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Deuterium Gas Charging Experiments with Pd Powders for Excess Heat Evolution

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Aim

It has been recently reported in ref. [1] that charging of highly pure D_2 gas into Pd nano-powders in the form of Pd/ZrO_2 nano-composite contained in a stainless-steel vacuum vessel has induced significant excess heat and ^4He generation.

We have constructed an experimental system to replicate the phenomenon of excess-heat (and ^4He generation) and **investigate the underlying physics for D(H)-charged Pd powders**.

[1] Y. Arata, et al.; The special report on research project for creation of new energy, J. High Temperature Society, No. 1. 2008.

Outline of the Present Work

We constructed two identical chambers (**twin system**); one for D_2 gas foreground run and the other for H_2 gas background run. Each system has an inner reaction chamber containing Pd powders (Pd-black and **nano-Pd/ZrO_2**)and the outer chambers are evacuated for thermal insulation.

A water-cooling system is provided for flow calorimetry to estimate **heat production rates for two phases**.

D(H)/Pd ratios were measured for the 1st phase ("zero pressure interval").

Moreover, after the gas charging, elemental analysis of the Pd powder was performed by PIXE (Particle Induced X-ray Emission) analysis. Radioactivity was measured with a Hp-Ge detector. A REM counter was used for monitoring neutron emission. NaI scintillator was used for gamma-ray. Furthermore, ^{4}He analysis will be performed in the future.

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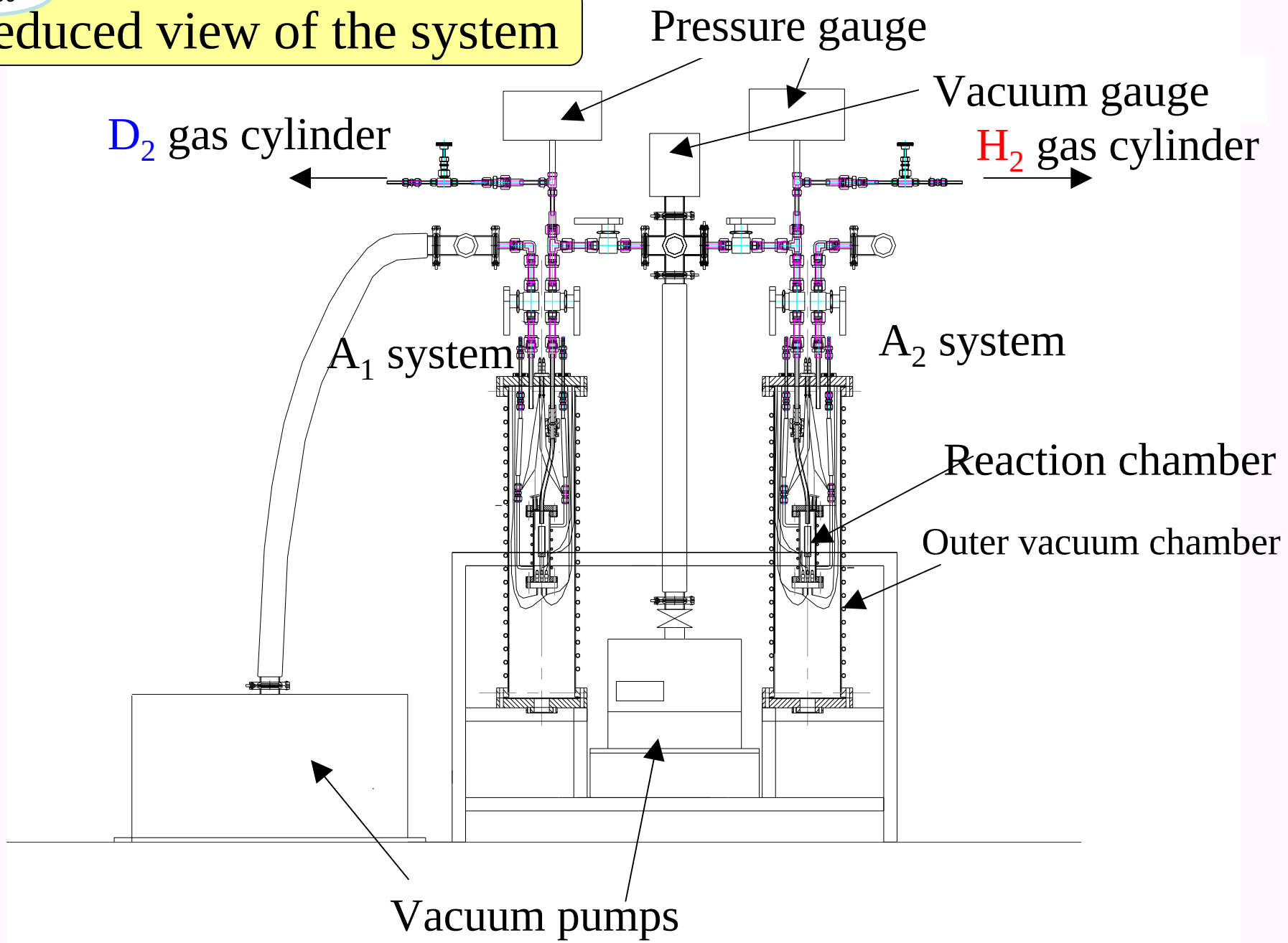
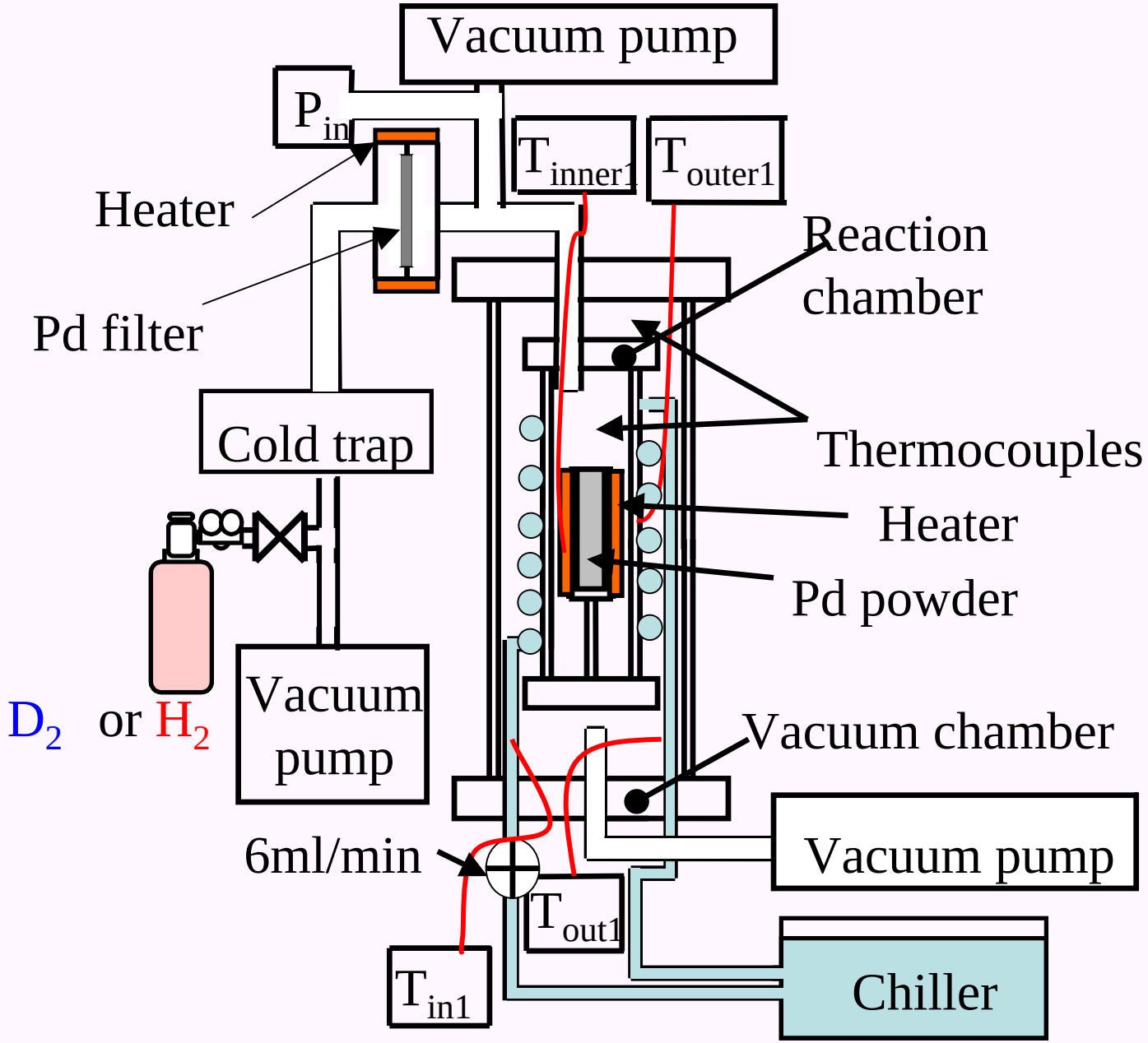
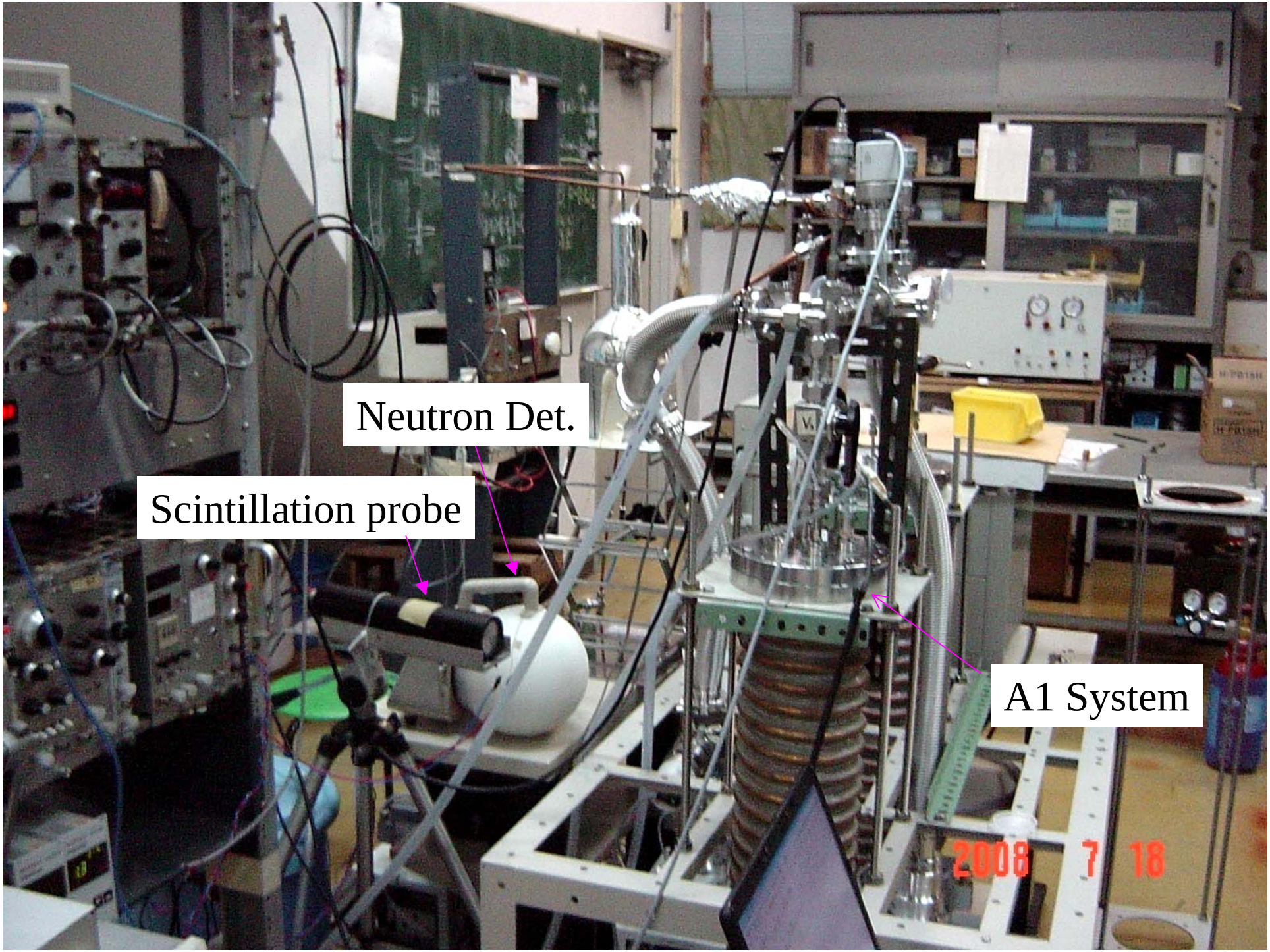
Reduced view of the system



Functional view of the A system (Old)




Neutron Det.
Scintillation probe
A1 System
2008 7 18

1. Calorimetry Calibration

Outline

The temperature of the reaction chamber is thermally isolated by evacuating the outer vacuum chamber.

Flow calorimetry is provided to measure heat output from the sample cup in the reaction chamber.

Calibration of the calorimetry system

- Input power: 0.5W, 1W, 3W, 6W and 10W.
- D_2 gas pressure in the reaction chamber: 0, 0.1, 0.3, and 1.0 MPa.
- Flow velocity of coolant water: 6 ml/min.

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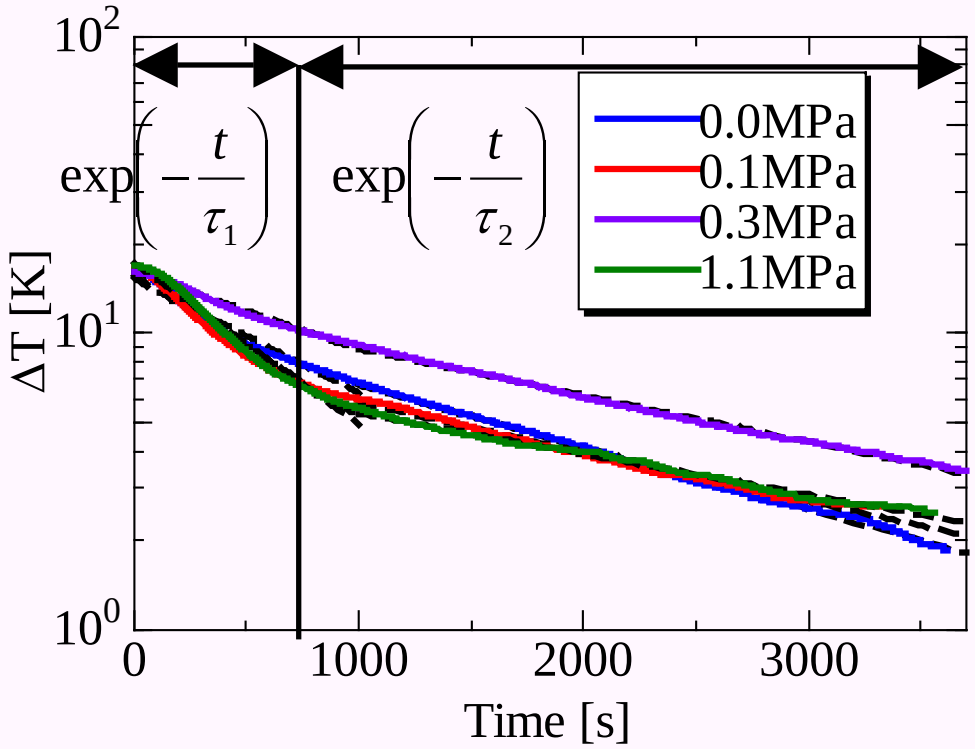
Results of calibration (Old A)

Pressure[MPa]	Input power [W]	Output power [W]	Heat recovery rate
0	10.0	5.9	59.3%
0	6.1	4.1	68.2%
0	3.0	2.2	72.5%
0	1.0	0.7	67.5%
3	10.0	7.0	70.2%
3	6.1	4.3	69.7%
3	3.0	2.2	71.8%
3	1.0	0.5	51.9%
1.1	10.0	6.8	68.1%
1.1	6.1	4.3	70.7%
1.1	3.0	2.0	68.3%
1.1	1.1	0.6	53.4%

Heat recovery rate is independent of pressure and input power, and is about 70% (±2%).

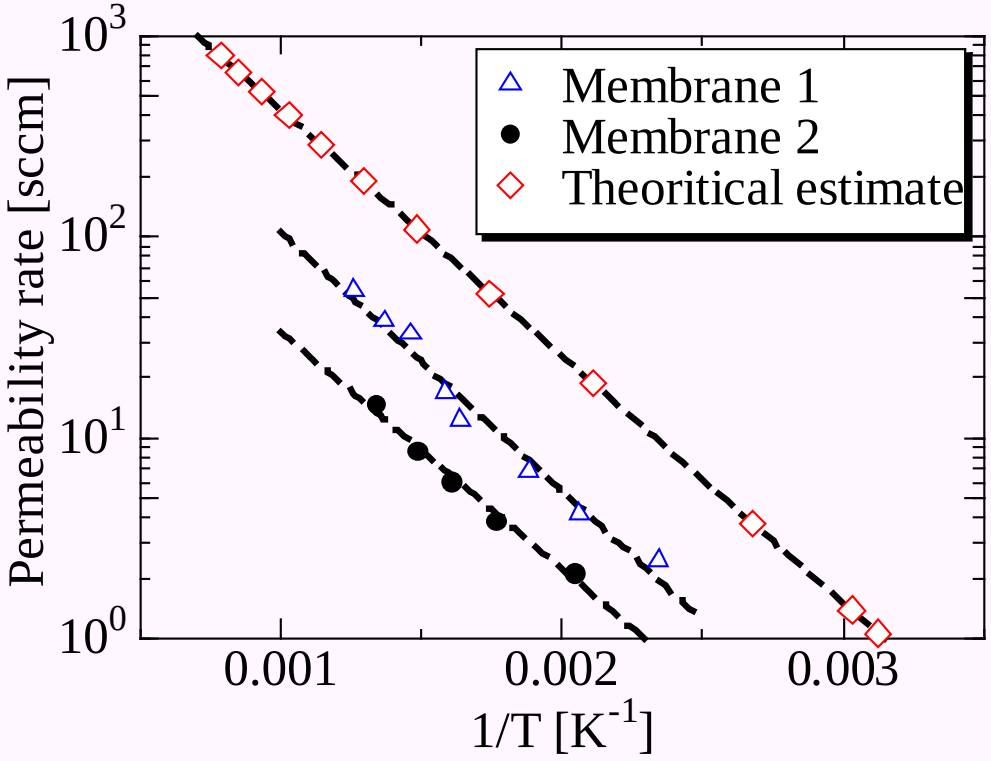
Thermal time constant: temperature change following the change in the input power.



MPa	τ_1 [s]	τ_2 [s]
0	1500	2700
0.1	690	3000
0.3	750	2600
1.1	930	2000

Thermal time constants will be used to determine the phases in absorption runs.

Performance test of Pd membrane filter

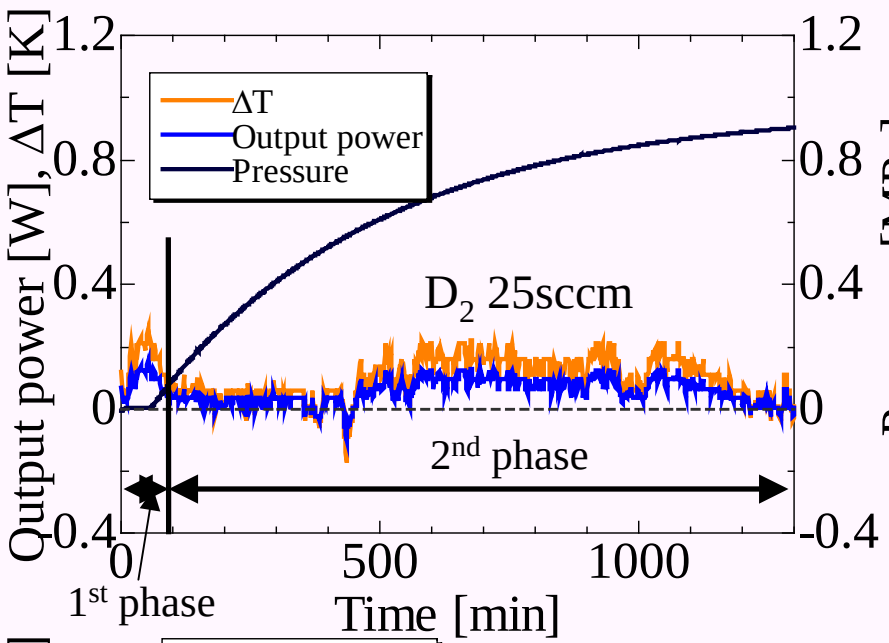


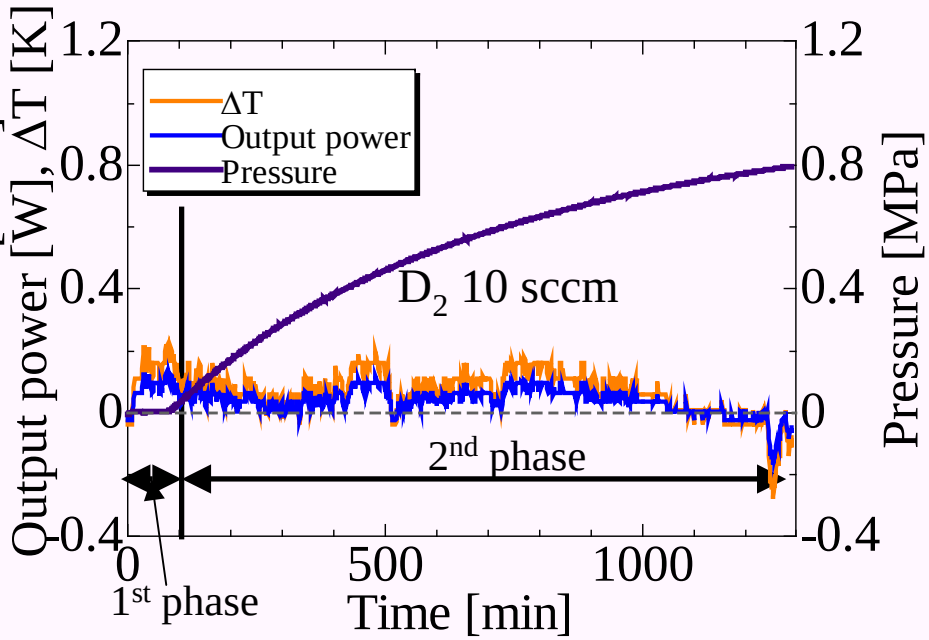
The Pd membrane (0.2 mm-t, 99.95%) separates the evacuated reaction chamber (1.6ℓ) and the gas reservoir filled with D_2 at 1 MPa.

