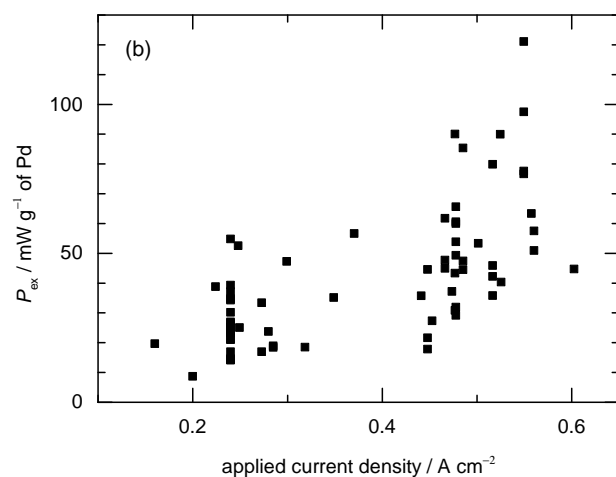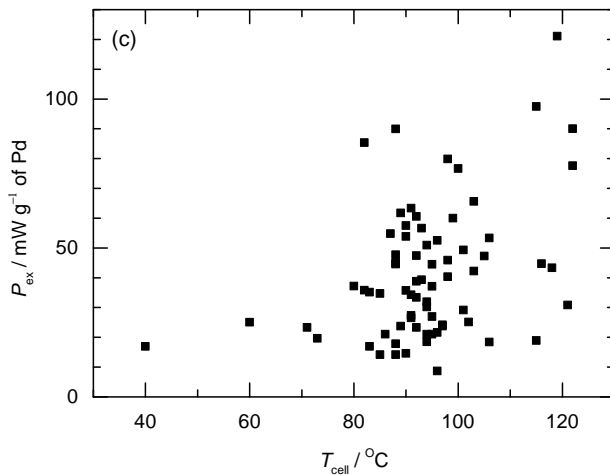

Fig. 6(a)

Fig. 6(b)

Fig. 6(c)

Fig. 6(d)

Figure 6. Specific excess power vs. (a) D/Pd ratio, (b) current density, (c) temperature, and (d) maximum temperature reached in pretreatments for 75 runs of positive calorimetric experiments with 21 samples from Dec. 23, 2008 to Mar. 28, 2015.

seems that history of H contamination suppresses excess heat production in Pd–D systems. Only Pd #2 and 4 in [5] were still active or could be activated by open electrolyzing thereafter.

In 2012, we tested Pd #5A from KIPM in 17 runs of calorimetry with four runs of open electrolyzing for activation; however, only one run (Exp. #120612) gave excess power of 73 ± 17 mW just after open electrolyzing (Exp. #120611). On Dec. 17, 2012, Pd #5A was cold rolled to 0.33 mm from original thickness of 0.5 mm and it was designated Pd #5B.

Table 1.   Summary of excess power for palladium samples pretreated with etching in aqua regia.

Pd #	Etching times	$P_{\text{ex,max}}$*/mW	Reproducibility	Exp. #
8	3	45 ± 18	1/4	See Table 3
9	1	-14 ± 18	0/2	130927/29
10	2	-34 ± 18	0/2	131008/11
11	1	-30 ± 19	0/1	131013
29B	1	24 ± 14	1/2	150705/07, 160423/26

*$P_{\text{ex,max}}$ is the maximum stable (always >1 h) excess power.

After soaking in sulfuric acid for 15 min and washing, it was assembled to the cell for electrolysis and calorimetry. It showed a sign of excess power of 32 ± 32 mW the next day (Exp. #121218). This sample showed excess heat in two runs over 12 runs of calorimetry with one run of open electrolyzing for activation. The maximum excess power was 59 ± 32 mW in Exp. #130110 at applied current of 3 A and a cell temperature of 92°C.

From Aug. 24 to Sep. 6, 2013, Pd #7 from GRINM was tested in five runs of calorimetry with three runs of open electrolyzing for activation. The maximum excess power was only 28 ± 26 mW in Exp. #130827 just after activation by open electrolyzing the day before. In our experience, it is difficult to produce excess heat with this batch of samples from GRINM.

As far as open electrolyzing is concerned, three processes take place in this procedure. The first is etching by acid, the second is heating in acid and the third is electrolyzing. To distinguishing the effects of these three processes, we designed three treatment methods with samples Pd #8 to 33, from September 2013, as shown in Table 1 and discussed below.

