Anomalous Heat Generation in Charging of Pd Powders with High Density Hydrogen Isotopes (II) Discussions on Experimental Results and Underlying Physics

A.Takahashi[1*], A. Kitamura[2], Y. Sasaki[2], Y. Miyoshi[2], T. Nohmi[2], A. Taniike[2], R. Seto[1], and Y. Fujita[1]

[1]Technova Inc. *akito@sutv.zaq.ne.jp

[2](Division of Marine Engineering, Graduate School of Maritime Sciences, Kobe University)

to be presented at ICCF15

October 5-9, 2009, Rome Italy

Aim

The Gas-Phase D(H)-Loading Method [1] with Nano-Fabricated Metal Powders is regarded promising for repeatable CMNS experiments.

We have constructed an experimental system to replicate the phenomenon of excess-heat (and ^{4}He 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 (100nm Pd, Pd-black and **nano-Pd/ZrO_2**).

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 1^{st} phase ("zero pressure interval"), for changing conditions (powder, gas-flow rate, base-cell temperature, etc.).

A REM counter was used for monitoring neutron emission. A NaI scintillator was used for monitoring gamma-ray. Furthermore, ^{4}He analysis will be performed in the future.

Fig. 1(a): A. Kitamura *et al*., Physics Letters A, 373 (2009) 3109-3112.