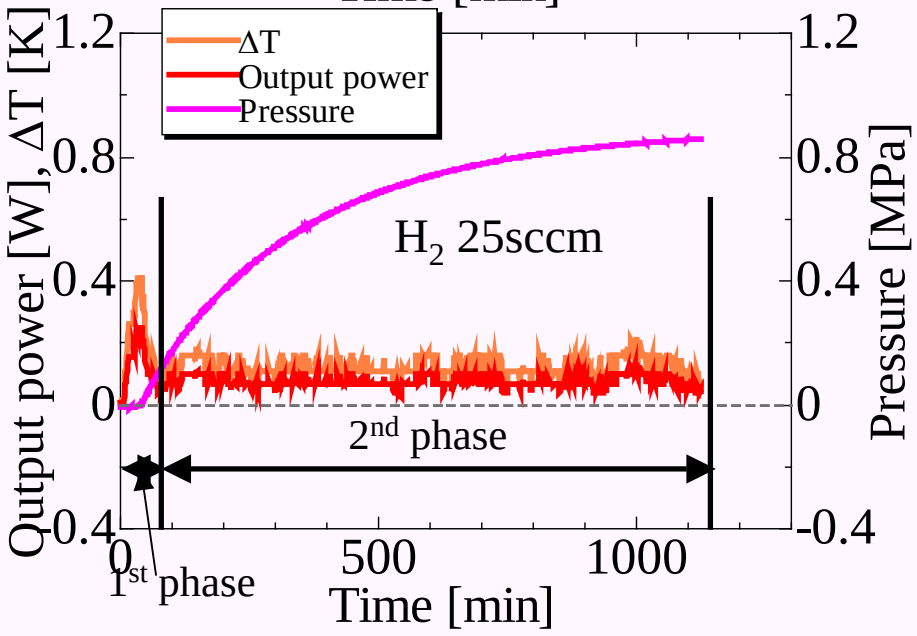
Permeation rate of D_2 gas into the reaction chamber was derived as a function of membrane temperature by measuring the rate of pressure increase after stopping evacuation.

D_2 gas flow rate is controllable between 0.1 and 25 sccm by varying the temperature from 298 K to 900 K.

Pd powders (ϕ0.1μm, 99.5%) – results



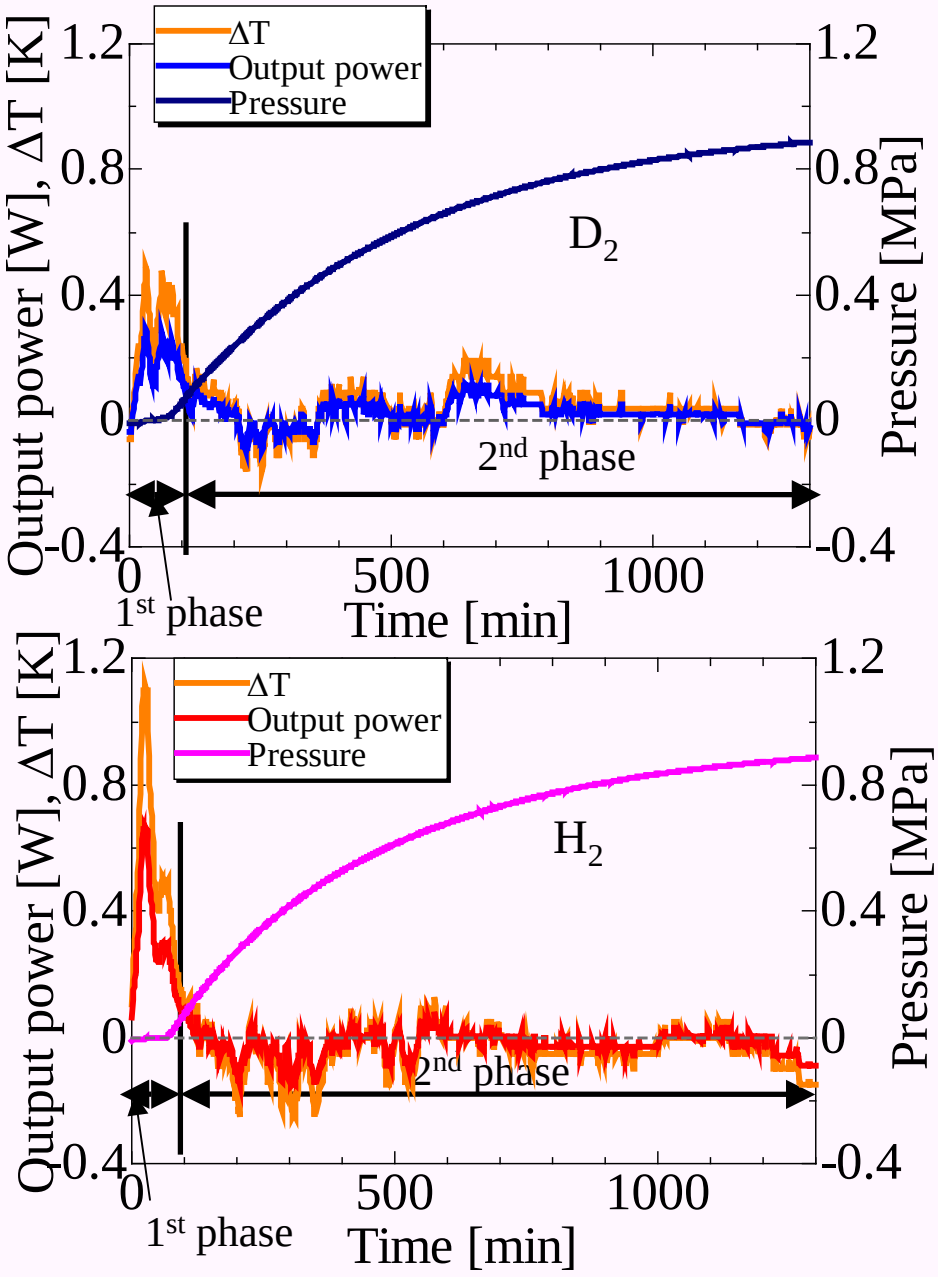




The evolution is divided into 2 phases by the time 30 minutes after the beginning of the pressure rise.

The release of heat of hydride formation should be completed in the 1st phase.

Pd black (300mesh, 99.9%) – results

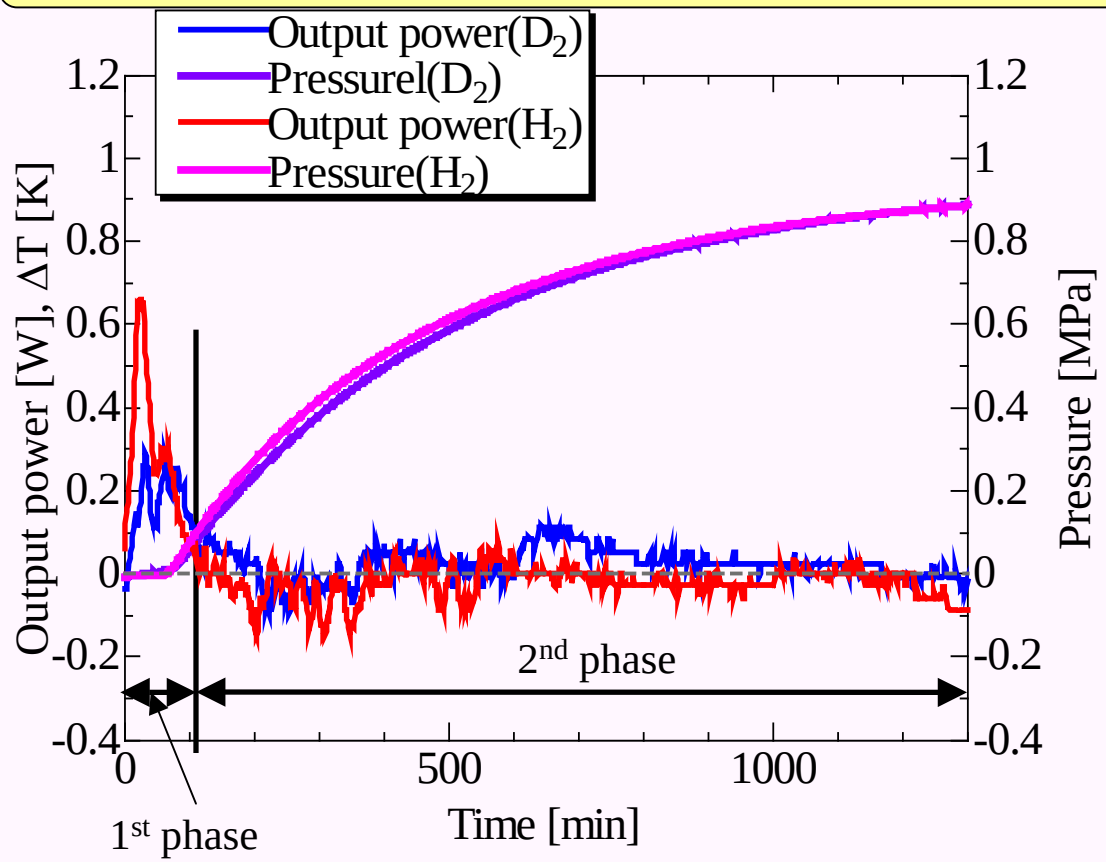


Likely to the case of Pd ϕ0.1μm sample, the evolution looks similar.

The evolution can be divided into 2 phases by the time 30 minutes after the beginning of the pressure rise.

The release of heat of hydride formation should be completed in the 1st phase.

B. Pd black (300 mesh, 99.9%) – comparison of Heat balance



Heat balance

	D_2	H_2
1st phase	5.4E+2 J/g	4.5E+2 J/g
2nd phase	2.6E+3 J/g	-6.2E+2 J/g

- The output energies in the 1st phase are almost the same for both cases, but seem to be somewhat larger than the nominal values of 100 – 405 J/g (H_2) and 80 - 330 J/g (D_2)
- On the contrary, the output energy in the 2nd phase appears to be larger for D_2 than H_2.

Summary of experimental results for the 1st Series

Sample	weight [g]	Gas	Nominal flow rate [sccm]	Measured flow rate [sccm]	1st phase [J/g]	2nd phase [J/g]	Total [J/g]	D/Pd or H/Pd	Absorption [scc]
0.1μϕ−Pd	5	D_2	10	2.7	1.0E+02	5.2E+02	6.2E+02	**0.46**	245±8
0.1μϕ-Pd	5	D_2	25	3.5	9.7E+01	7.9E+02	8.9E+02	**0.43**	224±8
0.1μϕ-Pd	5	H_2	25	5.4	1.2E+02	1.1E+03	1.2E+03	**0.45**	236±8
Pd black	3.2	D_2	25	3.3	5.4E+02	**2.6E+03**	3.1E+03	**0.85**	288±8
Pd black	3.6	H_2	25	3.9	4.5E+02	**-6.2E+02**	-6.5E+02	**0.78**	298±8

(1)D (H) absorption rates -D/Pd or H/Pd- for Pd black were about twice of those for Pd ϕ0.1μm for the phase 1 charging.

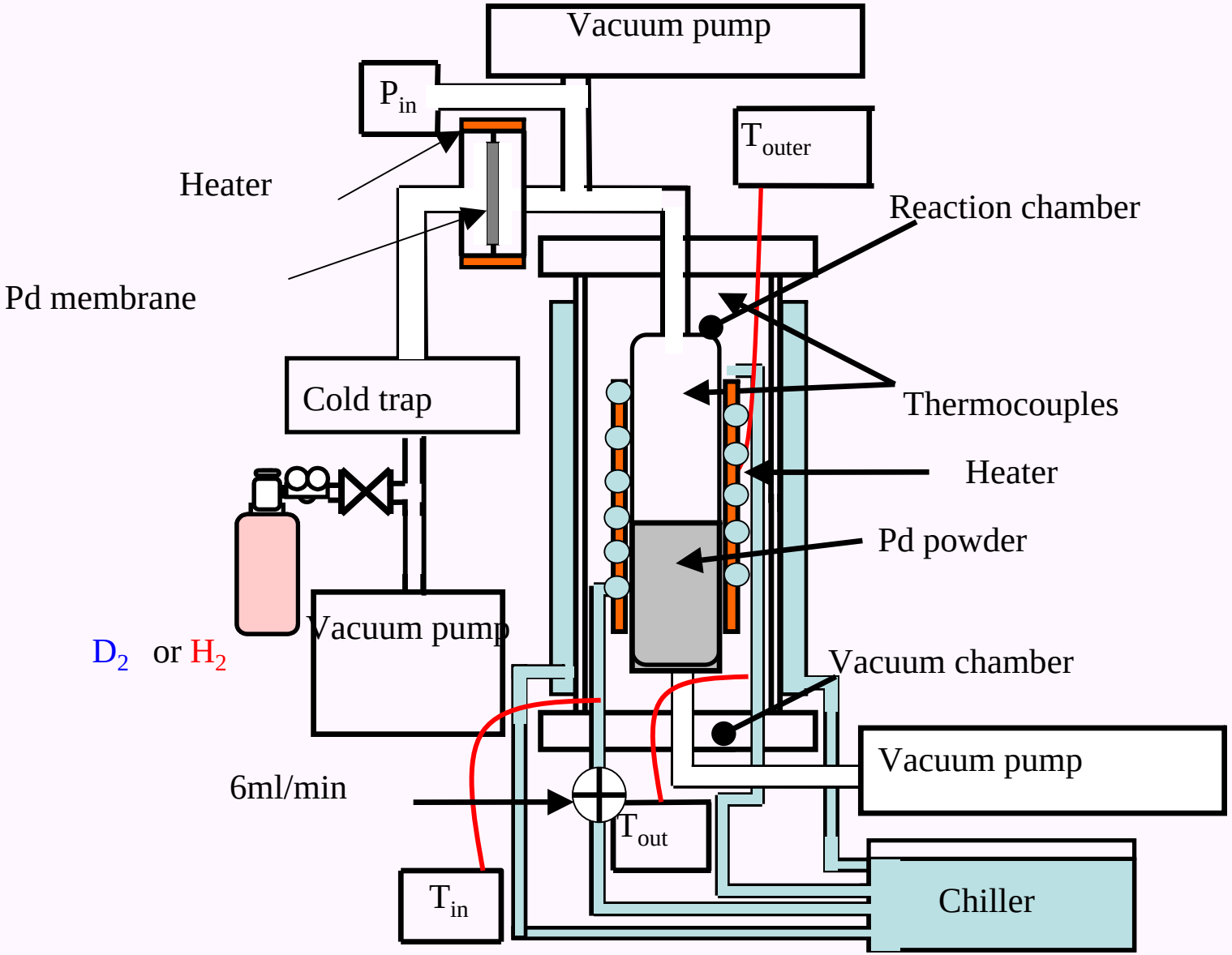
(2)Apparent excess heat about 2.6 kJ/g was observed for Pd black with D_2 gas charging.

Summary Remarks for the 1st Series Experiments

- The Pd-H_2 / D_2 gas absorption system using commercial Pd powder has been installed which enables a flow calorimetry and nuclear diagnosis.
- The calibration examination and the first experimental results have been described.
- When D_2 gas was used for the Pd-black sample, trend of excess heat was observed.
- Calorimetry time constant is yet to be made small by making heat capacity of the reaction chamber small.
- Clearer results of heat evolution will be obtained also by increasing the amount of samples.
- Nano-sized Pd powders will also be examined.

The 2nd Series Experiments

New A: Shorter FC Time-Constant (5min) and Larger Cell Volume



New A: Stability of Flow Calorimeter with Zero Input Power

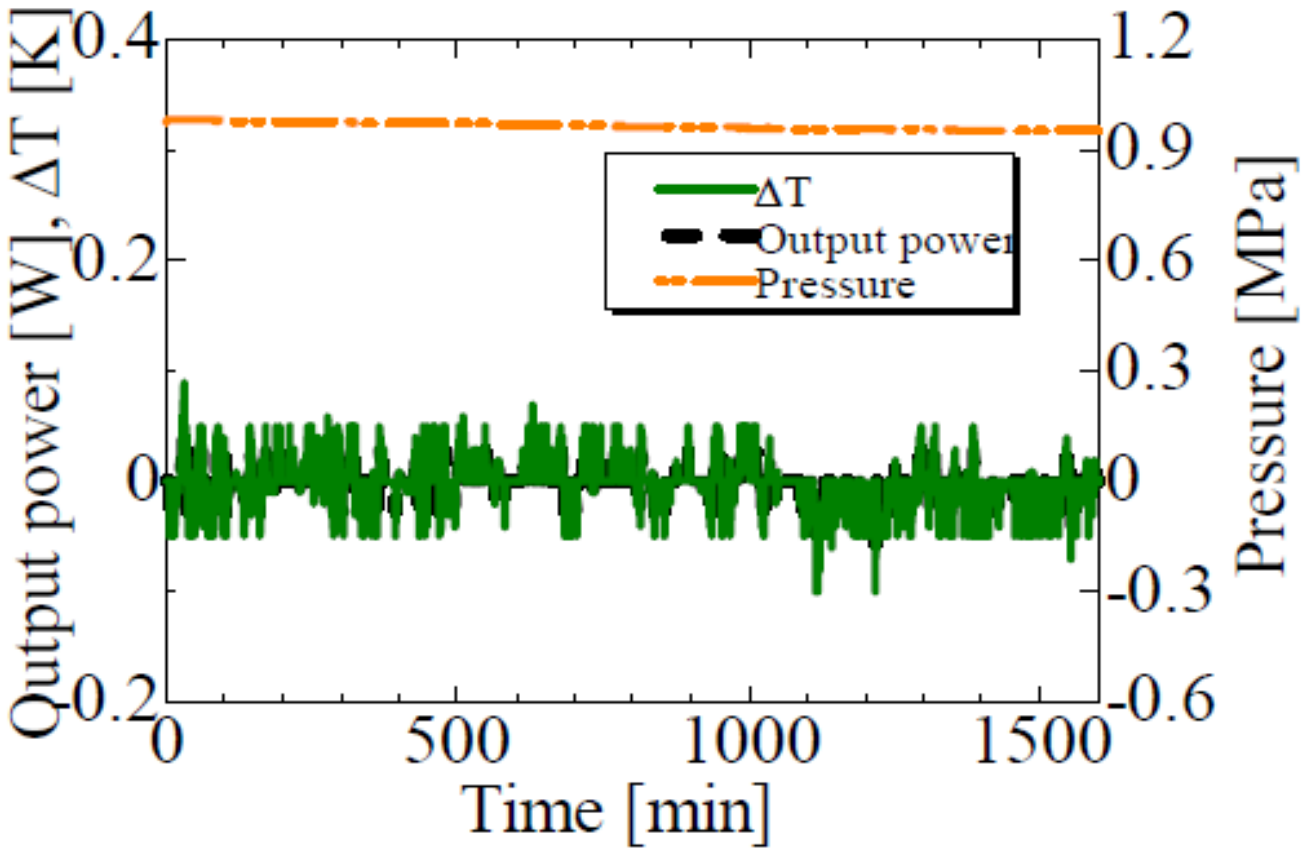
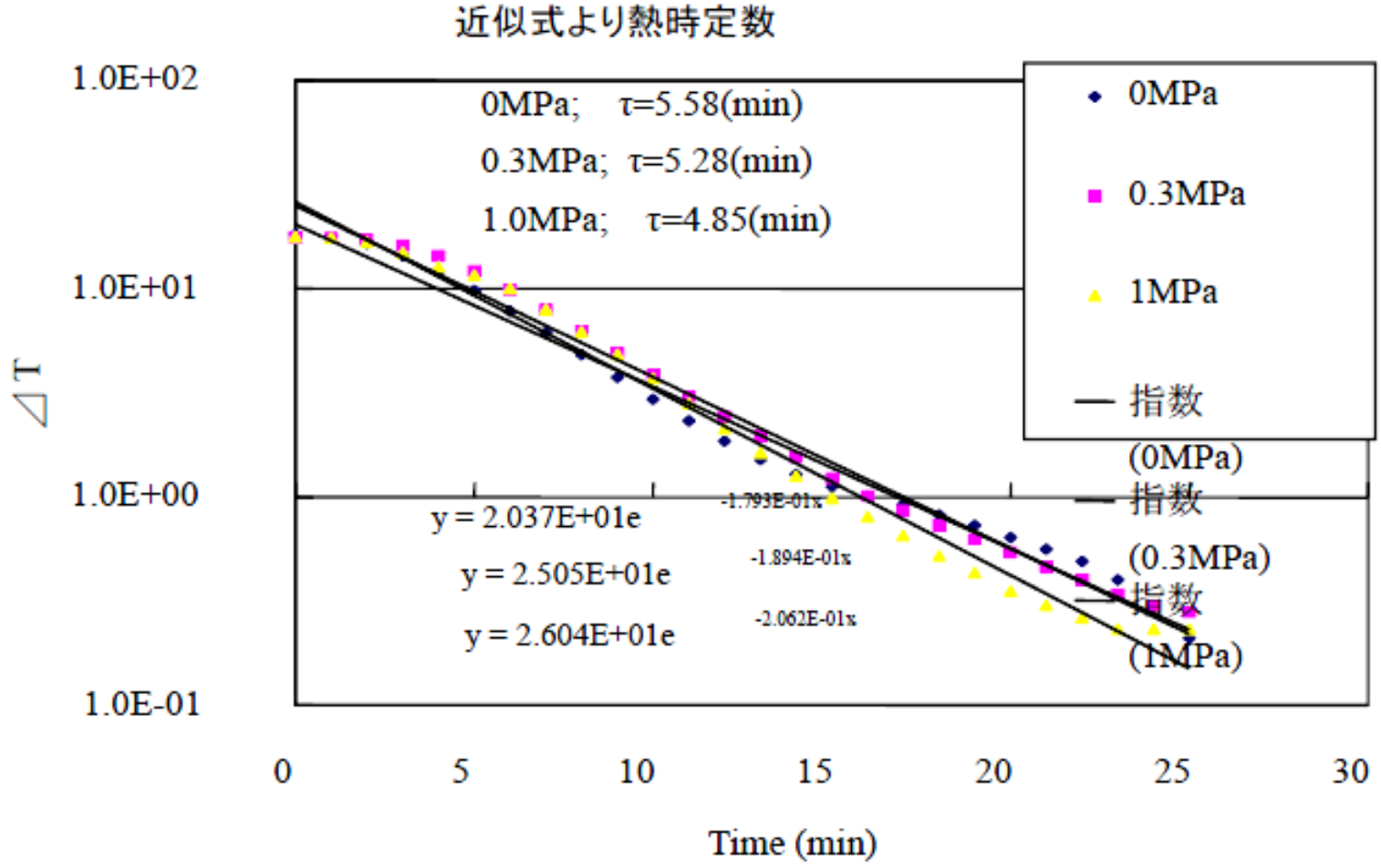


Fig. 4-2. Evolution of temperature; D_2 gas contained with 1MPa in the reaction chamber.