3.2.1. *Etching in aqua regia*

Five samples (Pd #8 to 11, 29B) were pretreated with etching in aqua regia, and 11 runs of calorimetry were carried out. Most of these runs did not produce any excess heat, as shown in Table 2. Now we take Pd #8 as an example to illustrate the calorimetric results shown in Table 3. We find that only a little excess heat was observed in Exp. #130917 when Pd was etched in aqua regia for 15 min and then electrolyzed for 12 h at 3 A, whereas there was no excess power in the other three runs with this sample (Exp. #130919/23/25).

Because mass losses from the cell were prominent in experiments during 2013, we tested this pretreatment method again in 2015. We chose Pd #29A, which had given the maximum excess heat after pretreated with open electrolyzing (see Section 3.2.3), and we cold rolled it to the thickness of 0.12 mm and designated it Pd #29B. It was etched in aqua regia for 72 s and about 6.4 μm of thickness from the surface was removed, according to its mass loss (from 1.0624 to 0.9496 g). The subsequent electrolysis at 3 A for 12 h only gave excess power of 6 ± 14 mW (Exp. #150705). The mass loss of this run was only 28 mg. All experiments listed in Tables 2 and 3 show that etching alone has no significant effect on excess heat production.

Table 2.   Summary of excess power for Pd #8 pretreated with etching in aqua regia.

Exp. #	Etching time	$I \times t$ (A h)	Mass loss (mg)	T_{cel}(°C)	P_{in}(W)	P_{ex}(mW)	D/Pd
130917	15 min	3.0×12	257	85	7.984	45 ± 18	0.57
130919	None	3.2×10	218	88	9.747	-11 ± 18	0.47
130923	20 min	3.3×12	272	90	9.310	1 ± 18	0.52
130925	30 min	3.3×12	506	91	8.866	-27 ± 18	0.54

Table 3. Summary of excess power for palladium samples pretreated with heating in D_2SO_4.

Pd #	Heating times	$P_{ex,max}$*/mW	Reproducibility	Exp. #
15	4	87 ± 24	4/4	131129, 131222/24/26
16	5	117 ± 24	6/7	See Table 5
17	3	27 ± 16	1/3	140112/14/16
18	2	48 ± 16	1/2	140118/20
19	2	30 ± 16	1/2	140211/14
20	4	45 ± 33	2/3	140218/20/22
21	1	23 ± 33	0/1	140226
22$^\$$	3	70 ± 33	2/3	140301/13/15
23$^\$$	3	40 ± 14	1/3	140319/21/25
24	1	26 ± 14	1/1	140327
28	2	61 ± 19	2/3	141121/27/29

* $P_{ex,max}$ is the maximum stable excess power.
$^\$$ See Table 8.

3.2.2. *Heating in D_2SO_4*

Thirty-two runs of calorimetry with 11 samples were conducted to study the effects of pretreatment by heating in D_2SO_4 on subsequent electrolysis, as shown in Table 4. Details of Pd #16 as an example are listed in Table 5; we find that most runs with this sample show excess heat after activation. It produced maximum excess power of 117 ± 24 mW in Exp. #140107 after being heated for 2 h and reaching the maximum temperature of 244°C in pretreatment. In all 11 samples listed in Table 4, 9 samples produced excess power but only four of them give maximum excess power $P_{ex,max} > 3\sigma$, the rest are not so activated, although reproducibility is high for this method.

3.2.3. *Electrolyzing in D_2SO_4*

Fifty runs of calorimetry with 12 Pd samples were performed to test the effect of open electrolyzing in pretreatment on excess heat production in subsequent electrolysis, as shown in Table 6. All runs with Pd #29A as an example are listed in Table 7. Before open electrolyzing, PTFE sealing tape is used to wrap the cell cap to protect the O-ring from corrosion by evolution gas, an open bottle is filled with D_2SO_4 until the Pd cathode is completely immersed, and the electrolysis current is usually set as 4 A. During 3 h of open electrolyzing in Exp. #141209 with Pd #29A, the maximum temperature reached 228°C at 2.5 h. In subsequent electrolysis in a closed cell at 4 A for 15 h, the stable excess power P_{ex} reached 103 ± 19 mW from 10 to 11 h. The activity of this sample continued in the next two runs as observed before [5]. It gave 128 ± 19 and 82 ± 19 mW in Exp. #141212 and 141214, respectively, without any pretreatment, as shown in Table 7. From Table 6, we find the reproducibility of this method is 25/50 (50%), which is somewhat less than the heating method of 21/32 (66%); however, there are six samples giving excess power of

Table 4. Summary of excess power for Pd #16 pretreated with heating in D_2SO_4.