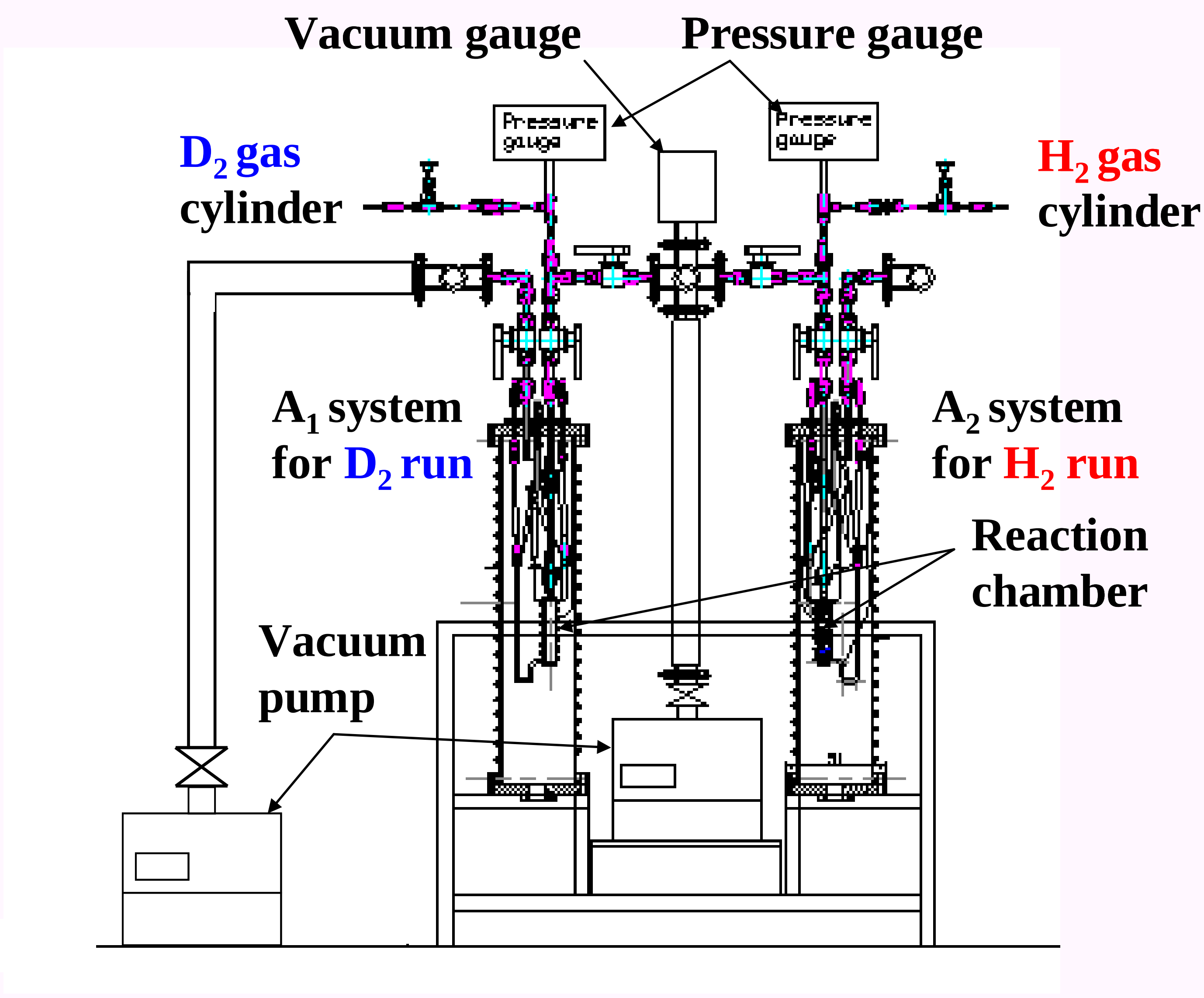
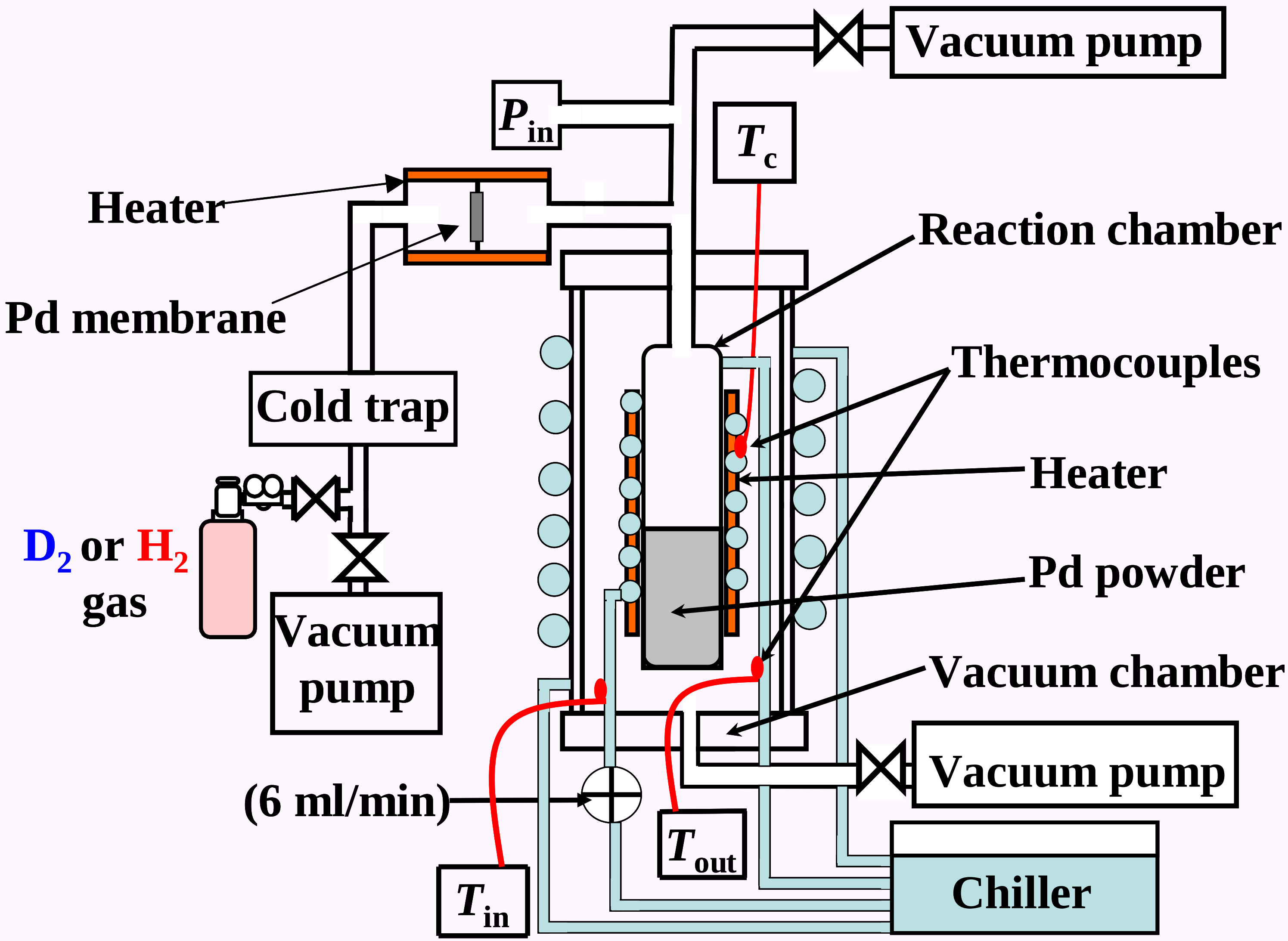