Time Constant for Heat Removal (75.5 %)



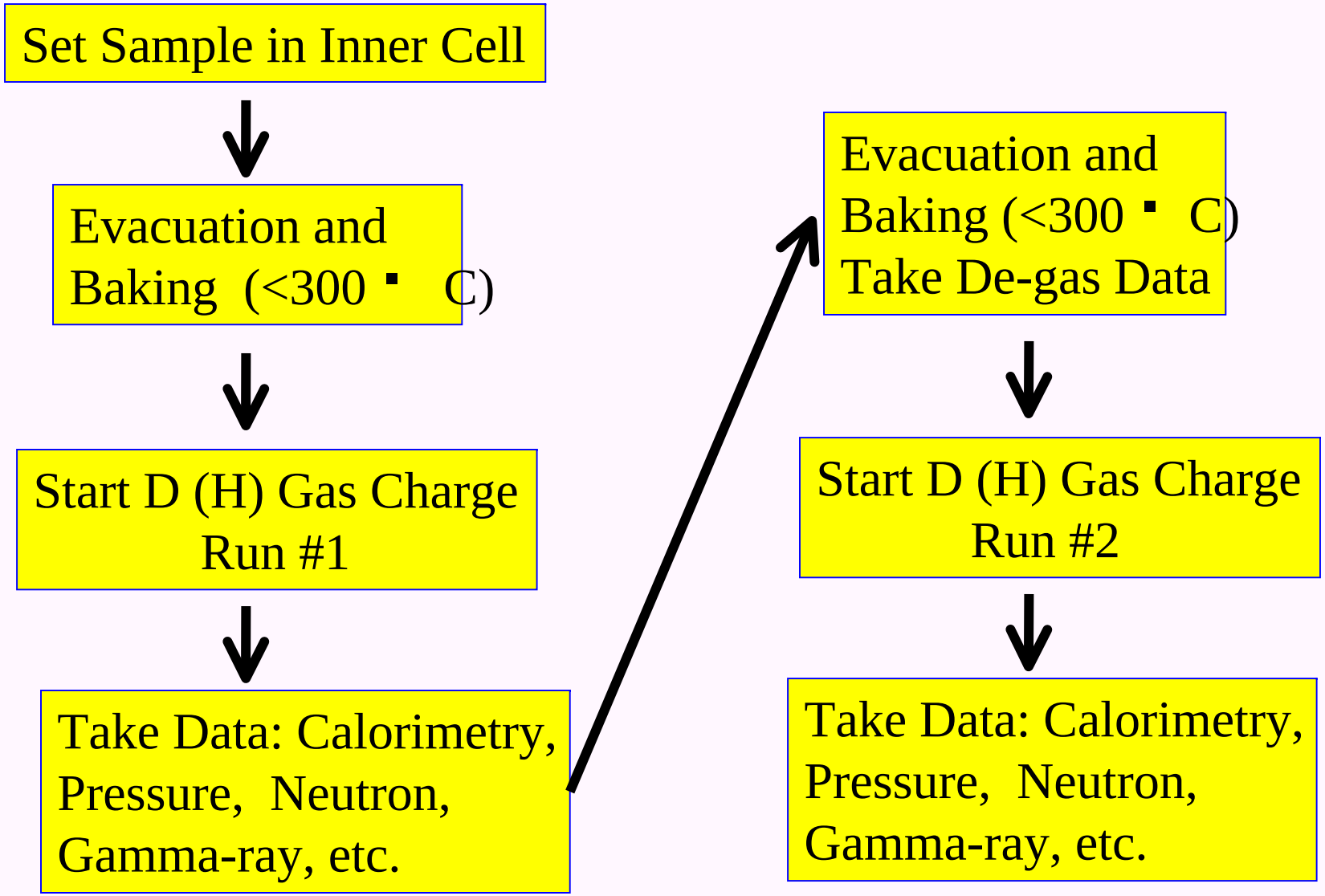
Old A-System

MPa	Thermal time constant τ_1 [s]	Thermal time constant τ_2 [s]
0.0	1463	2731
0.1	686	3016
0.3	746	2566
1.1	927	2048

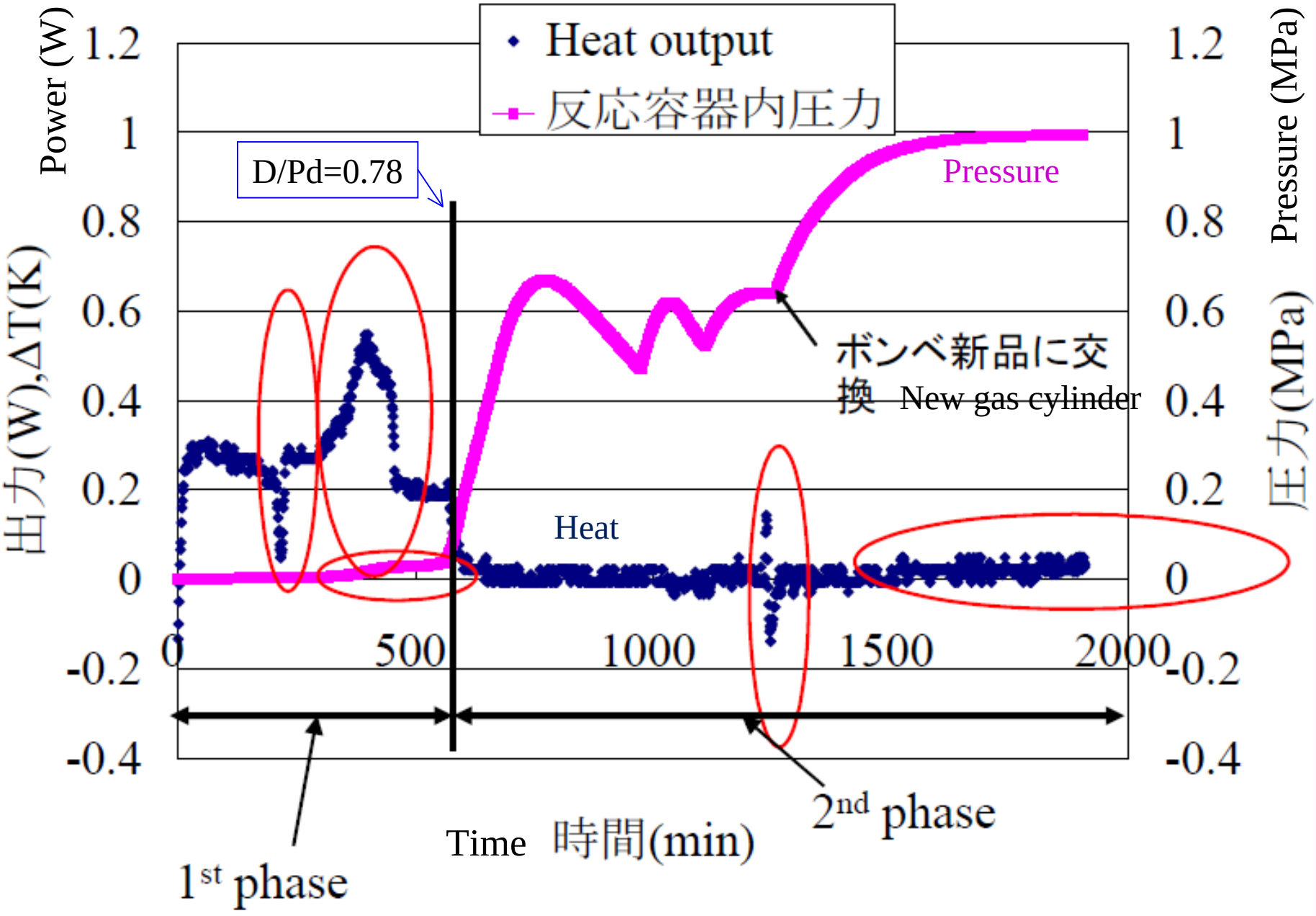
New A-System

MPa	Thermal time constant τ [s]
0.0	335
0.3	317
1.0	291

2. Experimental Procedure



Pd-black (20g) / D-gas charge #1: Nov. 2009



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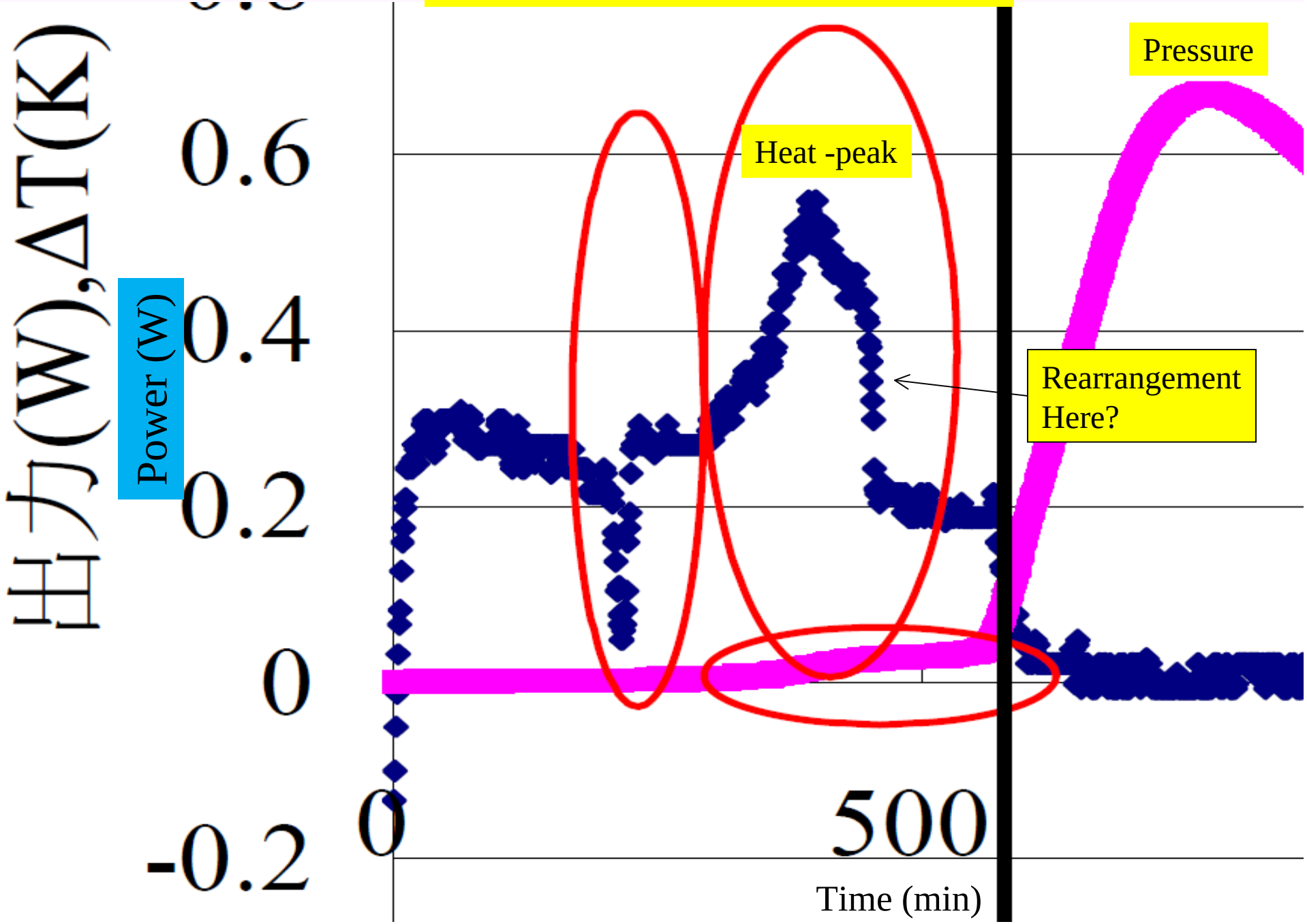
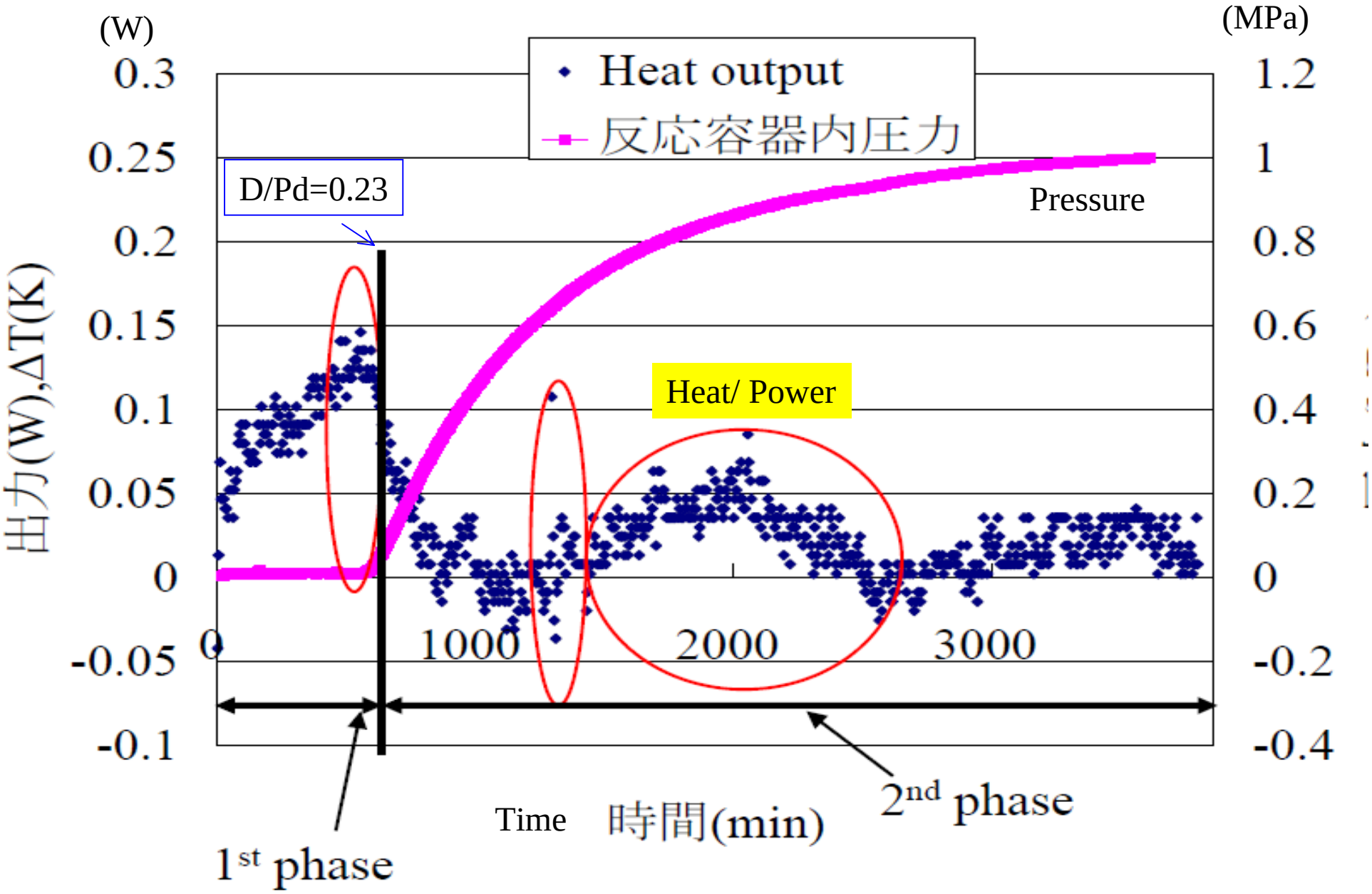
Pd-black / D-gas charge #1 data



Decreased absorption and heat level for #2

Pd-black (20g)/ D-gas #2



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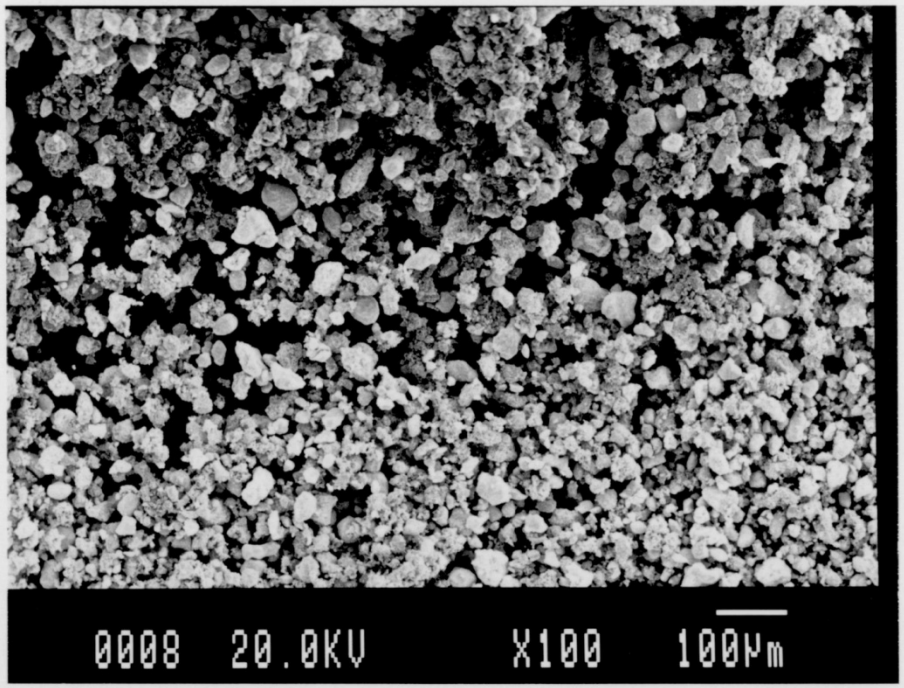
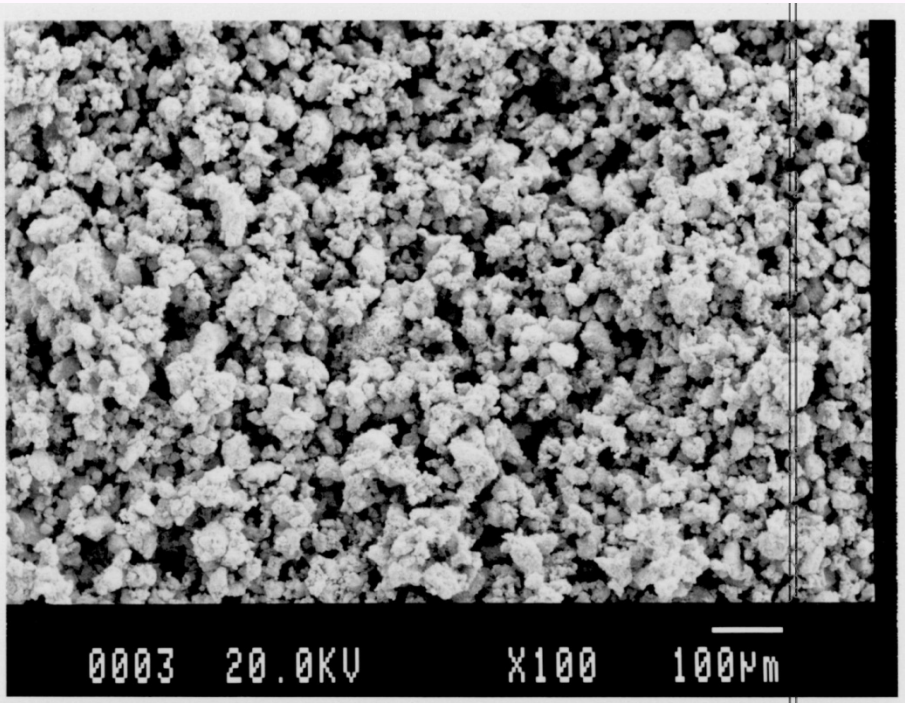
Before Runs



After Runs



Magnification: ×100 SEM Image

After experiments, Pd black powders stuck to be bigger sizes → Decrease of active surface area

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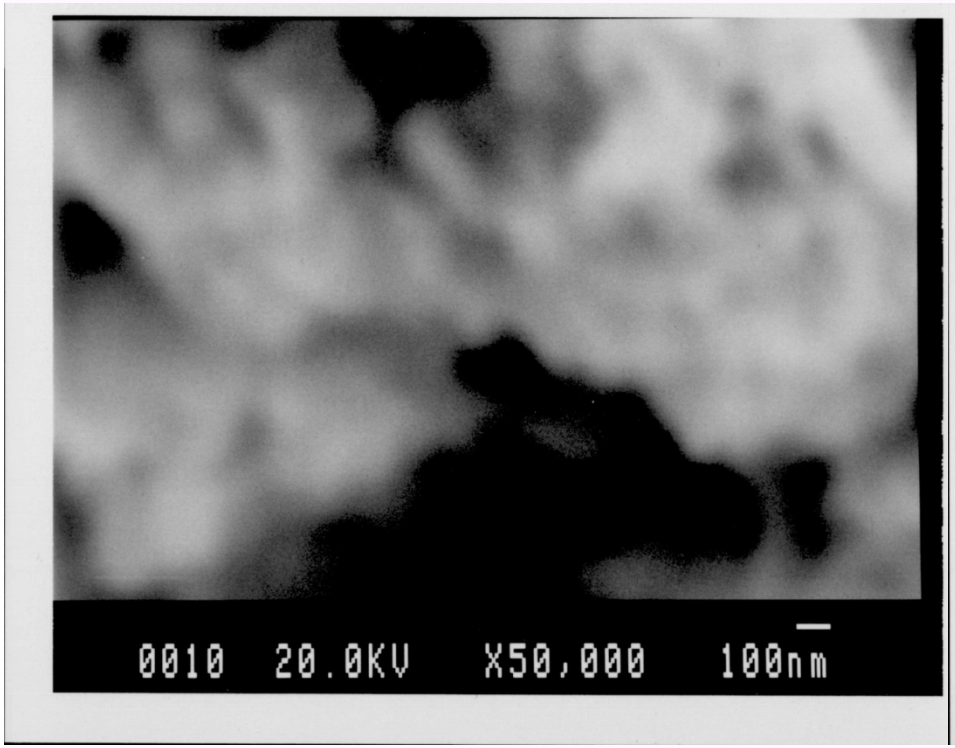
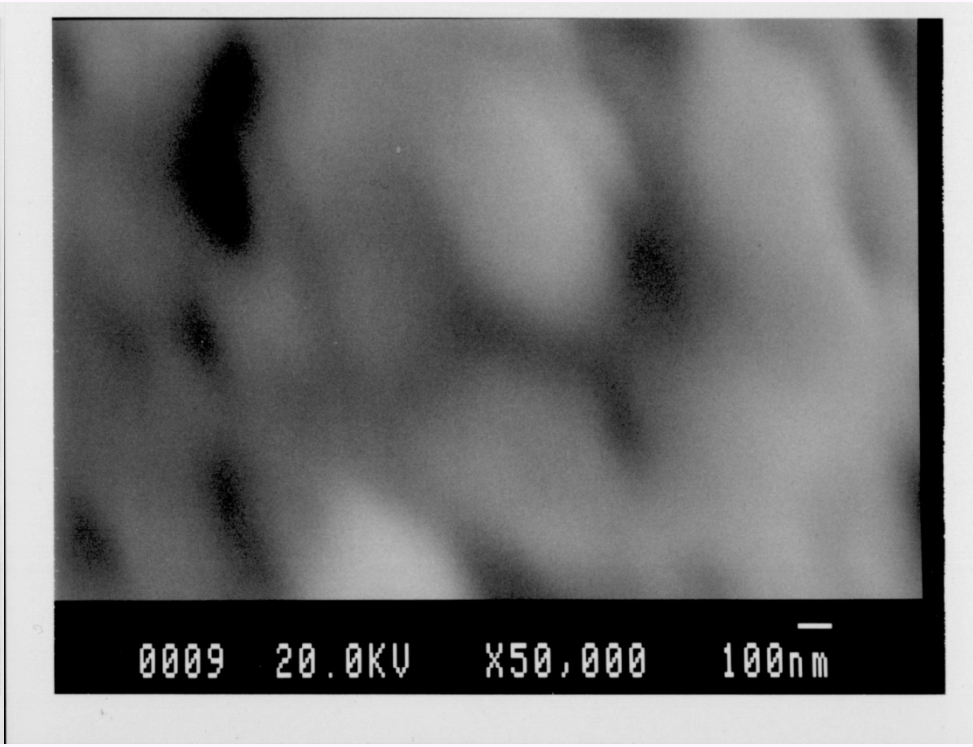
Before Runs