Exp. #	Heating time, maximum temperature	$I \times t$(A h)	Mass loss (mg)	T_{cell}(°C)	P_{in}(W)	P_{ex}(mW)	D/Pd
131231	1.5 h, 235°C	3.3×12	1372	95	9.357	61 ± 24	0.58
140102	1.5 h, 242°C	3.3×8	847	95	9.304	-12 ± 24	0.58
140104	2 h, 244°C	3.3×12	572	92	9.768	65 ± 24	0.52
140107	2 h, 244°C	3.3×24	135	82	9.813	117 ± 24	0.61
140110	None	$3.3 \times 1, 3 \times 11$	371	90	9.761	49 ± 16	0.60
140122	2 h, 241°C	$3.3 \times 1.5, 3 \times 10.5$	1624	90	9.260	29 ± 16	0.57
140123	None	$3.3 \times 0.8, 3 \times 10.3$		90	9.365	19 ± 16	0.58

Table 5. Summary of excess power for palladium samples pretreated with open electrolyzing in D_2SO_4.

Pd #	Times of open electrolyzing	$P_{ex,max}$*/mW	Reproducibility	Exp. #
11	2	16 ± 19	0/2	131018/23
12	3	42 ± 19	2/5	131028/29, 131101/03/05
13	2	66 ± 16	3/4	131109/10/12/15
14	3	101 ± 22	1/4	131120/21/23/26
25	1	31 ± 19	1/2	140412/0528
26	1	70 ± 19	1/1	140605
28	1	61 ± 19	3/4	141202
29A	2	128 ± 19	4/4	see Table 7
30	3	47 ± 32	1/3	141218/22/24
31	3	108 ± 32	3/3	141226/29/31
32	5	100 ± 32	5/10	150107/10/12/16/21,150309/11/13/15/26
33	3	61 ± 45	1/8	150328,150409/14150507/21/31

*$P_{ex,max}$ is the maximum stable (always > 1 h) excess power.

$P_{ex,max} > 3\sigma$ in all 11 samples tested. In comparison, this parameter is only four in all 11 samples for heating method in Table 4. This means open electrolyzing is apparently the most effective method of activation.

3.2.4. *Other activation methods*

It was reported that applying reverse current for 1 h in electrolysis can activate a Pd cathode for excess heat production [16]; however, we tested five samples in eight runs (Exp. #080731, 080804, 081125 & 081130 with Pd #1; Exp. #090527 with Pd #2; Exp. #121118 with Pd #6; Exp. #130914 with Pd #8; Exp. #140319 with Pd #23) and no significant excess heat was stimulated by this method.

We also tested reverse polarization in pretreatment during open electrolyzing (Exp. #090814, 090915 and 090921 with Pd #1), there was no excess heat observed in subsequent calorimetry for closed electrolysis. Only one positive example came from Pd #4, when we applied reverse polarization of 3 A for 20 min at the beginning of pretreatment with open electrolyzing, then normal current of 3.5 A was applied for 2 h and 3.75 A was applied for 1 h successively (Exp. #110728). The subsequent four runs of calorimetry with closed electrolysis gave excess power of 96 ± 15 mW in Exp. #110729, 117 ± 15 mW in Exp. #110802, 52 ± 15 mW in Exp. #110804, and 88 ± 15 mW in Exp. #110805. However, we are not sure of the role of reverse electrolysis here.

It has been said that an oxide layer on the palladium surface may be important for excess heat production [17,18]. In ICCF17, Dash et al. also reported that Pd and Ti foils being heated in flame at 700°C for 20–60 min had given excess power in subsequent electrolysis [19]. At our request, John Dash sent us three samples (Pd #6 in Table 1 and two Ti foils). We tested the Pd sample in six runs (Exp. #121013/14/16/17/24, 121115) at current of 3 A. Only three runs produced a little excess heat with the maximum value of 61 ± 23 mW in Exp. #121017. We also activated it by electrolyzing two times; however, it did not produce excess heat in the two subsequent runs (Exp. #121117/18) after

Table 6. Summary of excess power for Pd #29A pretreated with open electrolyzing in D_2SO_4.