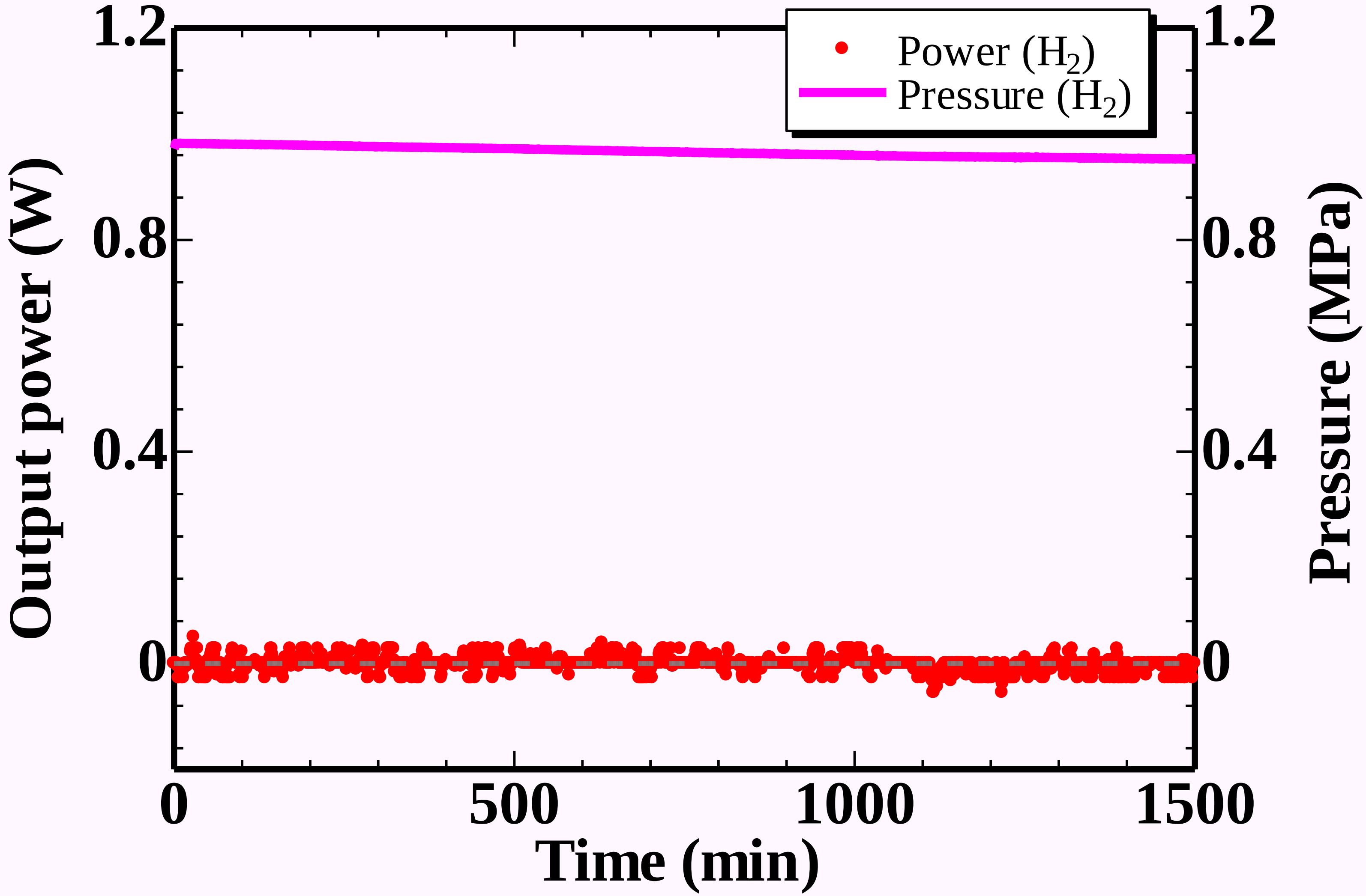