After Runs



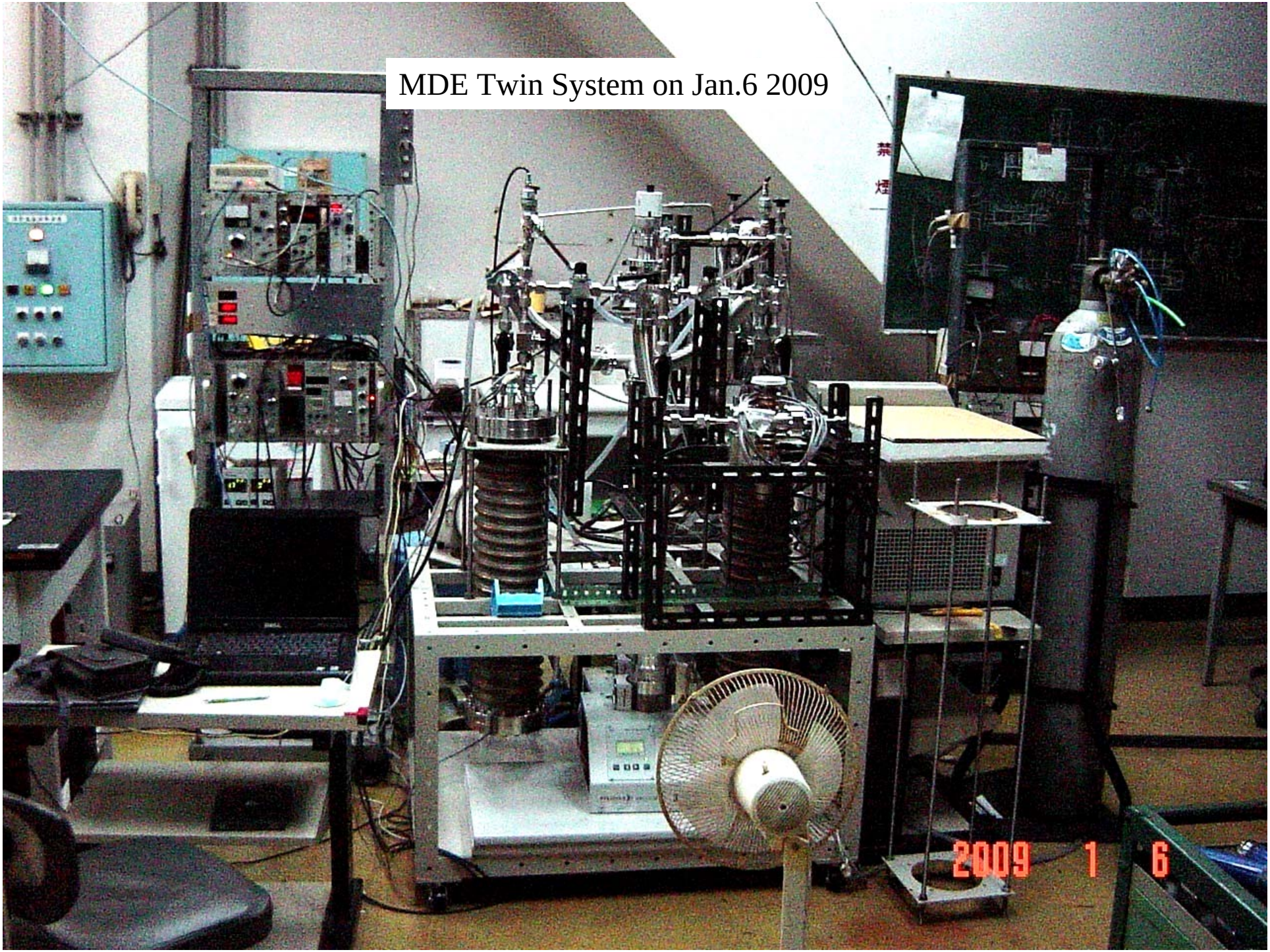
Magnification: ×50,000 SEM Image

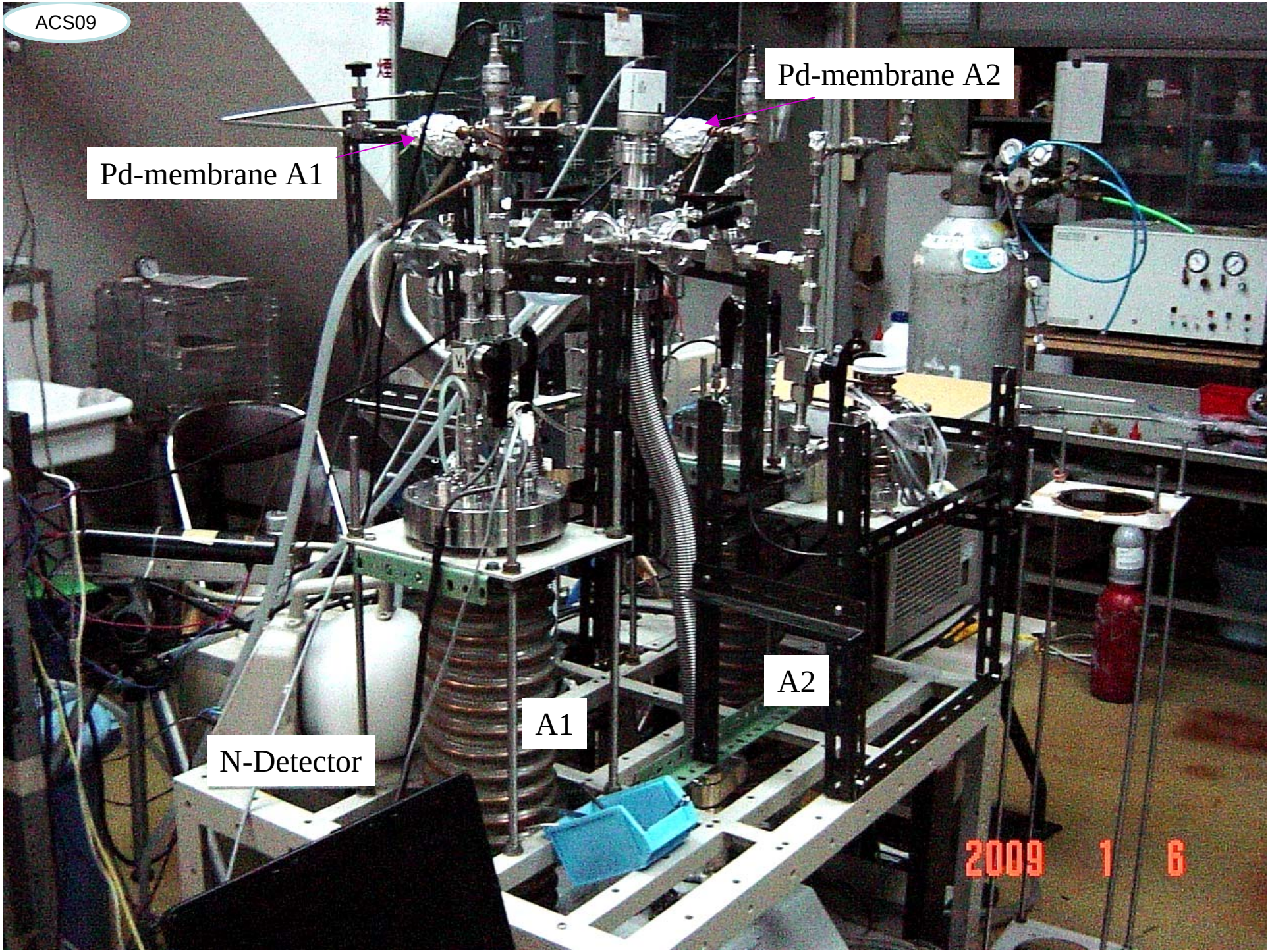
Before experiment, surface was fractal in nano-scale.

After experiment, surface became flatter in about 10 times larger scale → Decrease of active surface area

Summary for Pd-black

- There were seen excess heat in the 1st and 2nd phases, but smaller than those by Pd/ZrO_2
- Pd-black powders stuck to be bigger sizes (about 10 times diameter by SEM observation), after the #1 run.
- In the #2 run and following runs, no significant excess heat was seen.
- D/Pd ratio for #1 was 0.78 in the pressure zero condition under D-charge.
- D/Pd ratios for #2 and later runs, D/Pd was about 0.23 (much smaller).
- No transmuted elements were seen by PIXE.


MDE Twin System on Jan.6 2009
2009 1 6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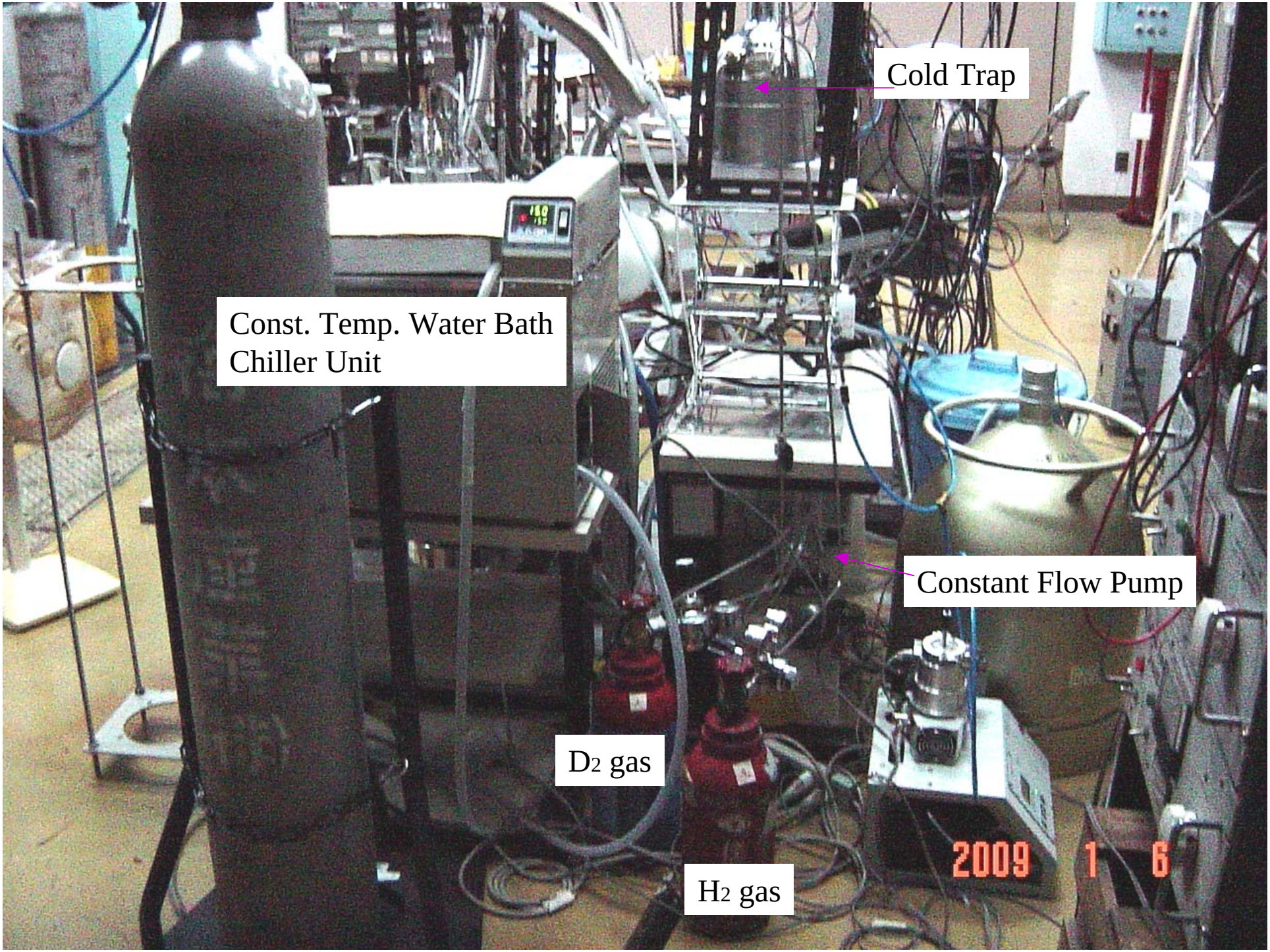
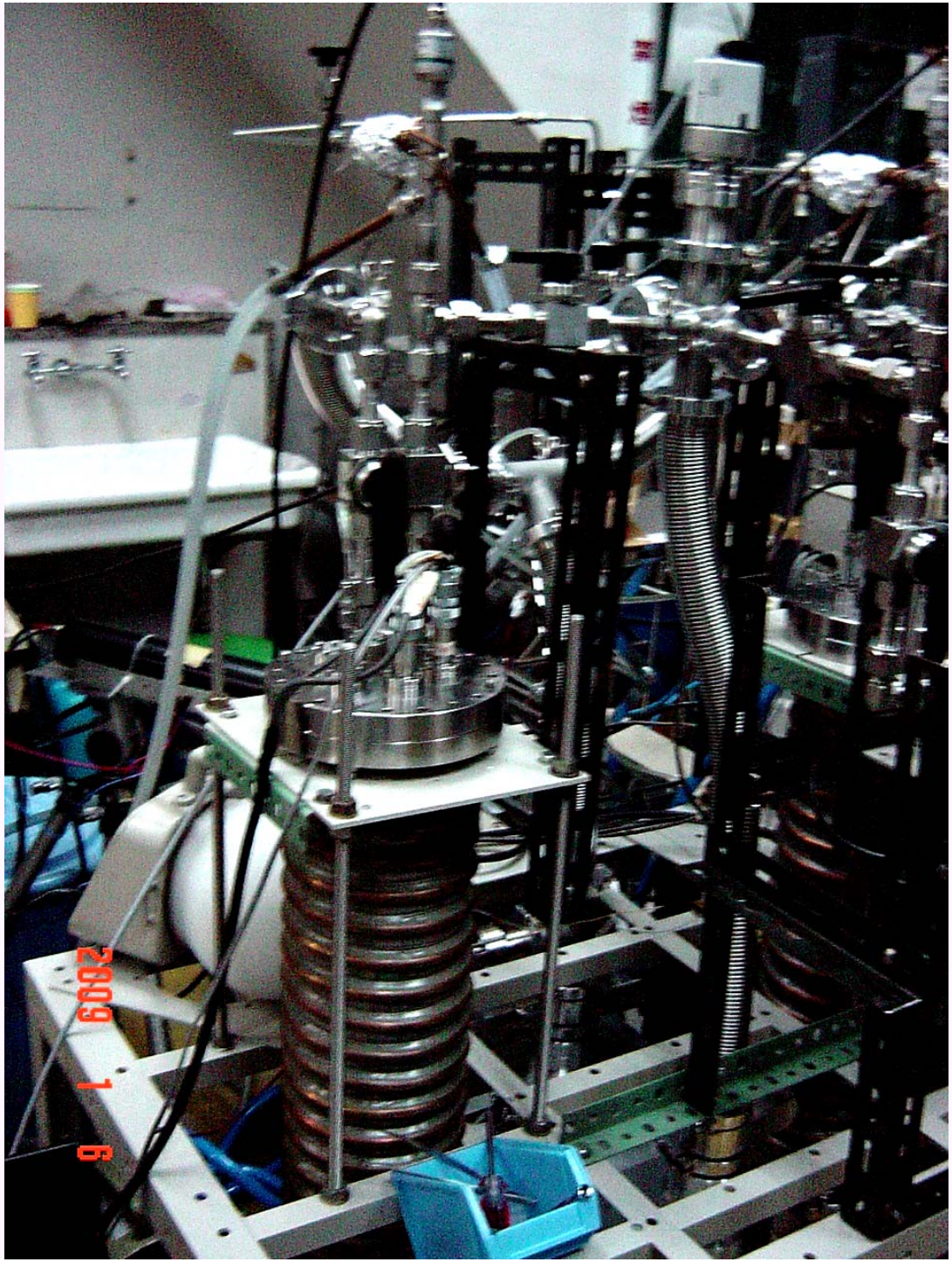
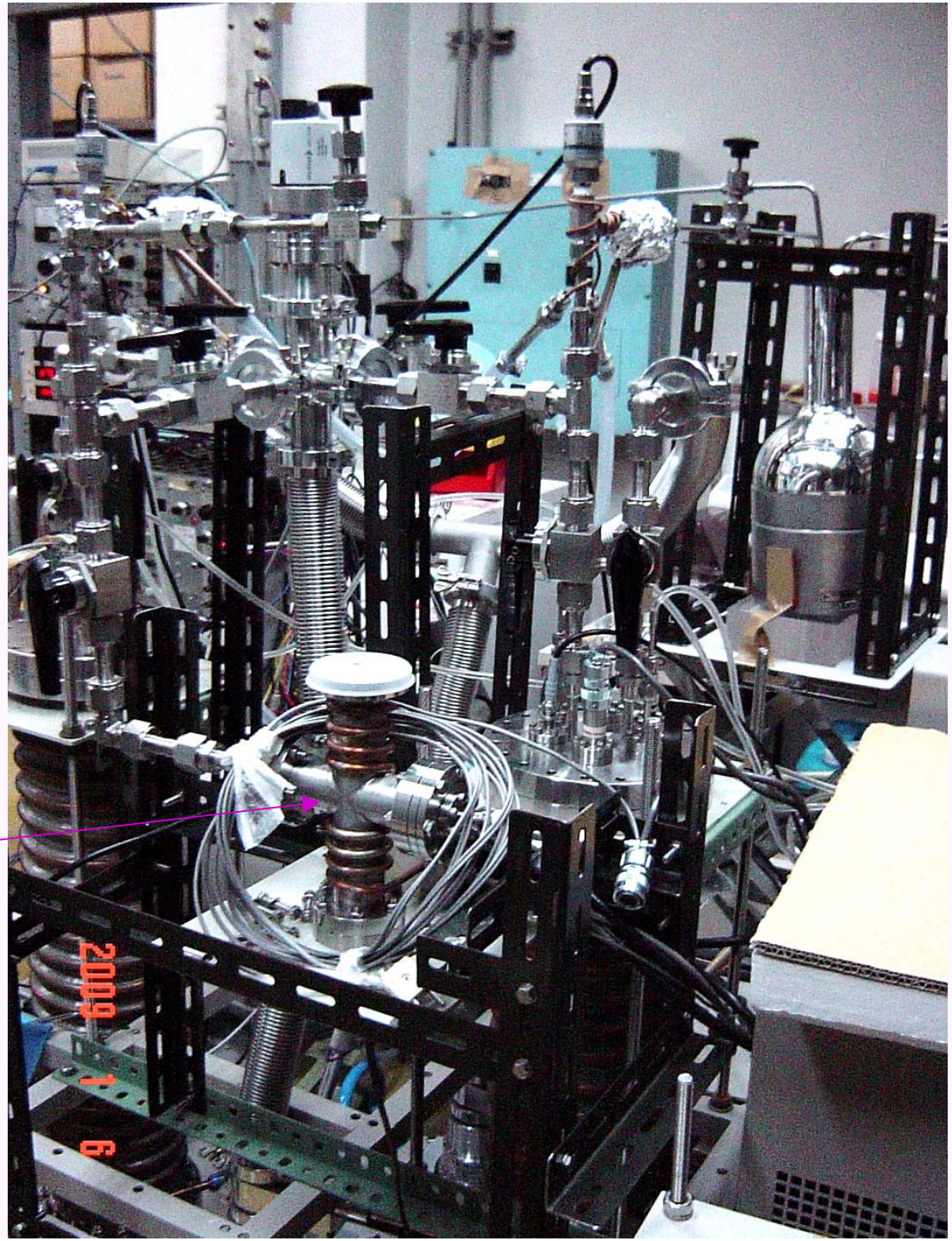
Pd-membrane A2
Pd-membrane A1
A2
A1
N-Detector
2009 1 6


Cold Trap
Const. Temp. Water Bath
Chiller Unit
Constant Flow Pump
D2 gas
H2 gas
2009 1 6