Exp. #	Electrolyzing time, maximum temperature	$I \times t$(A h)	Mass loss (mg)	T_{cell}(°C)	P (W)	P (mW)	D/Pd
141204	2 h, 214°C	4×15	1821	100	12.846	81 ± 19	0.55
141209	3 h, 228°C	4×15	127	115	12.545	103 ± 19	0.58
141212	None	4×15	982	119	13.105	128 ± 19	0.50
141214	None	4×15	662	122	12.397	82 ± 19	0.41

Table 7. Summary of excess power for Pd samples plated with Au and Cu.

Pd #	Exp. #	D/Pd	Anode	$I \times t$ (A min)	Plating thickness (μm)	P_{ex} (mW)
22	140301	0.74	Au	2.7 A $\times$ 45 min	–	70 $\pm$ 33
22	140313	0.73	Cu	1.0 A $\times$ 30 min	12.1	28 $\pm$ 14
22	140315	0.74	Cu	1.0 A $\times$ 1 min	3.37	34 $\pm$ 14
23	140319	0.56	Cu	0.1 A $\times$ 1 min	0.43	19 $\pm$ 14
23	140321	0.69	Cu	0.1 A $\times$ 1 min	0.45	25 $\pm$ 14

the first open electrolyzing (Exp. #121116). It only gave small excess power of 40 ± 26 mW in the first two of total four runs (Exp. #121120/21/22/29) after the second open electrolyzing (Exp. #121119). One Ti foil (0.6596 g, $0.4 \times 10 \times 39$ mm^3, Alfa Aesar, 99.99% metals basis) did not give excess heat in four runs of electrolysis (Exp. #130529/30/31 and 130602) too.

The situation was similar for Pd #21. It was soaked in fused potassium hydroxide (a.k.a. mercerizing) about 20 years ago and the surface is black. It did not produce excess heat in the first run of electrolysis (4 ± 33 mW in Exp. #140224). After heating in hot D_2SO_4, the excess power in subsequent electrolysis was still within the range of uncertainty (23 ± 33 mW in Exp. #140226).

We tried to deposit inert metals on the surface of palladium after deuterium was absorbed in order to seal the deuterium into the sample, thereby testing if this method could trigger excess heat. Two samples were tested in 5 runs, as shown in Table 8. Au or Cu was deposited on the Pd surface by means of electroplating. Firstly, one of the samples was heated in D_2SO_4 for 1–2 h, and then electrolysis was carried out for the Pd cathode in the cell used for calorimetry. After the D/Pd ratio reaching saturation value, the Pt anode shown in Fig. 1 was switched to Au or Cu (Alfa Aesar, 99.99%) for some minutes. Cu was easily plated; however, it was difficult to form an Au deposit because of the insolubility of Au in sulfuric acid. Both current and time affect the plating thickness, as shown in Table 8. There is no clear evidence that this method can improve excess heat production.

3.2.5. *Comparison of different treatment methods*

Table 9 compares the effects of different pretreatments on excess heat production for different Pd samples. We find that etching in aqua regia only gives the maximum excess power of 45 ± 18 mW and 18% reproducibility; heating in D_2SO_4 induces maximum excess power of 117 ± 24 mW and 66% reproducibility; open electrolyzing in D_2SO_4 leads to the maximum excess power of 128 ± 19 mW and 50% reproducibility. Although heating produced higher reproducibility than open electrolyzing, the latter method has a sample rate of 3/11 with $P_{ex} > 100$ mW while the former has only 1/11. This means that open electrolyzing is the most effective method of activation. Figure 6(d) shows effects of maximum temperature reached in pretreatment (heating or open electrolyzing of Pd in D_2SO_4) on excess heat, higher temperature of pretreatment will induce higher excess power as expected. We feel that we need to achieve much higher temperature in future research.

Of course, reproducibility is also source and sample dependent. Pd plates from GRINM were difficult to activate; four samples (Pd #3 in [5], Pd #7, 18 and 27 here) only gave maximum excess power of 48 ± 16 mW with reproducibility of 2/11. Generally, we only use this batch without any pretreatment in control experiments to test the

Table 8. Comparison of different pretreatments on excess power for samples Pd #8 to 33.