A1 System





B System
Under
Construction

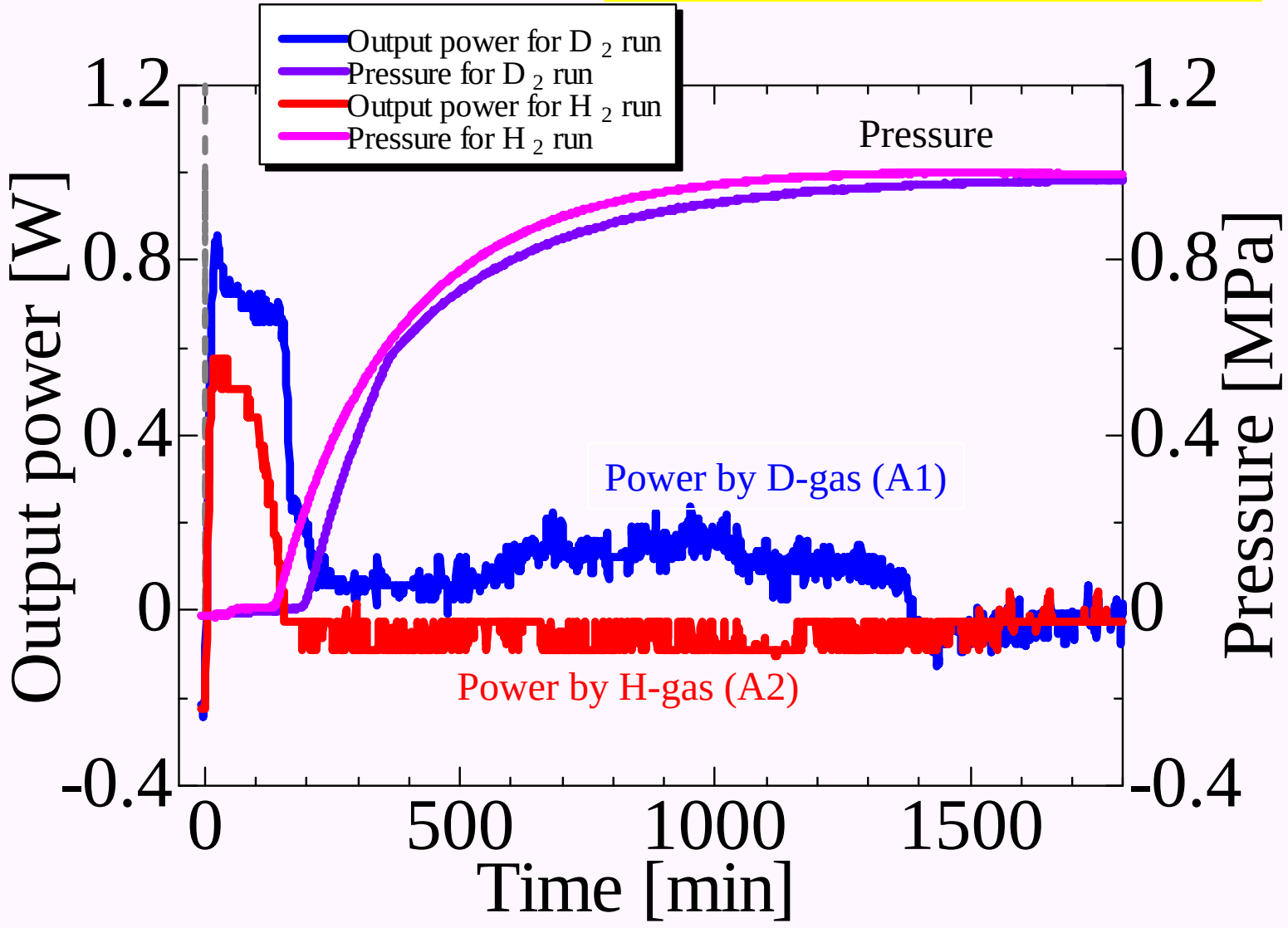
Experiments with Pd/PdO/ZrO_2 Dispersed Samples

10g (Net Pd weight : 4.3 g): Three trials for Santoku 1, Santoku 2 and Santoku 3 samples, #1 and #2 runs for each sample

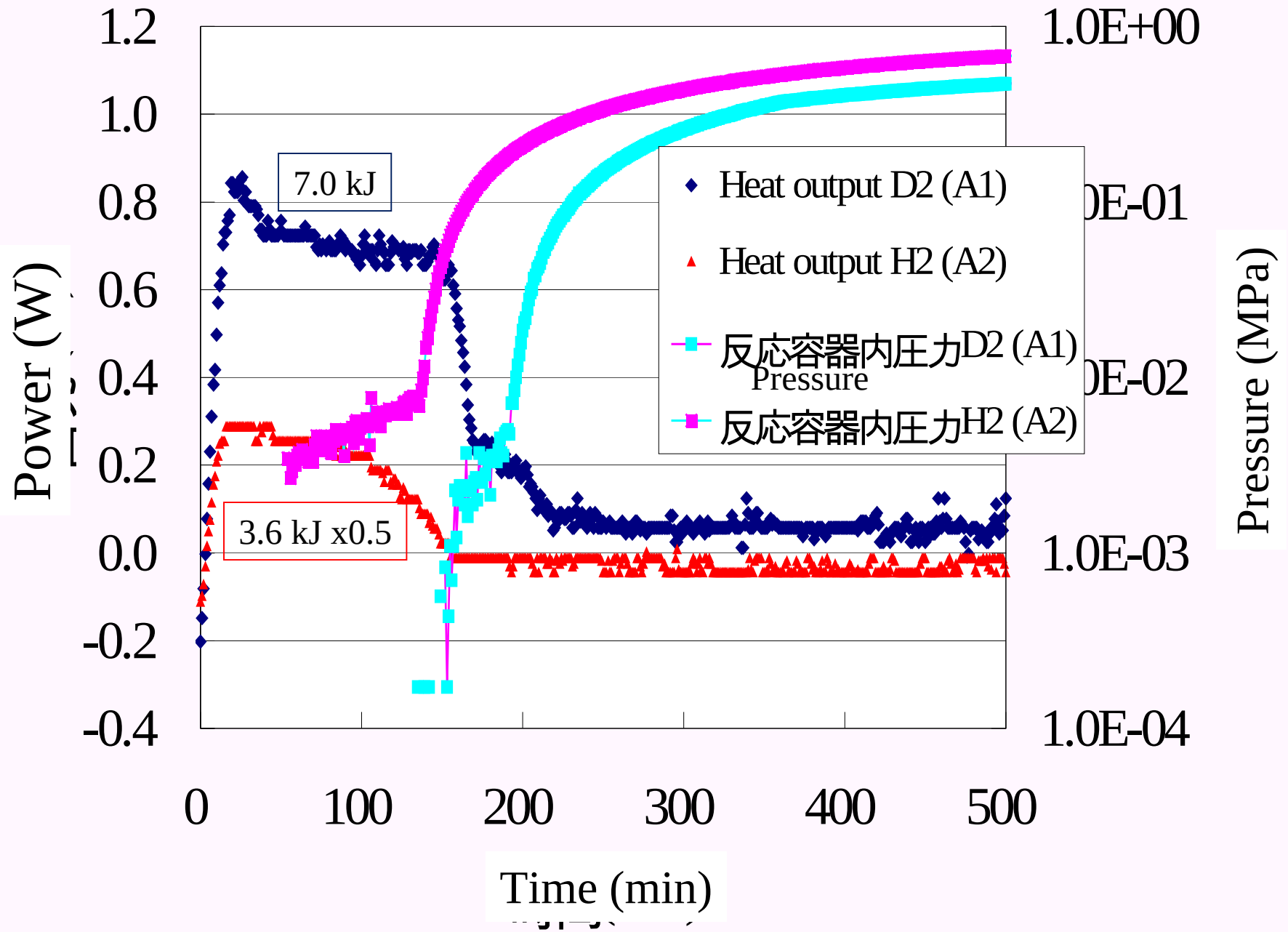
- Nano-Pd/ZrO_2 sample was produced by Santoku Co. Japan, based on different protocol from Inoue-Yamaura (Arata-Zhang).
- X-ray diffraction analysis showed composite of Pd/PdO/ZrO_2 .
- Pd particle size is less than 10nm.
- A1 system: 10g for D-gas charging (2-3sccm)
- A2 system: 10g for H-gas charging (2-4sccm)
- Water-flow calorimetry: 6cc/min flow rate

Santoku 1#1 Results of Heat Evolution

Gas flow rate: 2.8 (D) and 2.6(H) sccm



Santoku1 #1 Run: Expanded view for 1st phase



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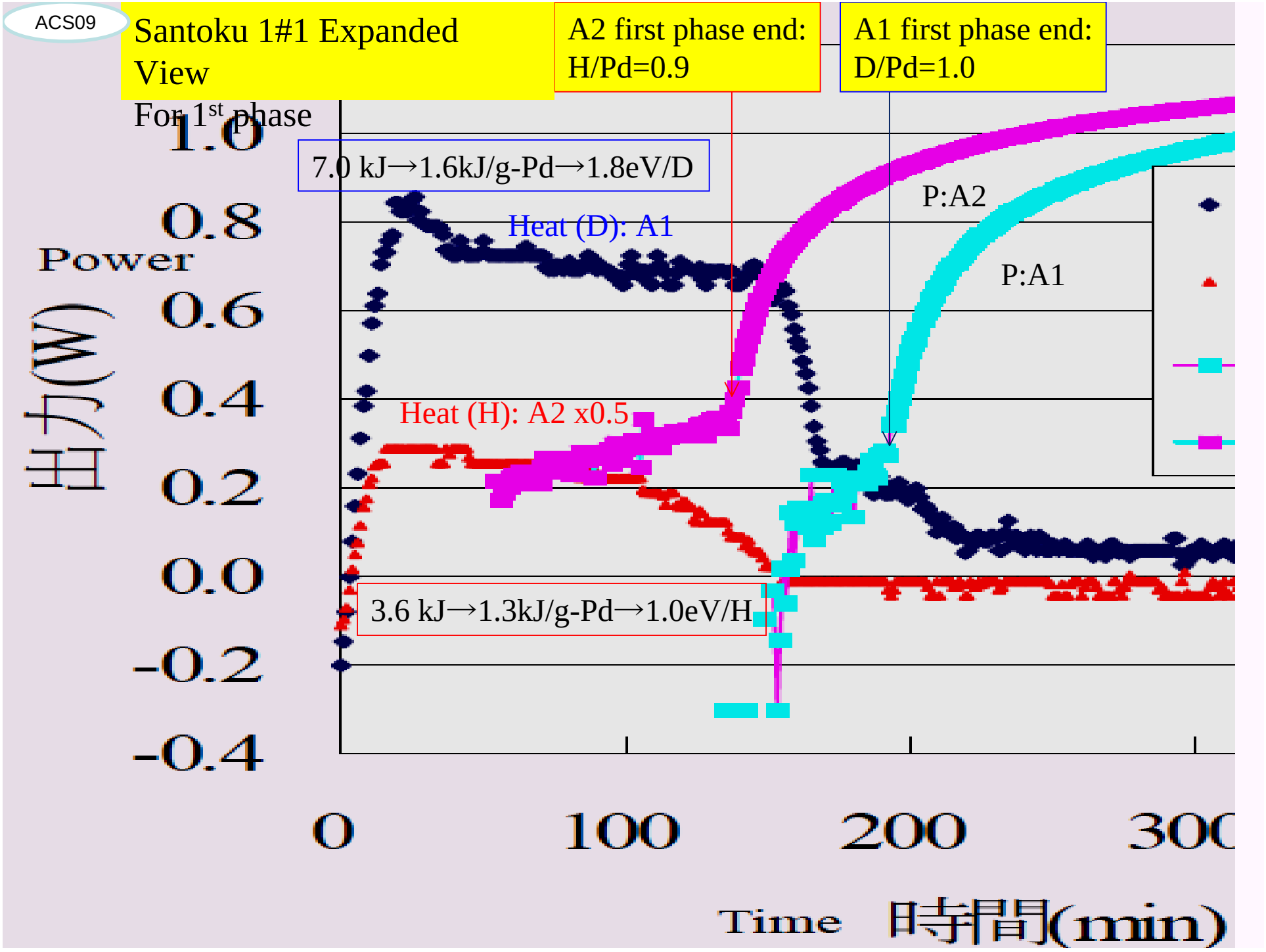
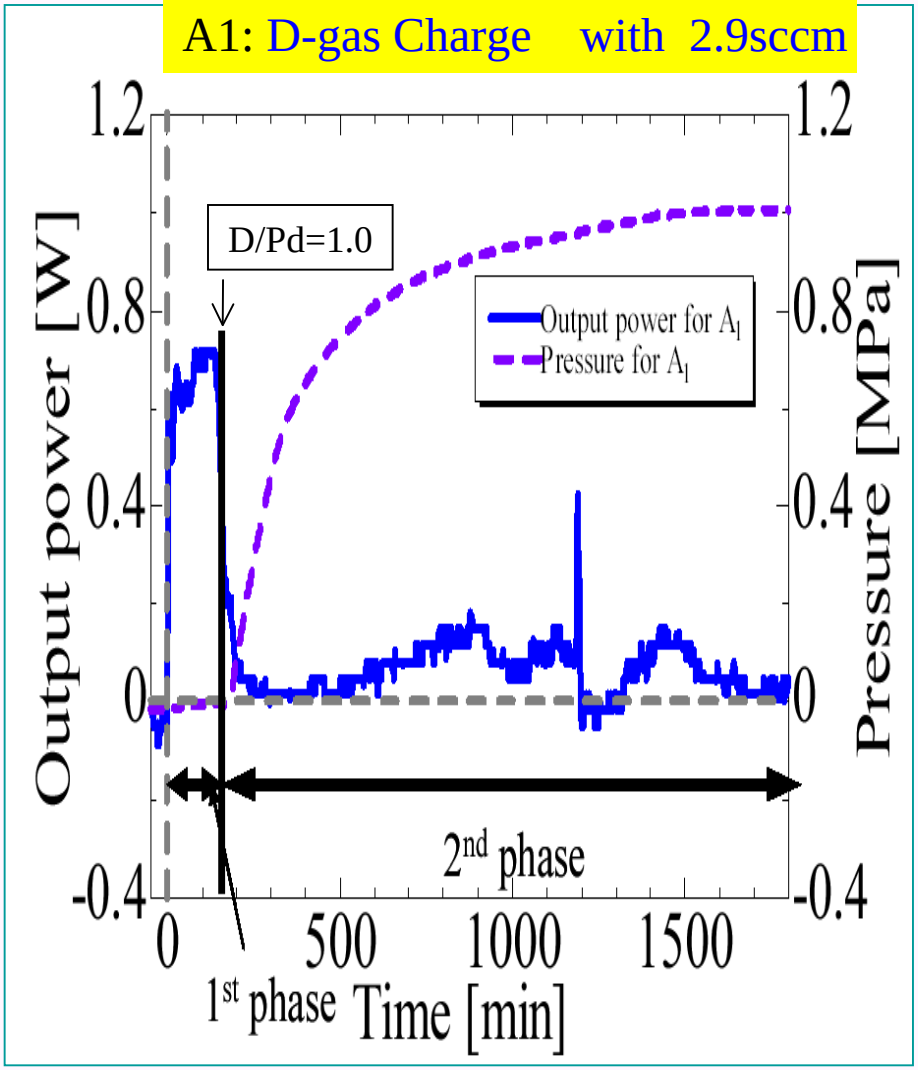
Santoku 1#1 Expanded View