Pd #	$P_{ex,max}$/mW	Reproducibility	Pretreatment method
8–11, 29B	45 $\pm$ 18	2/11 (18%)	Etching in aqua regia
15–24, 28	117 $\pm$ 24	21/32 (66%)	Heating in D_2SO_4
12–14, 25, 26, 28, 29A, 30–33	128 $\pm$ 19	25/50 (50%)	Electrolysis in hot D_2SO_4

accuracy and validity of our calorimetry. On the other hand, samples from one batch of Alfa Aesar showed different levels of excess heat production from one to another. For example, Pd #28 to 33 were all cut from a plate of Lot #J30Z002 and were all pretreated with open electrolyzing; however, Pd #33 only gave maximum excess power of 61 $\pm$ 45 mW (Exp. #150328) and reproducibility of 1/8 while both #31 and 32 gave excess power greater than 100 mW The reasons of this sample dependent on excess heat production are unknown at present.

3.3. Surface characteristics of Pd samples

As reported by the Violante group [8,9], the surface morphology of a Pd sample is very important for its excess heat production in electrolysis. For this purpose, we cut a small part from some typical Pd samples in every phase and studied them with light and electron microscopes. Now we take Pd #16 as an example to demonstrate our primary results. This sample was pretreated by heating in D_2SO_4 and gave excess power up to 117 ± 24 mW, as shown in Tables 1 and 5. Its photos in three different phases are shown in Fig. 7; we find its surface becomes rough after heating and electrolysis in D_2SO_4, as expected.

3.3.1. *Changes of surface roughness*

To quantitatively characterize the surface morphology, we used a non-contact 3D optical profiler (BRUKER ContourGT) to measure roughness, as shown in Fig. 8 and listed in Table 10. It is clear that all roughness parameters under different definitions increase by around one order of magnitude after heating in D_2SO_4, and they increase again by 1/10 to 1/2 after electrolysis for 12 h. AFM study on Pd #14 also support this conclusion, i.e. open electrolyzing also roughens the surface. These results agree with the discovery of the Violante group [8,9]. Of course, more study on comparison of different pretreatments on surface properties is needed. Without this we cannot determine the detailed requirements for excess heat production.

3.3.2. *SEM and EDS characteristics*

Similar to our previous work [2,3], we also studied SEM as shown in Fig. 9, and element composition with EDS, as shown in Tables 11 and 12 for different phases of Pd #16. Figure 9(a) is an SEM of the fresh sample and there is only base metal Pd and some C and O on the surface (see Table 11). After heating in D_2SO_4 for 2 h, many microstructures appear on the Pd surface as shown in Fig. 9(b). After electrolysis, new elements S, Ag and Pt occur on the surface as shown in Fig. 9(c) and listed in Table 12. For these new elements, S comes from the electrolyte; Pt comes from
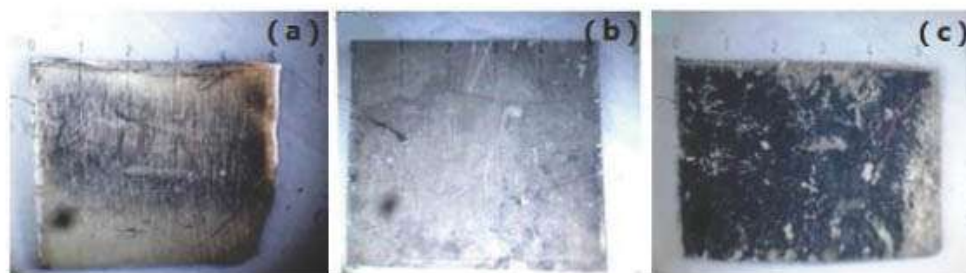

Figure 7. Optical photos of Pd #16 just cold rolled (a), after heating in D_2SO_4 for 2 h (b) and after electrolysis for 12 h (c). The units of scale are in mm.

Table 9. Roughness parameters of surface shown in Fig. 8.

Figure #	R_a (μm)	R_p (μm)	R_q (μm)	R_v (μm)
a	0.235	1.807	0.307	-2.014
b	2.426	14.046	3.055	-14.084
c	3.545	15.382	4.307	-16.492

Note: R_a, arithmetic average; R_p, maximum peak height; R_q, root mean squared; R_V, maximum valley depth.