For 1st phase



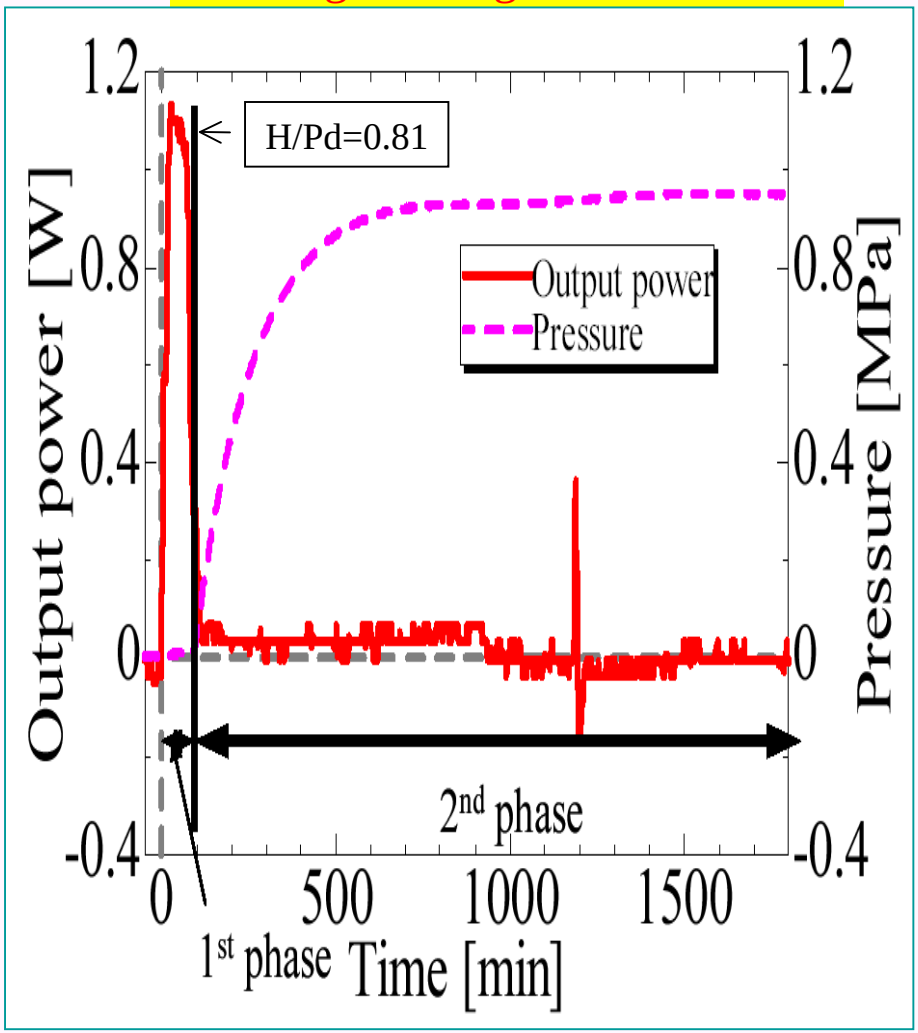
Results of Santoku2#1 run

A1: D-gas Charge with 2.9sccm



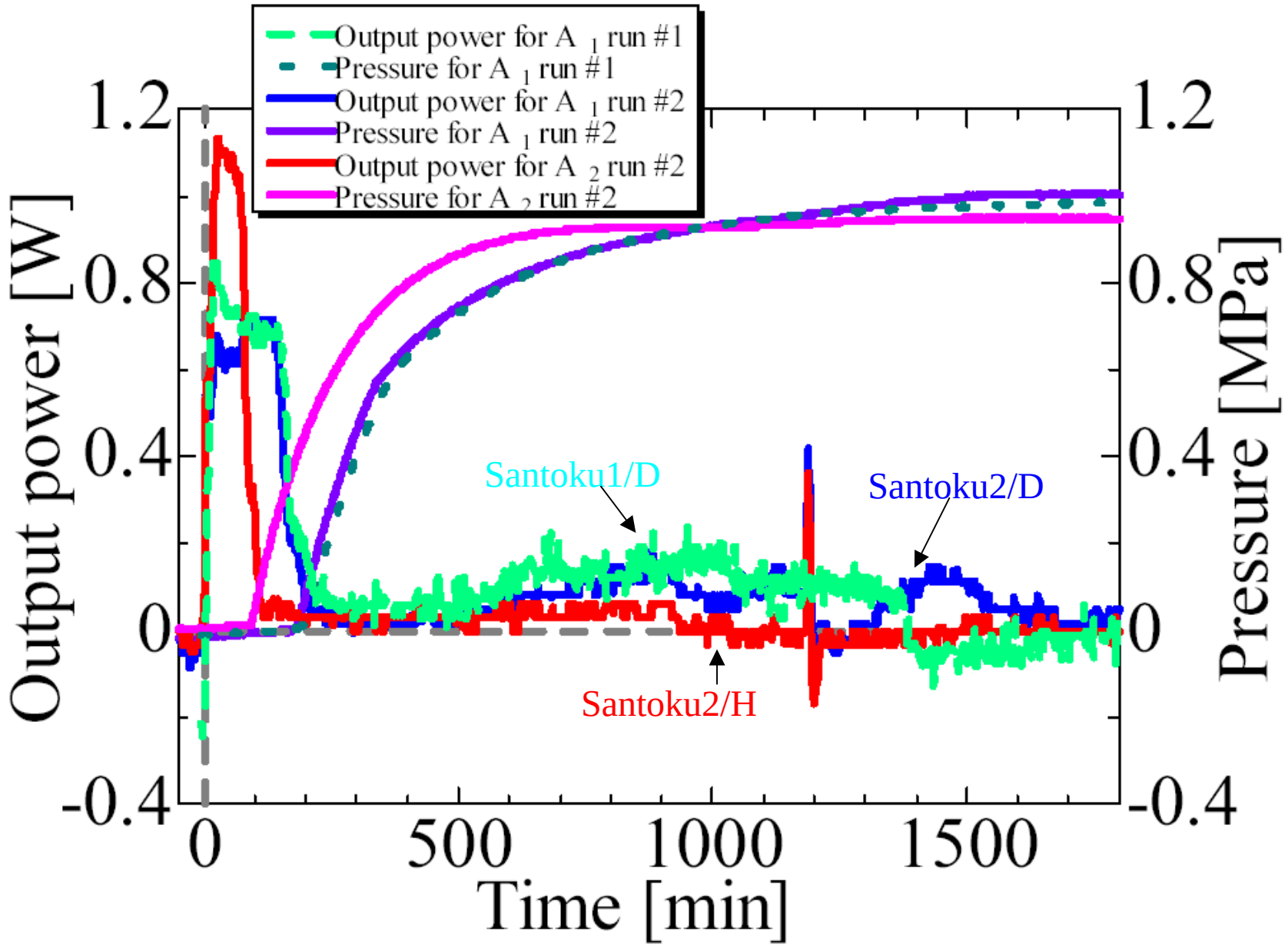
D-gas Charging to Santoku2#1

A2: H-gas Charge with 3.5sccm

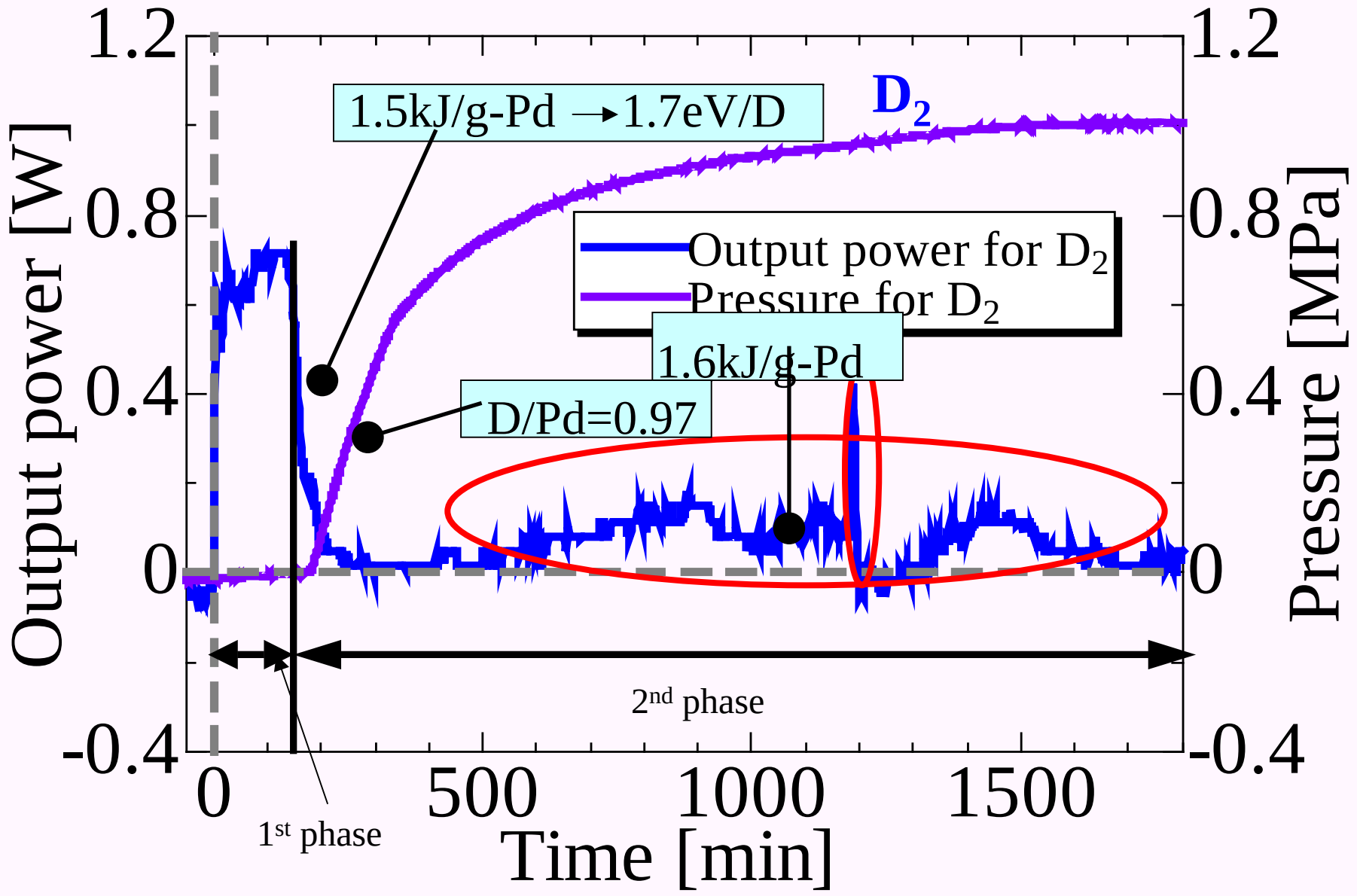


H-gas Charging to Santoku2#1

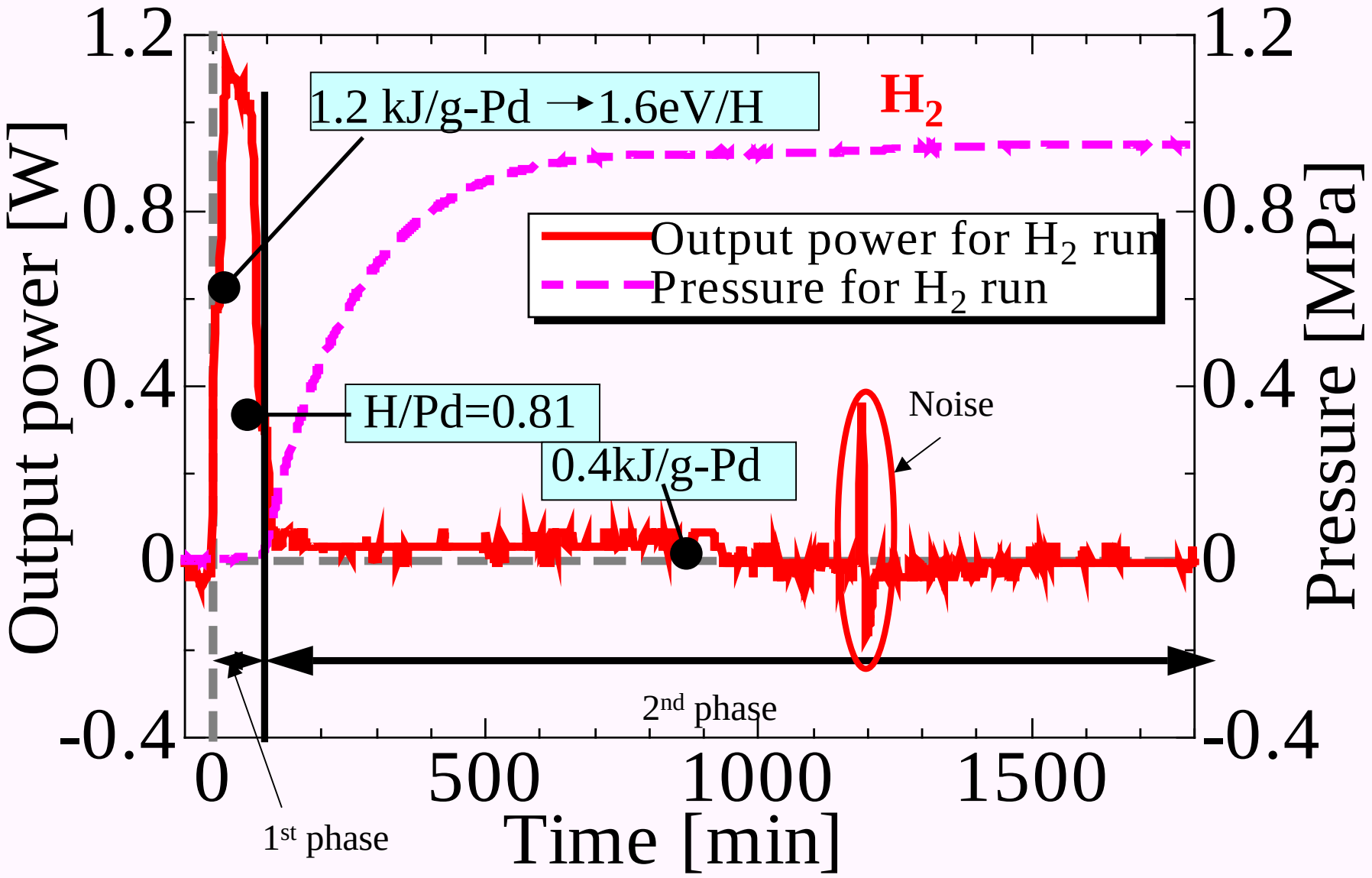
Comparison of Results for Santoku1#1 and Santoku2#1



Pd･ZrO2 Santoku 2 #1 Run (A1) for D-gas Charge



Pd･ZrO2 Santoku 2 #1 Run (A2) for H-gas Charge



Integrated Data for Pd/ZrO2 Santoku #1 Runs

Significant **isotopic effects** are seen for D(H)/Pd =x loading ratios , and out-put energies per Pd (and D(H) atom), for the 1st phase.
Significant excess heat by D-gas charge in the 2nd phase.

Santoku 2#1

Run number	Specific output energy[kJ/g]		Composition; x for	Output energy per D/H
	1st phase	2nd phase		
D_2	1.5±0.0	1.6±0.2	0.97	1.71± 0.05
H_2	1.2±0.0	0.4±0.2	0.81	1.67 ± 0.03

Santoku 1#1

D2	1.6±0.0	1.7±0.2	1.0	1.8±0.05
H2	0.8±0.0	(-)	0.89	1.0±0.03

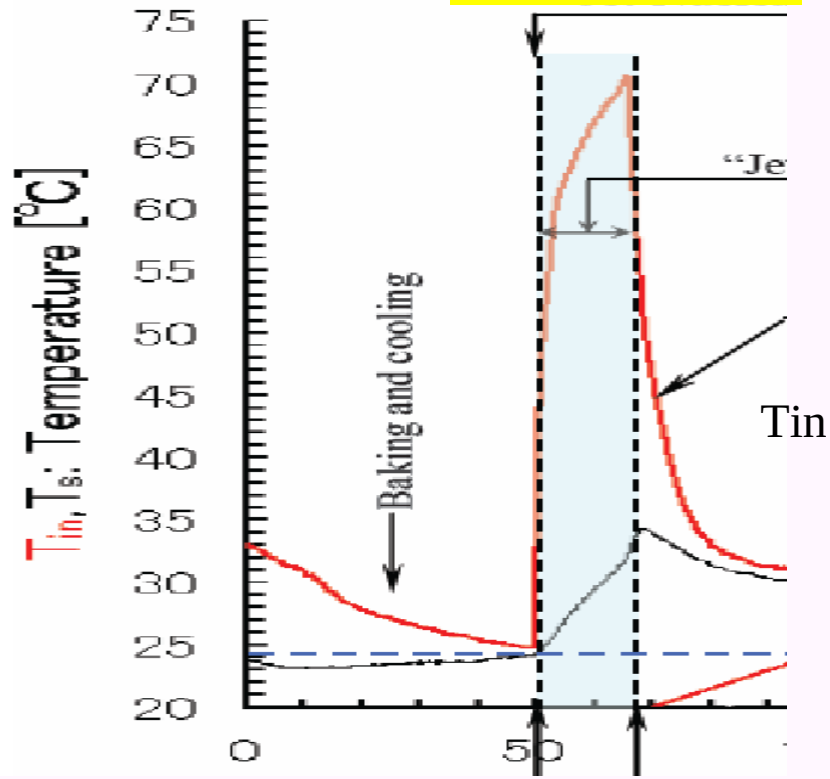
Summary Table of Integrated Data for #1 Runs With Santoku Pd/PdO/Zr_2O nano-composite samples

Time-Interval: 0-1,800 min

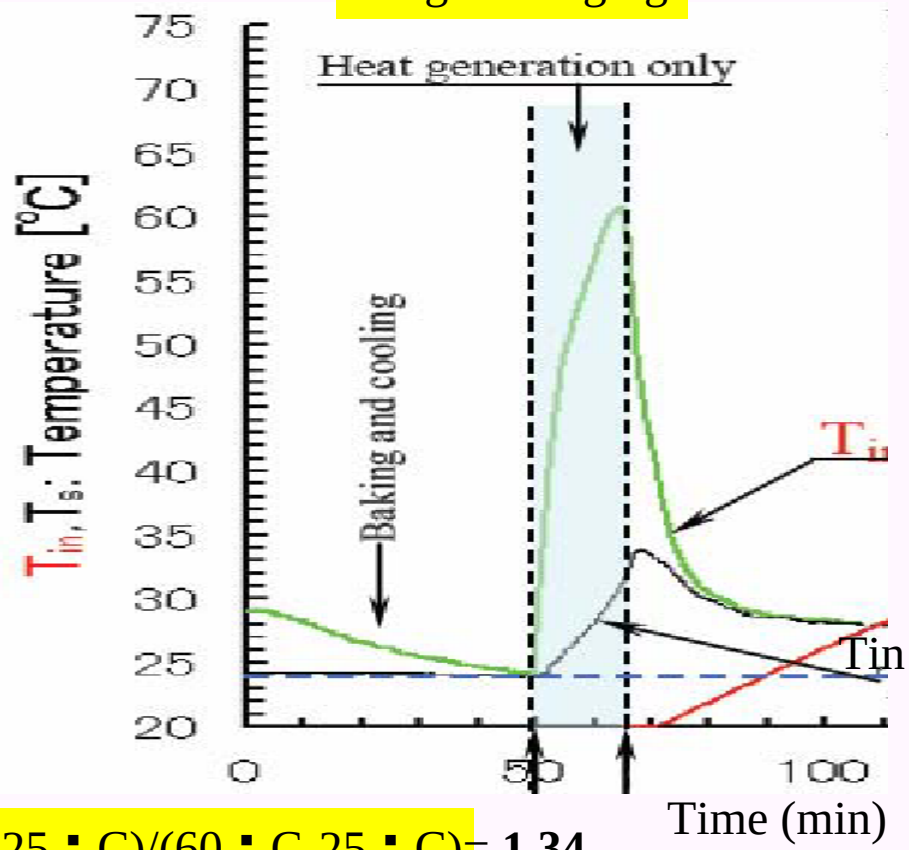
Run number	flow rate [sccm]	Output energy [kJ]		Specific output energy[kJ/g]		Composition; x for PdDx/PdHx	Output energy per D/H in the 1st phase [eV]
		1st phase	2nd phase	1st phase	2nd phase		
D-PZ1#1	2.8	7.0±0.2	6.8±1.3	1.6±0.0	1.6±0.3	1.0	1.80 ± 0.05
Corrected H-PZ1#1	2.6	3.6±0.1	-5.1±1.4	0.8±0.0	-1.2±0.3	0.89	1.02 ± 0.03
D-PZ2#1	2.9	6.4±0.2	5.5±0.8	1.5±0.0	1.2±0.2	0.97	1.71± 0.05
H-PZ2#1	3.5	5.1±0.1	1.7±0.9	1.2±0.0	0.4±0.2	0.81	1.67 ± 0.03

Arata-Zhang's 1st Phase Data for Pd/ZrO2 (7g)

D2-gas charging



H2-gas charging



Arata-Zhang: [Heat(D)/Heat(H)] ~ (72C-25 ▪ C)/(60 ▪ C-25 ▪ C)= **1.34**

Our Exp. Santoku1: [Heat(D)/Heat(H)] = (7.0kJ)/(3.6kJ) = **1.94**

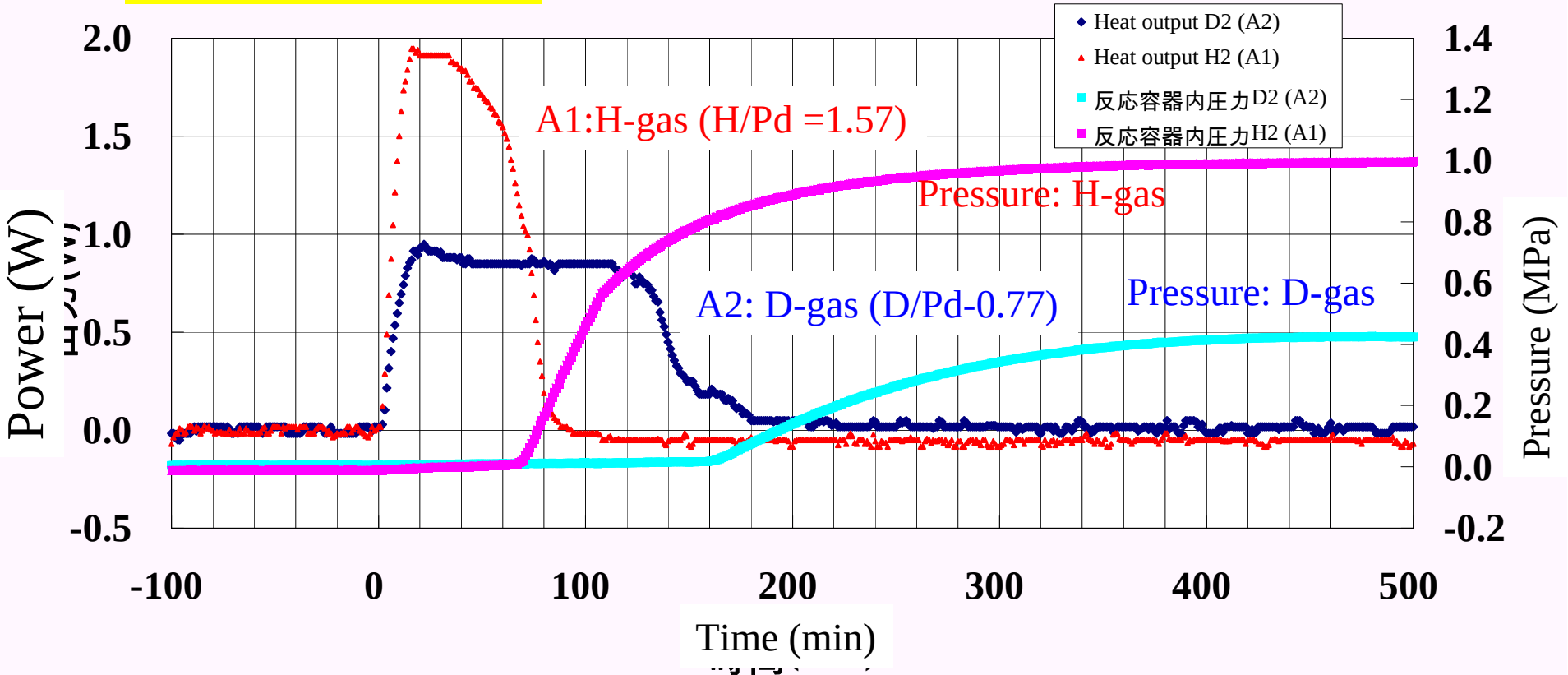
Our Exp. Santoku2: [Heat(D)/Heat(H)] = (6.4kJ)/(5.1kJ) = **1.26**

Agreed!

Results by Large H-Flow Rate And Low D-Gas Pressure

A1: H-gas, Flow Rate = **9.96** sccm
A2: D-gas, Flow Rate = **2.1** sccm

Santoku **3#1** Run



run	1st phase [kJ]	2nd phase [kJ]	1st phase [J/g]	2nd phase [J/g]
D_2-3-1	7.14±0.15	1.26±1.36	1661±35	293±316
H_2-3-1	7.07±0.07	-0.23±1.44	1644±18	-54±334

Table. : Integrated Data for the First Phase ("zero" pressure interval)

Run	gas	Heat (kJ/g-Pd)	D/Pd or H/Pd	Eout/Pd (eV)	Eout/D(H) (eV)	comment
0.1 μ Pd#2	D	0.097±0.05	0.43	0.11	0. 25±0. 13	Old A
ibid	H	0.12 ±0. 03	0.45	0.13	0.29±0. 07	Old A
Pd-black(I)	D	0.54 ±0. 10	0.85	0.59	**0. 70±0. 13**	Old A
ibid	H	0.45 ±0. 08	0.78	0.50	**0.63±0. 11**	Old A
Pd-black(II)#1	D	0.47 ±0. 06	0.78	0.52	**0. 66±0. 08**	Baking T≦170℃
Pd-black(II)#2	D	0.17 ±0. 03	0.23	0.19	**0. 81±0. 14**	stuck
Pd-black(II)#4	D	0.16 ±0. 02	0.24	0.18	**0. 75±0. 09**	stuck
Pd-black(II)#2	H	0.16 ±0. 01	0.22	0.18	**0. 80±0. 05**	stuck
Santoku 1 #1 **Pd/PdO/ZrO_2**	D	**1.63 ±0. 01**	**1.0**	1.80	**1.80**±0. 01	Baking T≦300℃
ibid	H	**0.80 ±0. 01**	**0.89**	0.91	**1.02**±0. 02	ibid
Santoku 2 #1	D	**1.49 ±0. 01**	**0.97**	1.70	**1.71**±0. 02	Baking T≦170℃
ibid	H	**1.30 ±0. 01**	**0.81**	1.48	**1.67**±0. 02	ibid
Santoku 3 #1	D	**1.66 ±0. 03**	0.77	1.89	**2.38**±0. 02	A2, 2.1sccm
ibid	H	**1.64 ±0. 02**	1.57	1.87	**1.15**±0. 02	A1, 10sccm

Note-1: $H_2O \rightarrow 2H + O - 1.48eV$, and $D_2O \rightarrow 2D + O - 1.52eV$ (0.75 eV per H(D))

Note-2: Eout/D(H) values for chemical heat are 0.6 to 0.8 eV per D (or H), for nano-powders of Pd-black

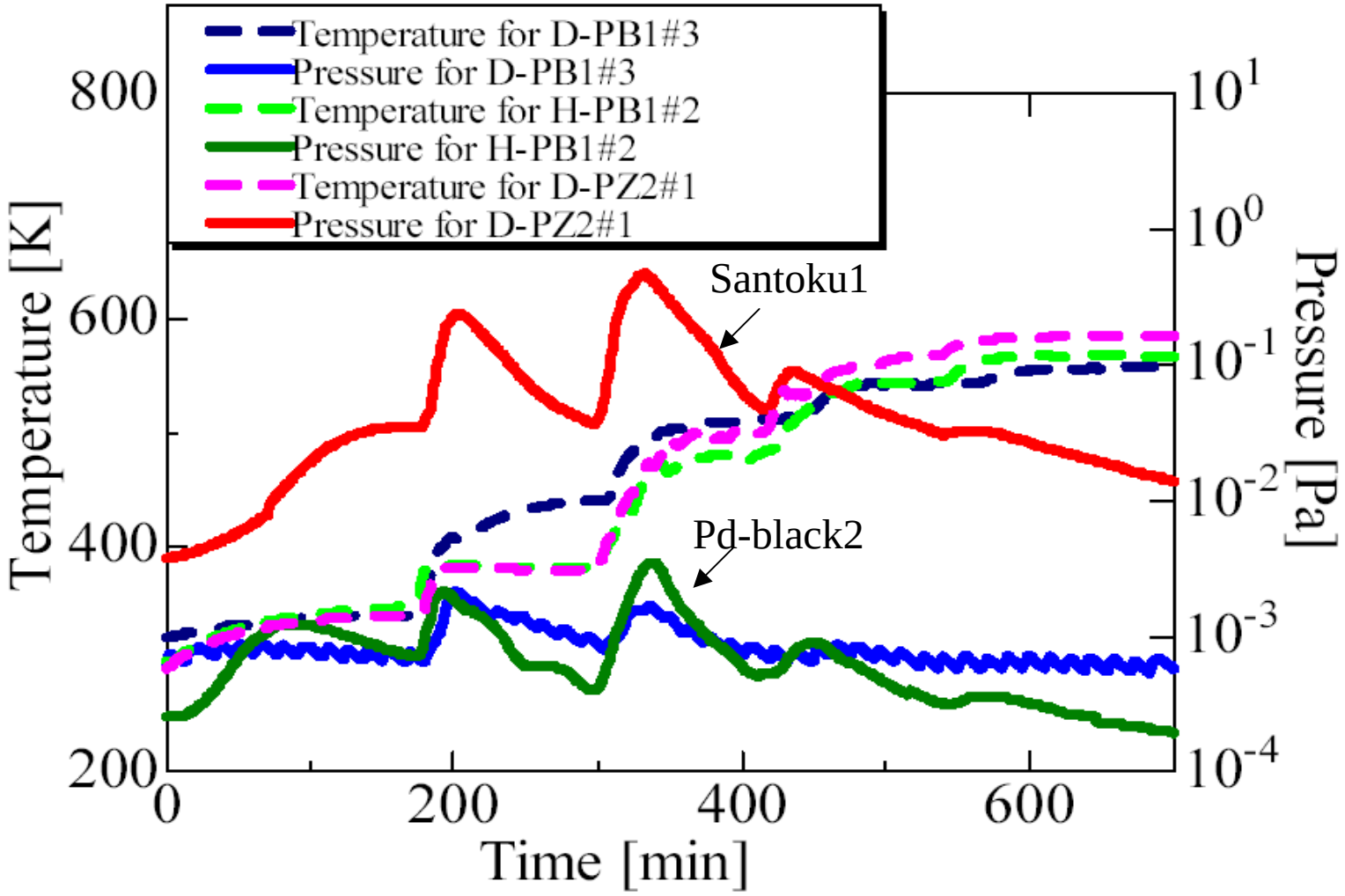
Note-3: Eout/D value 1.7-2.3eV for Santoku-nano-Pd powder anomalously large. And Eout/H values are also anomalously large compared to known chemical values.

Note-4: Pd-black powder stuck to be bigger sizes after #1 run, but heat/D(H) is same to show some surface reaction active.