Table 10. Relative atomic percent concentrations at spots shown in Fig. 9(a).

Element	#1	#2	#3
C	37.3	68.1	22.9
O	0.0	15.2	0.0
Pd	62.7	16.7	77.1

the anode and Ag may be the product of transmutation as reported before [2,3]. Spot #1 in Fig. 9(c) is the center of a crater, where should be the place of deuterium bubbles evolved from and silver is prominent. This situation is the same as Fig. 9 in [3]. This means that silver is transmuted in the deuterium electrode reaction.

4. Discussions and Conclusion

Although we can observe excess heat with some reproducibility, the amplitude of excess power is still very small now and we need to increase it by 2 or 3 times at least. Otherwise, the scientific community may have doubts about the calorimetry. Regarding the Pd surface pretreatment, we need more research to clarify the surface properties and their physical effects. This may be the key step to amplifying excess power.
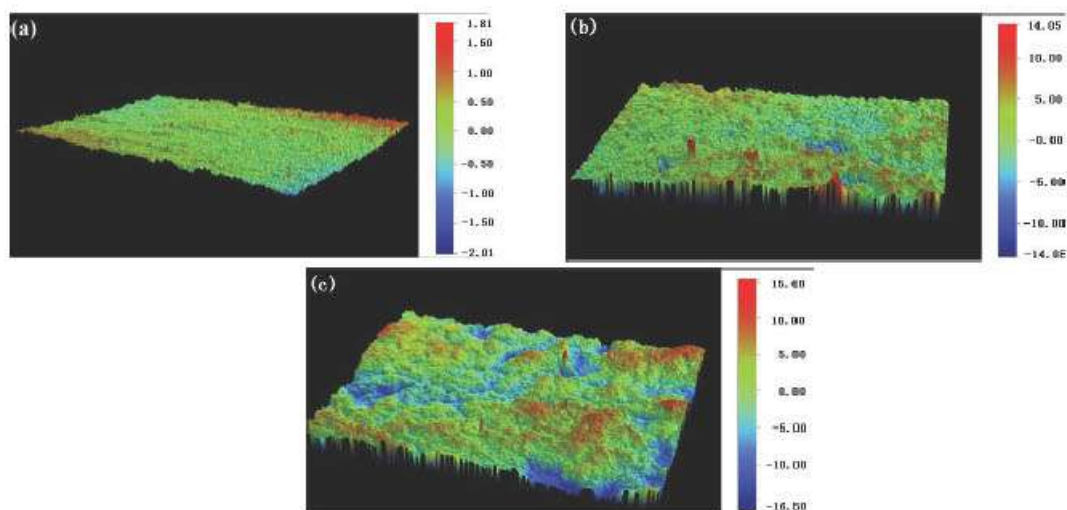

Figure 8. Typical 3D morphology of Pd #16. Regions of (a)–(c) are chosen from Figs. 7(a)–(c), respectively. The areas are 0.234×0.310 mm^2 for (a) and (c), and 0.223×0.299 mm^2 for (b); the units of height on the right side are in μm.
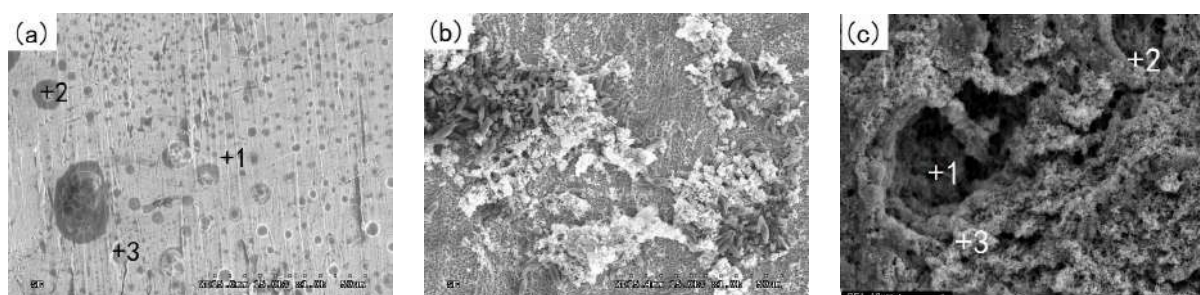
Figure 9. SEM of Pd #16, (a)–(c) are chosen from Figs. 7(a)–(c), respectively.

Table 11. Relative atomic percent concentrations at spots shown in Fig. 9(c).

Element	#1	#2	#3
C	20.1	0.0	24.0
O	4.0	0.0	0.0
S	6.9	0.0	0.0
Pd	45.5	8.1	46.7
Ag	3.0	0.0	0.6
Pt	20.5	91.9	28.7

In conclusion, we find that high loading ratios of D/Pd are unnecessary for excess heat production in Pd|D$_2$O electrolytic cells. Additionally, the temperature is more important than the D/Pd ratio as demonstrated by 75 runs of calorimetry. On the other hand, pretreatments of surface are another necessary step to activate Pd cathodes. Comparing three methods, i.e. etching in aqua regia, heating in D$_2$SO$_4$ and open electrolyzing in D$_2$SO$_4$, we found that the latter two are effective ways to activate a Pd sample to produce excess heat in subsequent electrolysis. Light and electron microscopy indicate that pretreatments roughen the surface and this may be responsible for the excess heat production.

Acknowledgments

References

[1]   Z.-L. Zhang, W.-S. Zhang, M.-H. Zhong and F. Tan, *Proc. ICCF8*, Bologna, Italy, May 21 to 26, 2000, p. 91.
[2]   W.-S. Zhang, J. Dash and Q. Wang, *Proc. ICCF12*, Yokohama, Japan, Nov. 27 to Dec. 2, 2005, p. 86.
[3]   W.-S. Zhang and J. Dash, *Proc. ICCF13*, Dagomys, Sochi, Russia, June 25 to July 1, 2007, p. 202.
[4]   W.-S. Zhang, J. Dash and Z.-L. Zhang, *Proc. ICCF14*, Washington DC, USA, Aug. 8–10, 2008, p. 26.
[5]   W.-S. Zhang, *Proc. ICCF15*, Roma, Italy, Oct. 5–9, 2009, p. 27.
[6]   M.C.H. McKubre, S. Crouch-Baker, A.M. Riley, S.I. Smedley and F.L. Tanzella, *Proc. ICCF3*. Nagoya, Japan, Oct. 21–25, 1992, p. 5.
[7]   K. Kunimatsu, N. Hasegawa, A. Kubota, N. Imai, M. Ishikawa, H. Akita and Y. Tsuchida, *Proc. ICCF3*, Nagoya, Japan, Oct. 21–25, 1992, p. 31.
[8]   V. Violante, F. Sarto, E. Castagna, M. Sansovini, S. Lecci, D.L. Knies, K.S. Grabowski and G.K. Hubler, *Proc. ICCF14*, Washington DC, USA, Aug. 8–10, 2008, p. 429.
[9]   E. Castagna, S. Lecci, M. Sansovini, F. Sarto and V. Violante, *J. Condensed Matter Nucl. Sci.* **8** (2012) 49.

[10] W.-S. Zhang, Z.-F. Zhang and Z.-L. Zhang, *J. Electroanal. Chem.* **528** (2002) 1.
[11] W.-S. Zhang, *Thermochim. Acta* **499** (2010) 128.
[12] M.C.H. McKubre and F.L. Tanzella, *Proc. ICCF12*, Yokohama, Japan, Nov. 27 to Dec. 2, 2005, p. 392.
[13] A. Spallone, F. Celani, P. Marini and V. Di Stefano, *Proc. ICCF12*, Yokohama, Japan, Nov. 27 to Dec. 2, 2005, p. 404.
[14] W.-S. Zhang, Z.-L. Zhang and X.-W. Zhang, *J. Electroanal. Chem*. **481** (2000) 13.
[15] E. Storms, *J. Condensed Matter Nucl. Sci*. **20** (2016) 81.
[16] J. Dash and A. Ambadkar, *Proc. ICCF11*, Marseille, France, Oct. 31 to Nov. 5, 2004, p. 477.
[17] D.D. Dominguez, D.A. Kidwell, D.L. Knies, K.S. Grabowski, G.K. Hubler, J.H. He, V. Violante, *J. Condensed Matter Nucl. Sci.* **8** (2012) 219.
[18] J.-P. Biberian, I. Parchamazad and M.H. Miles, *J. Condensed Matter Nucl. Sci.* **13** (2014) 38
[19] J. Dash, J. Solomon and M. Zhu, *J. Condensed Matter Nucl. Sci*. **13** (2014) 80.