Discussions for the 1st Phase

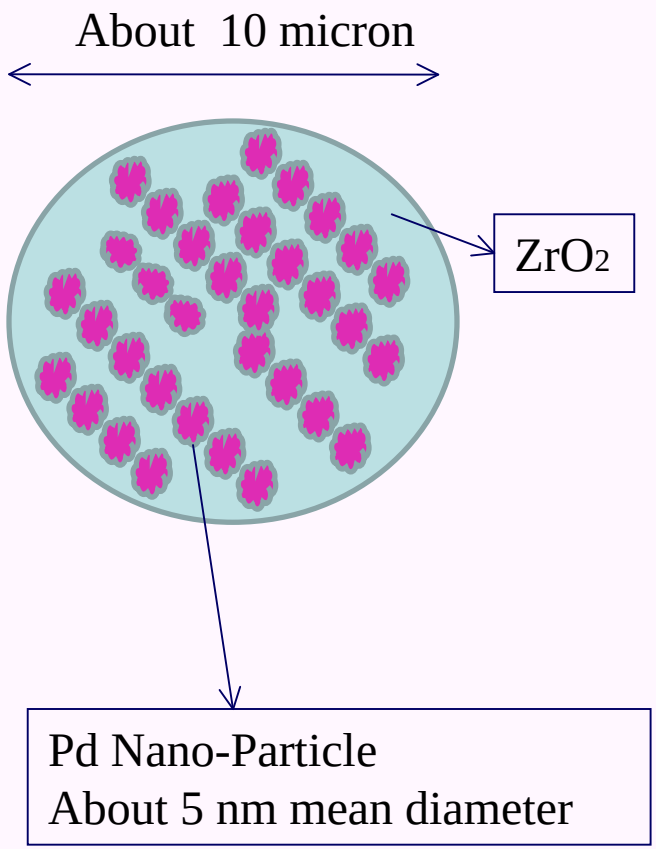
- Pd-black: (Heat/D)av = 0.70 (±0.15) eV (cf: 0.2-0.3 for 100nm Pd)
  (Heat/H)av = 0.69 (±0.1) eV
- Santoku1: (Heat/D) = 1.80 (±0.02) eV (2.38 for Santoku3#1)
  (Heat/H) = 1.02 (±0.02) eV (1.15 for Santoku3#1)
- Santoku2: (Heat/D) = 1.71 (±0.02) eV
  (Heat/H) = 1.67 (±0.02) eV (* flow rate larger for H-gas)
- After Fukai book: 0.2eV/H for bulk H absorption.
  100kJ/mol-H_2 : 0.5eV/H for surface adsorption.
- Reaction may be Surface Mesoscopic Phenomenon for the 1st Phase ("zero pressure" interval). Isotopic effect (**2.0eV/1.3eV**) is visible.
- Pd nano-particle makes deep trapping potential of D(H), probably in fractal defects of its surface!?
- This is the reason of high loading "in vacuum" for Pd-nano.

After evacuation, Santoku sample retains much more (100 times) D(H) than Pd-black: due to mesoscopic effect (rearrangement of surface and lattice) of Pd nano-particles.



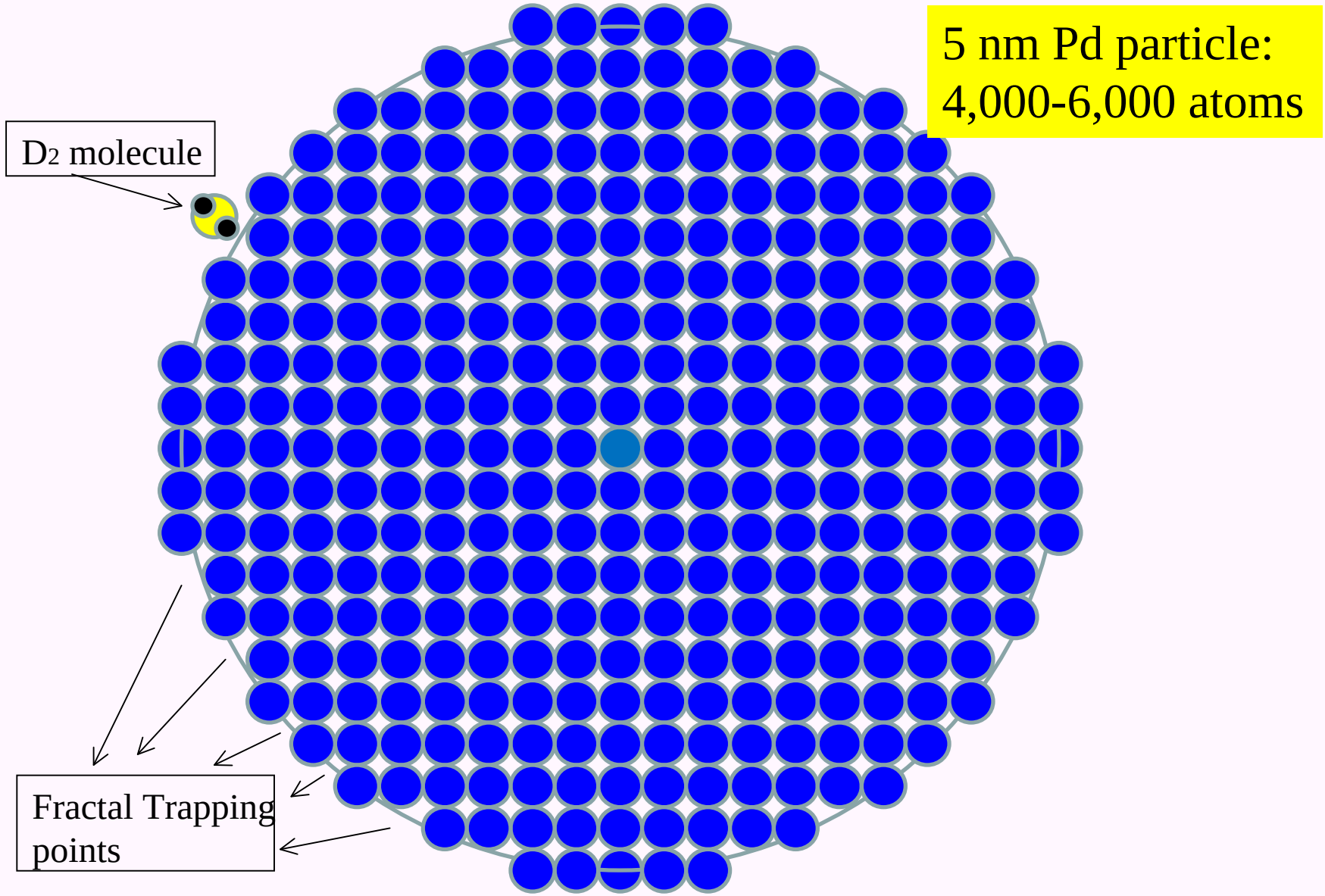
4-3. Variation of pressure during sample baking for outgassing.

Metal-Oxide-Nano-Pd Composite



- PdDx
- **X=1.0** by Arachi et al.;
  D-Absorption in O-sites of Pd-Lattice
  (We support this data)
- X=2.0 by Yamaura et al; deuterons at Pd-ZrO_2 interface (Voids?)
- Arata claimed: **x=2.5**

Irregular and Fractal Sites should form on surface of nano-particle



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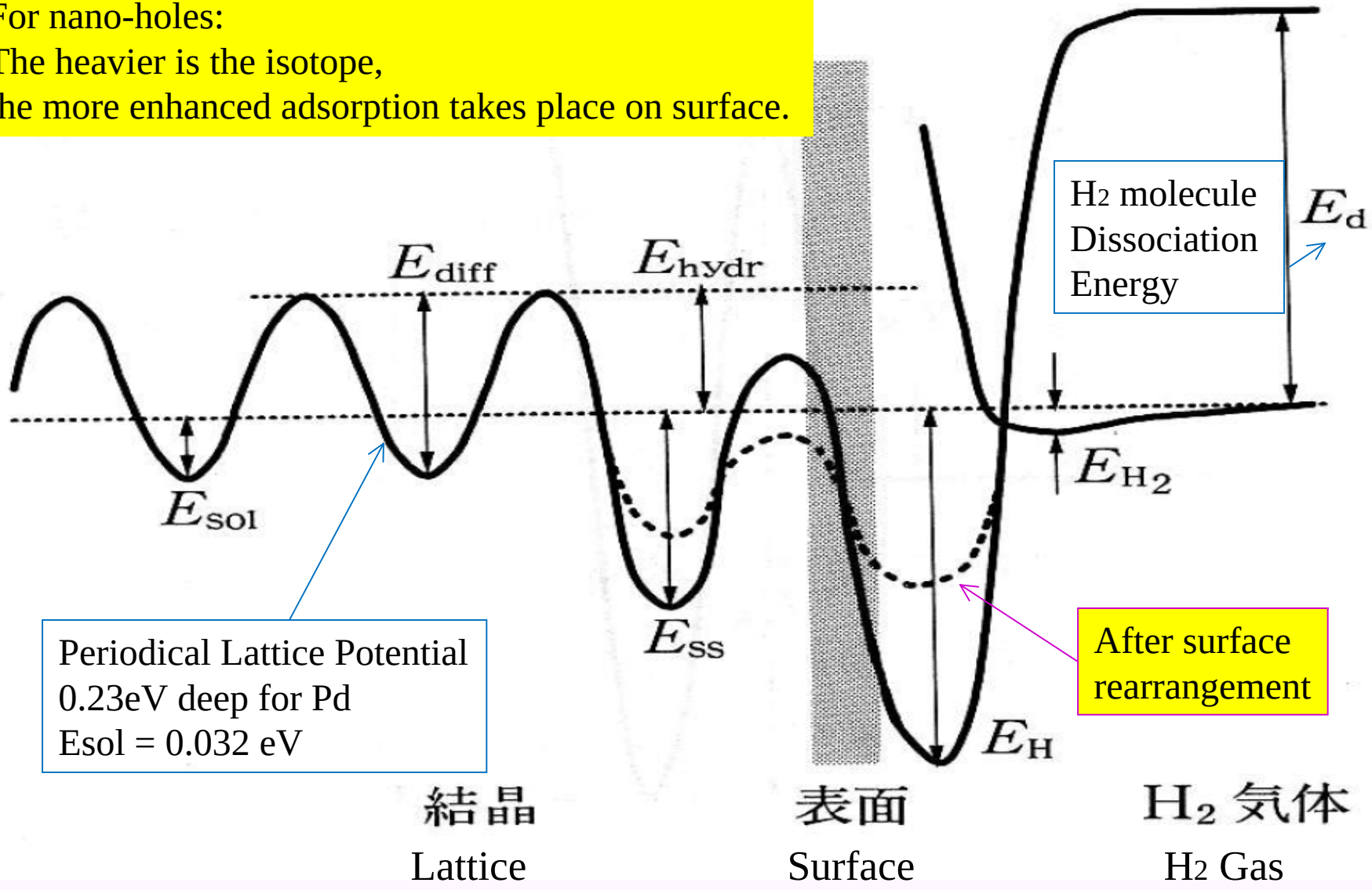
Potential form of hydrogen adsorption and absorption near surface

For nano-holes:
The heavier is the isotope,
the more enhanced adsorption takes place on surface.



Arata-Zhang Exp.: HTSJ, Vol.34, No.2 (2008)

Long time lasting heat by D-charge without input power: 29.2kJ Total by 24.4g Pd/ZrO2 sample

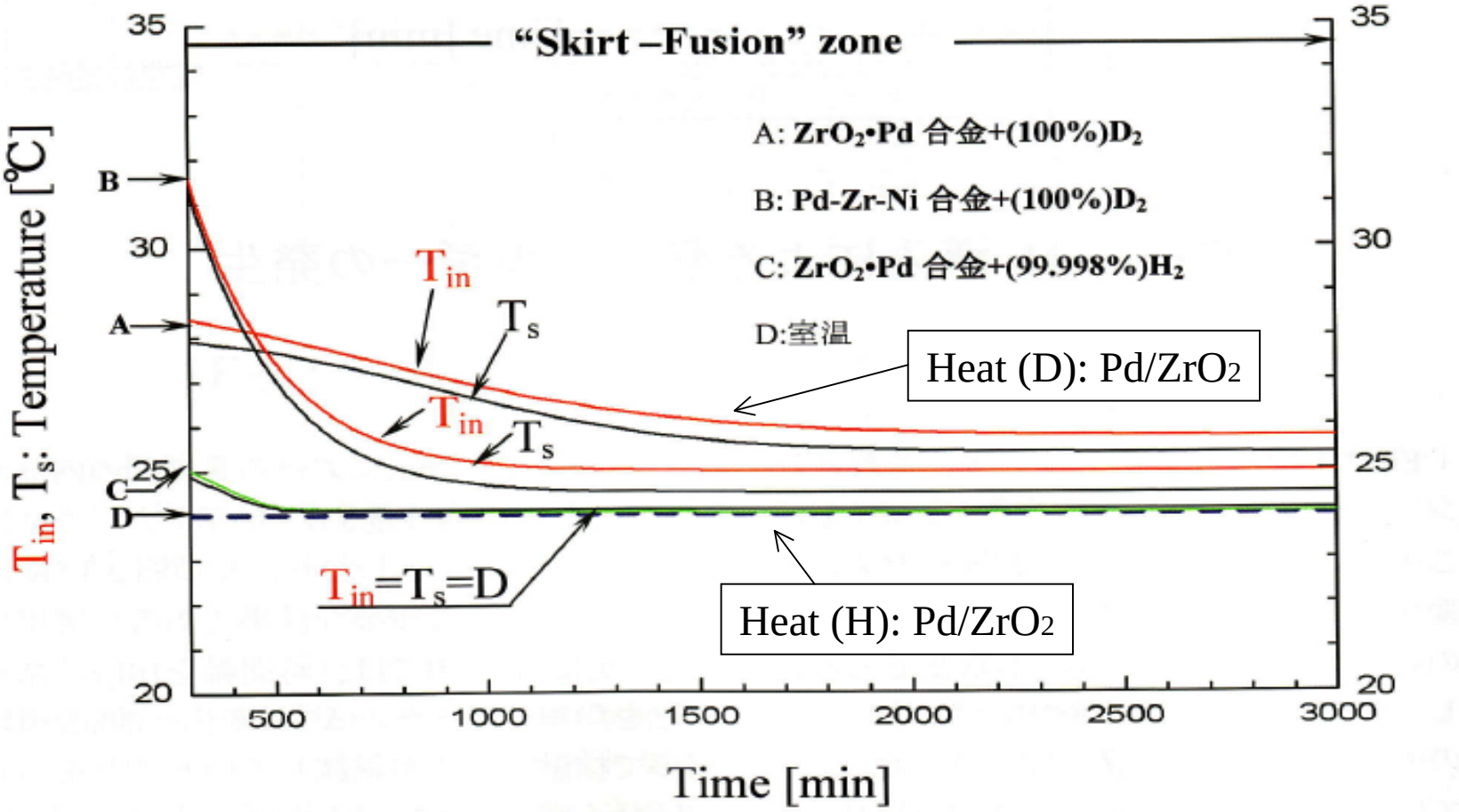


Fig.5B "Skirt-Fusion" zone における各燃料にたいする Nuclear fusion の発生特性の比較(after 300min)

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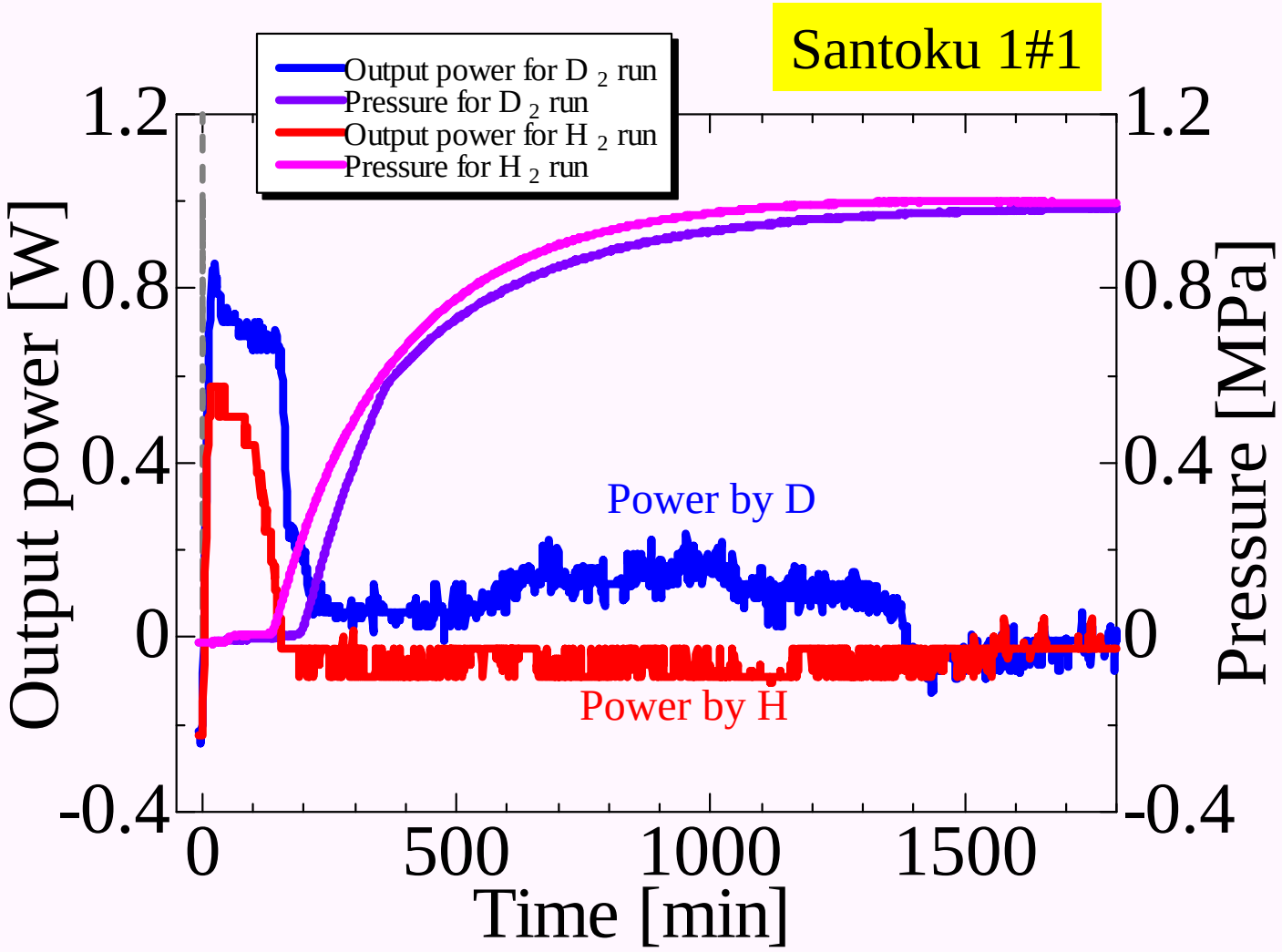


Run number	flow rate [sccm]	Output energy [kJ]		Specific output energy[kJ/g]		Composition; x for PdDx/PdHx	Output energy per D/H in the 1st phase [eV]
		1st phase	2nd phase	1st phase	2nd phase		
D-PZ1#1	2.8	7.0±0.2	6.8±1.3	1.6±0.0	1.6±0.3	1.0	1.80 ± 0.05
Corrected H-PZ1#1	2.6	3.6±0.1	-5.1±1.4	0.8±0.0	-1.2±0.3	0.89	1.02 ± 0.03

Discussions on Total Excess Heat Rates for #1 Runs: Our results are comparable to Arata's.

- **Arata-Zhang Exp.**
- Sample Pd/ZrO_2 by Fukuda P. M. Co.

  weight: 24.4 g

  net Pd weight: 10.5 g
- Observed Excess Heat

  (0-3000min): 29.2 kJ
- Excess Heat Rate:

  2.77 (kJ/g-Pd)

(Anomalous heat by H about 1 kJ/g inclusive)

→ Net Value ~ 1.8（kJ/g-Pd）

- **Our Exp.**
- Sample Pd/PdO/ZrO2 by Santoku Co.

  weight: 10 g

  net Pd weight: 4.3 g
- Observed Excess Heat

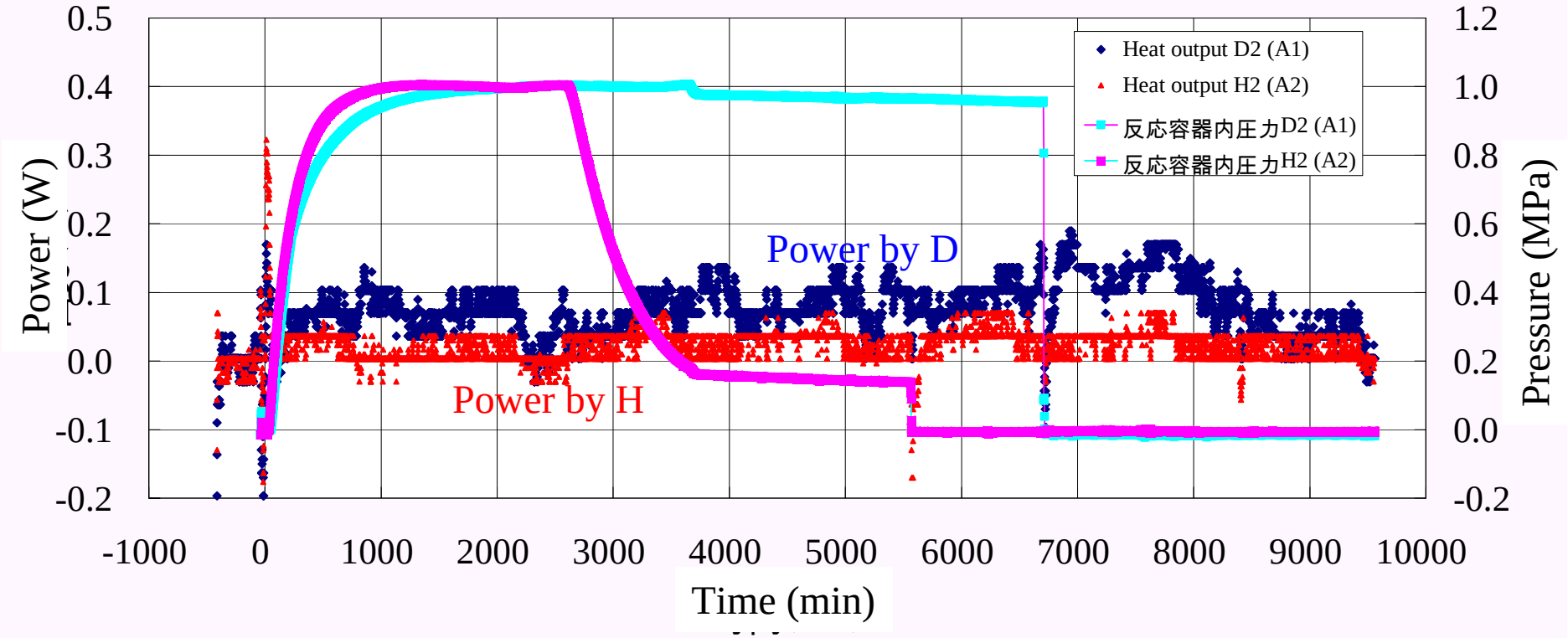
  (Example for S2, 0-3000min)

  S2: (6.4-5.1)+7.0 = **8.3** ±1.2 kJ
- Excess Heat Rate:

S1: 2.64 ± 0.30 (kJ/g-Pd)

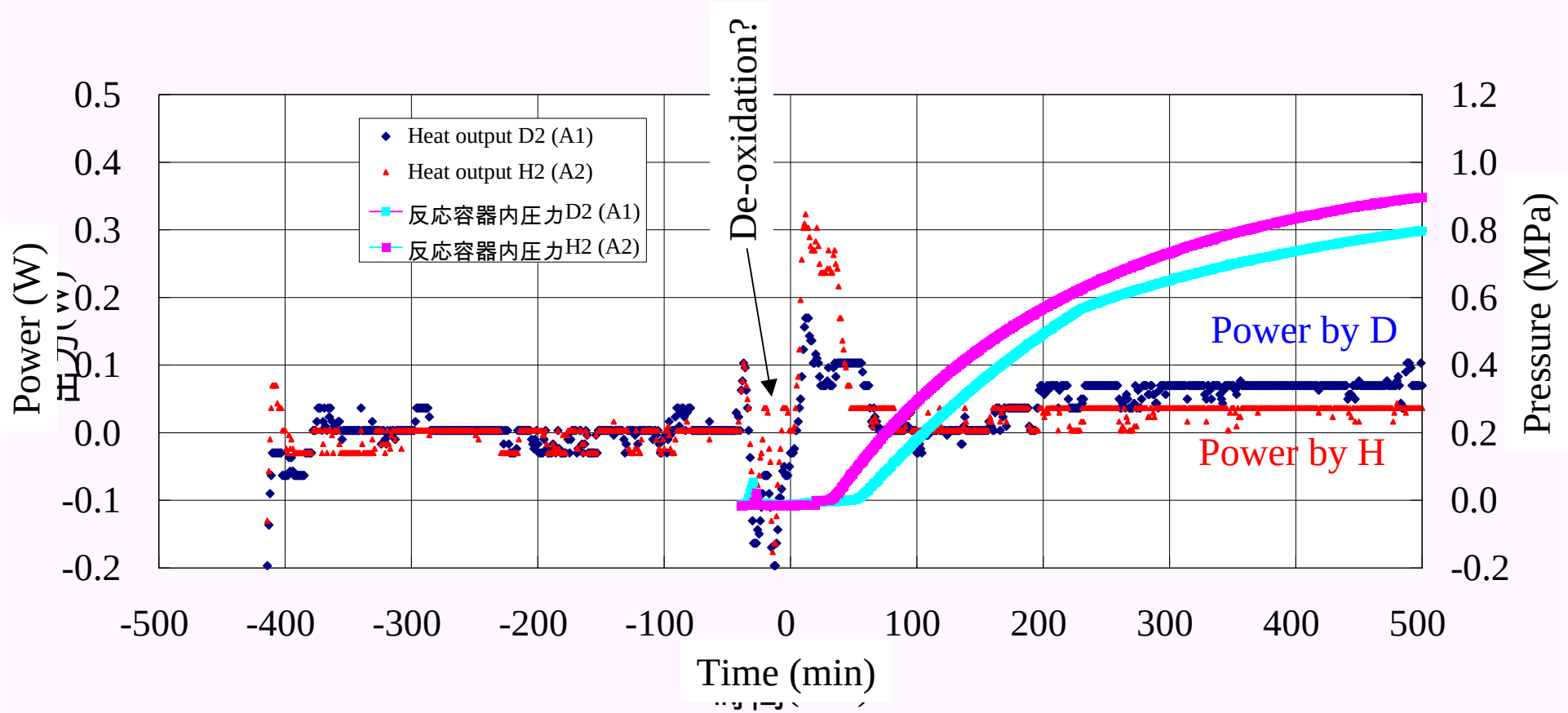
S2: 1.93 ± 0.30

Long Time Lasting Excess Heat by Run: Santoku 2#2

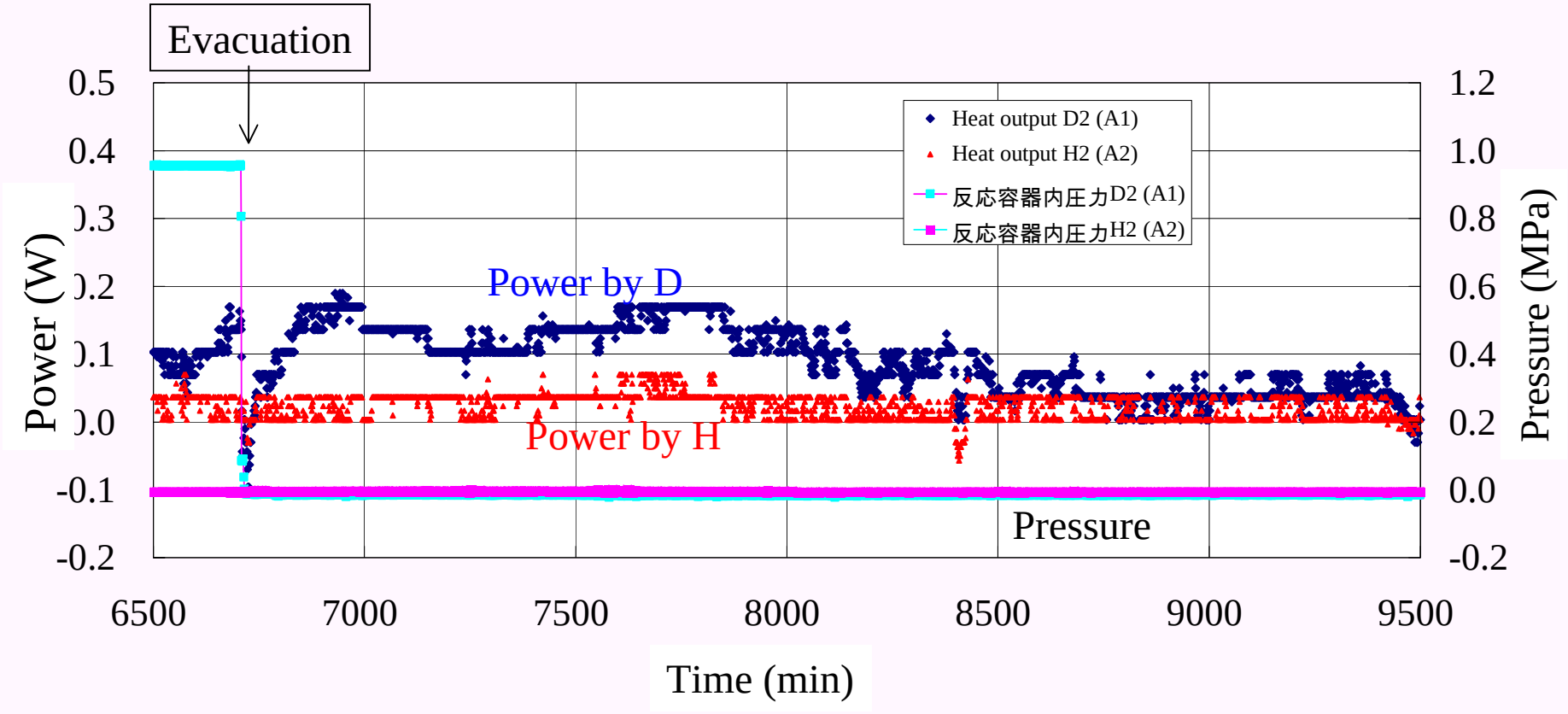


run	Gas	Measured flow rate [sccm]	1st phase [kJ]	2nd phase [kJ]	1st phase [J/g]	2nd phase [J/g]	D/Pd or H/Pd
D_2-2-2	D	3.87	0.17±0.03	9.89±1.48	40±7.0	2300±345	0.47
H_2-2-2	H	3.62	0.58±0.05	1.68±1.46	136±10.9	391±341	0.28

Run: Santoku 2#2: Expanded View of Early –Time Evolution

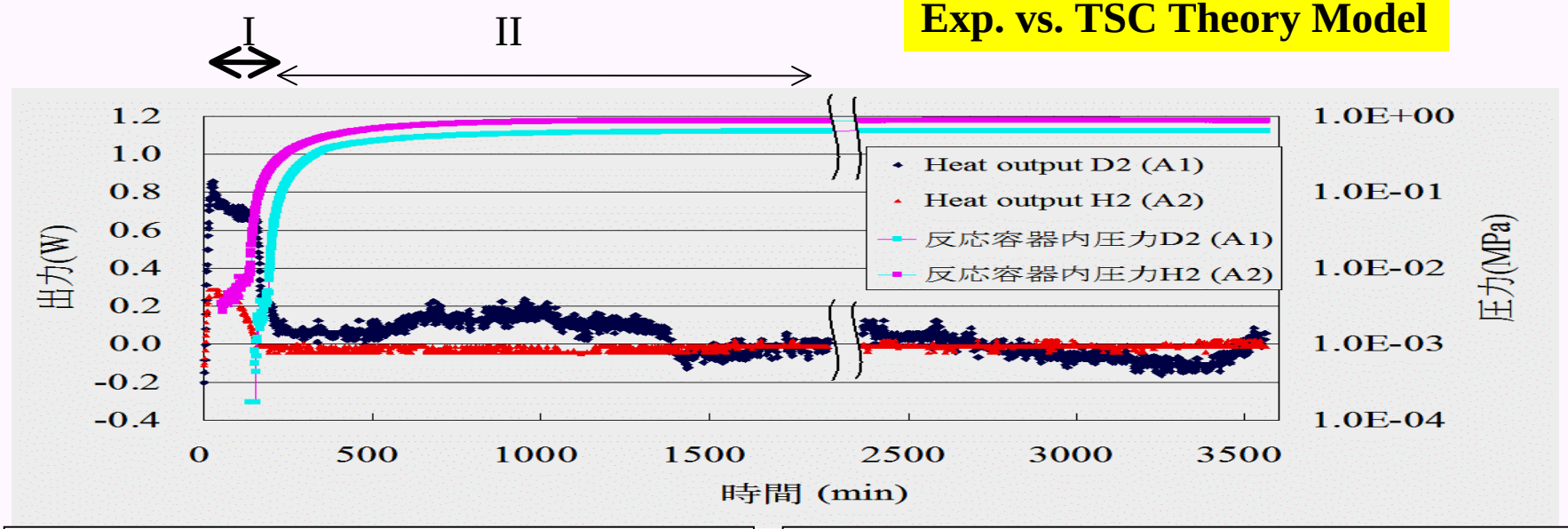


Run: Santoku 2**#2**: Expanded View of Heat Evolution after Evacuation- “Heat after Death”



Is Evacuation STIMULUS?

Exp. vs. TSC Theory Model



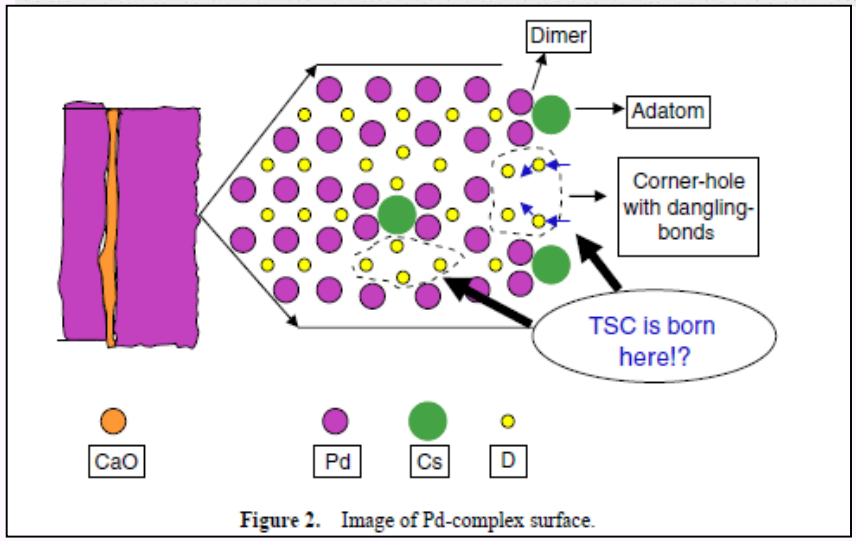
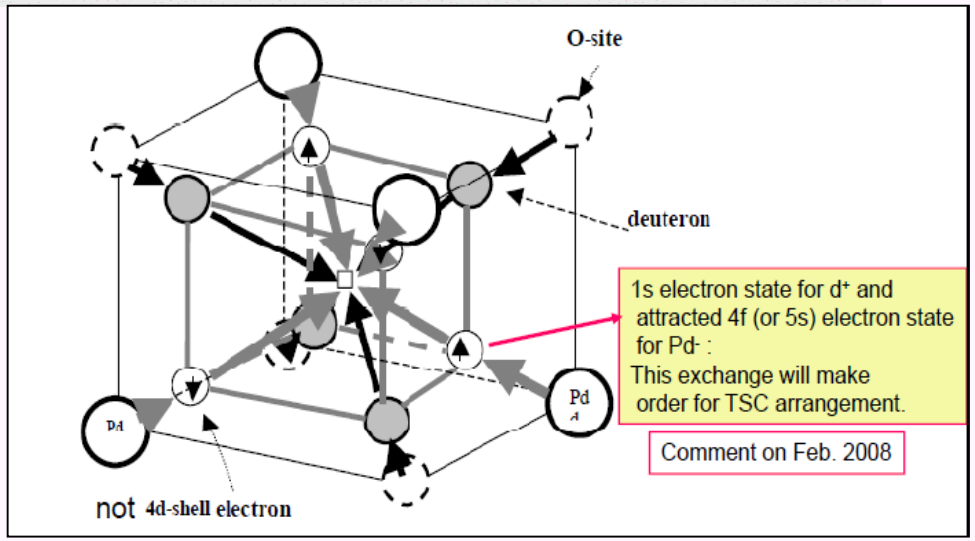


Figure 2. Image of Pd-complex surface.

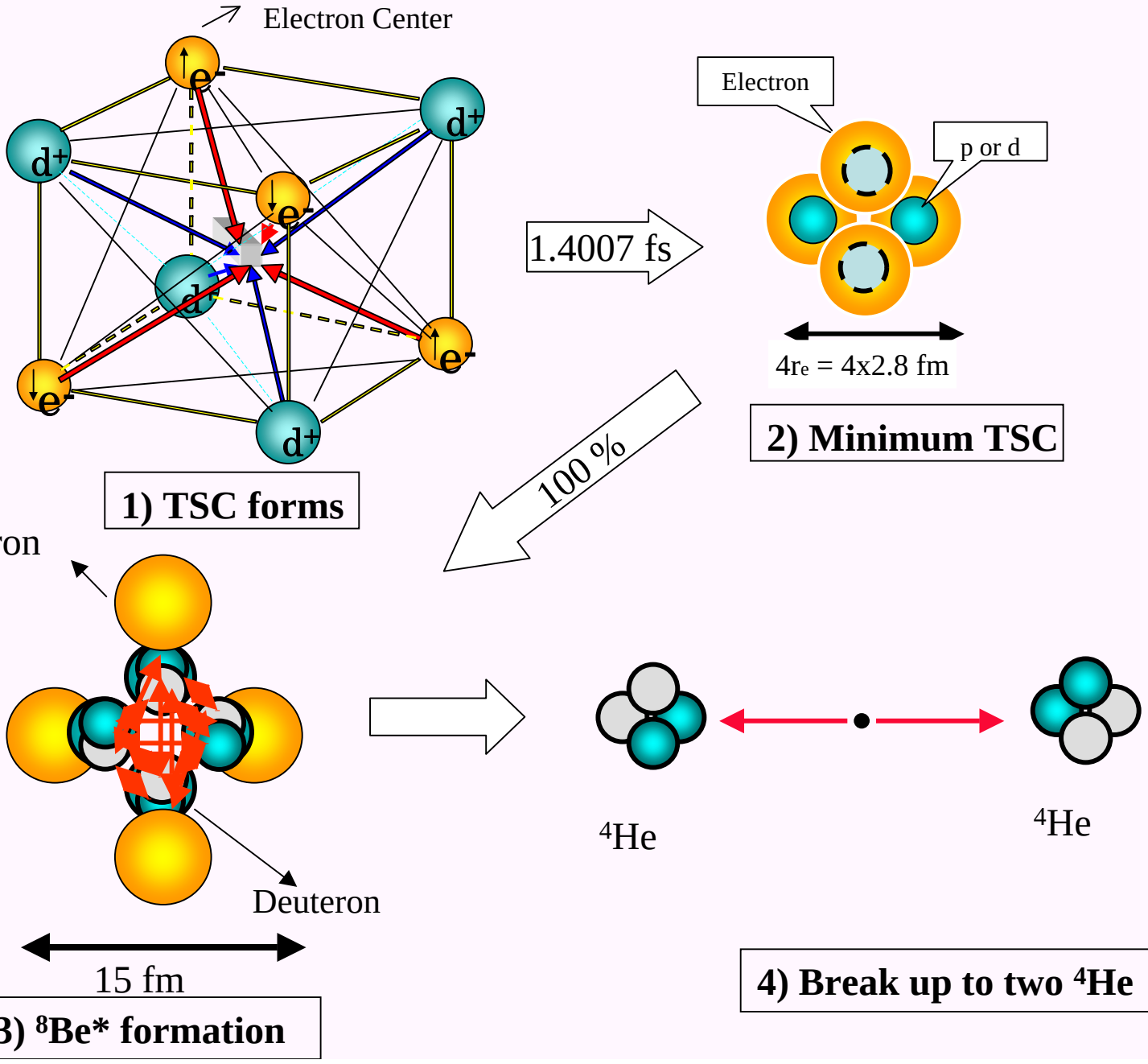


Model b) may correspond to **I.**

Model a) may correspond to **II.**

$4D/TSC \rightarrow {}^{4}He + {}^{4}He + 47.6MeV$

Result of Dynamic Condensation of 4D/TSC by Langevin Equation



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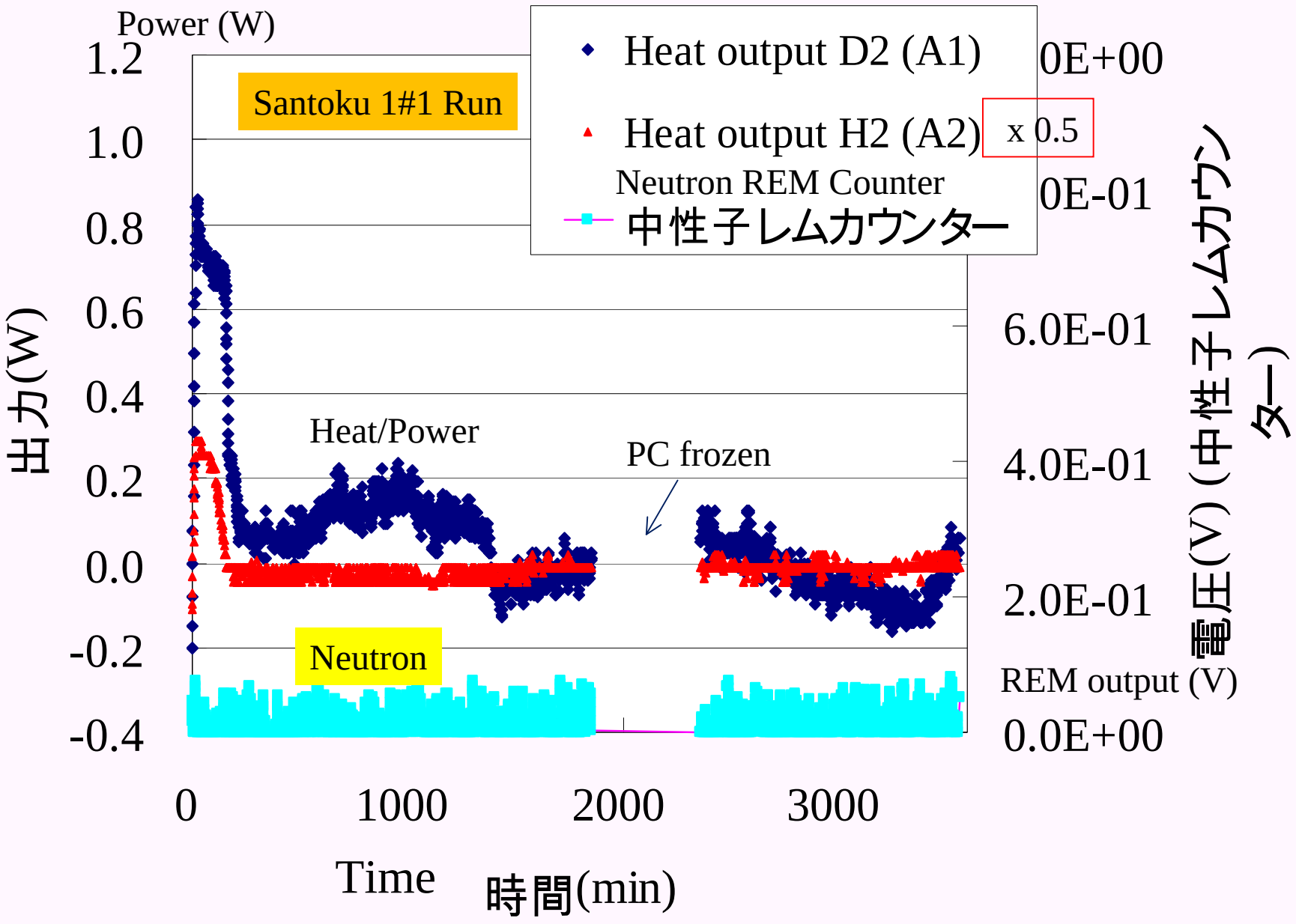
No increase of neutron count rate by REM counter was seen, gamma-ray either.



Conclusions-1

- Arata-Zhang's Excess Heat Result was replicated quantitatively.
- For Pd/PdO/ZrO_2 powder (Santoku):

  1) D-gas charge in the 1st phase (zero pressure) gave 20-90% excess heat than H-gas charge.

  2) **In the 2nd phase, significant excess heat (about 2 kJ/g-Pd) for D-gas charge**, while zero level for H-gas charge.
- No increase of neutron counts was seen.
- D/Pd ratio in the end of 1st phase was 1.0, while H/Pd was about 0.8 - 0.9. Flow rate dependence.
- Further experiments changing conditions will be fruitful for developing clean energy devices.

Conclusions-2

- Nano-Pd dispersed sample (Santoku, Pd/ZrO_2) retained 100 times more D(H) atoms after evacuation, than the Pd-black case.
- Mesoscopic effect by Pd-nano-particle, namely surface and lattice rearrangement probably makes deep D(H) trapping potentials (1.0-2.3eV). We need study for D(H)-gas flow-rate dependence.
- Stable excess heat production is expected for #2 and later runs. We need further study for this.
- Detection of nuclear products by the B-system is expected.
- Replication by other groups is important.