Fig. 1(b): A. Kitamura *et al*., Physics Letters A, 373 (2009) 3109-3112.



New A: Stability of Flow Calorimeter with Zero Input Power
Standard deviation = 14 mW



2. Experimental Procedure

Set Sample in Inner Cell

↓

Evacuation and
Baking (<300° C)

↓

Start D (H) Gas Charge
Run #1

↓

Take Data: Calorimetry,
Pressure, Neutron,
Gamma-ray, etc.

↗

Evacuation and
Baking (<300° C)
Take De-gas Data

↓

Start D (H) Gas Charge
Run #2

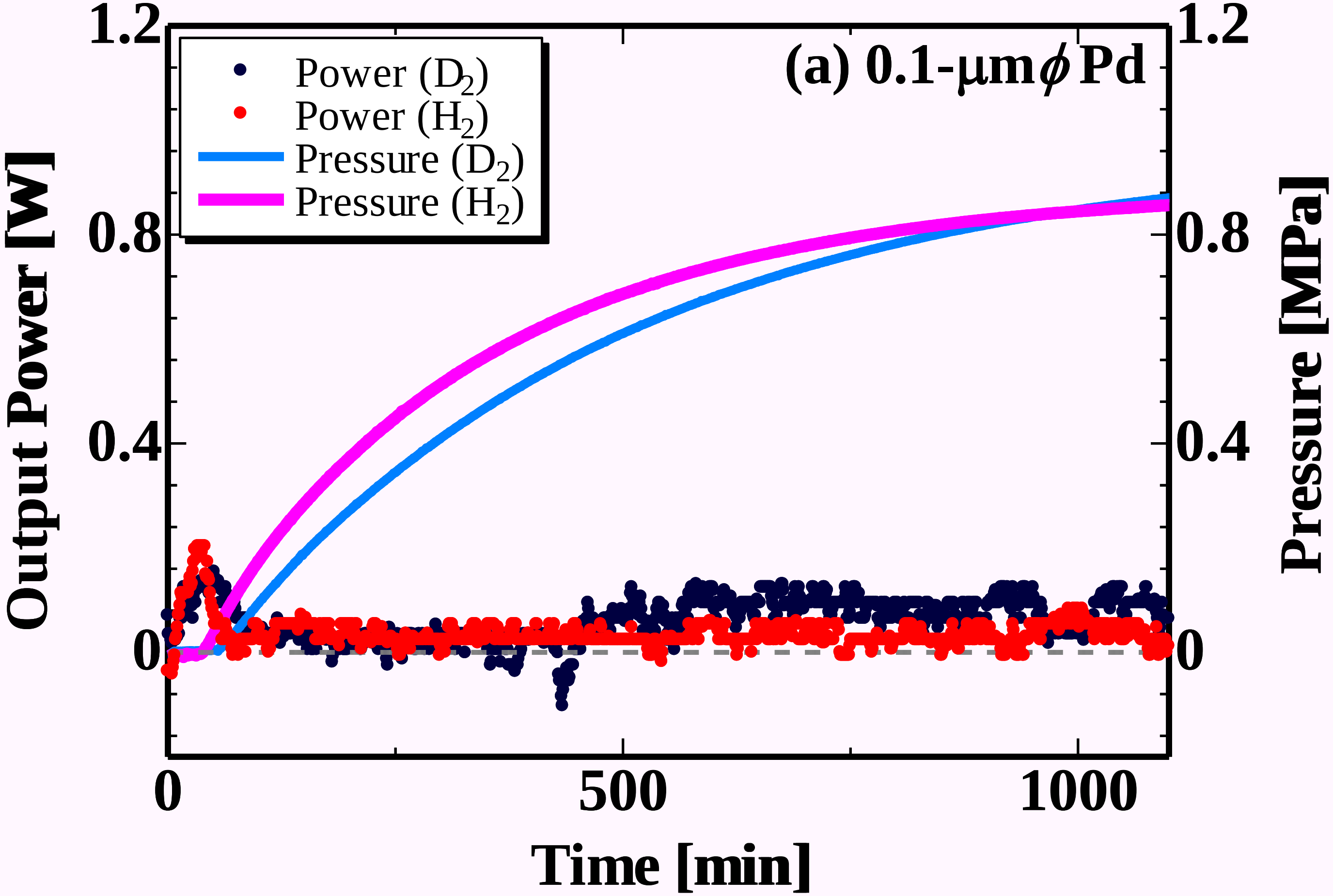
↓

Take Data: Calorimetry,
Pressure, Neutron,
Gamma-ray, etc.

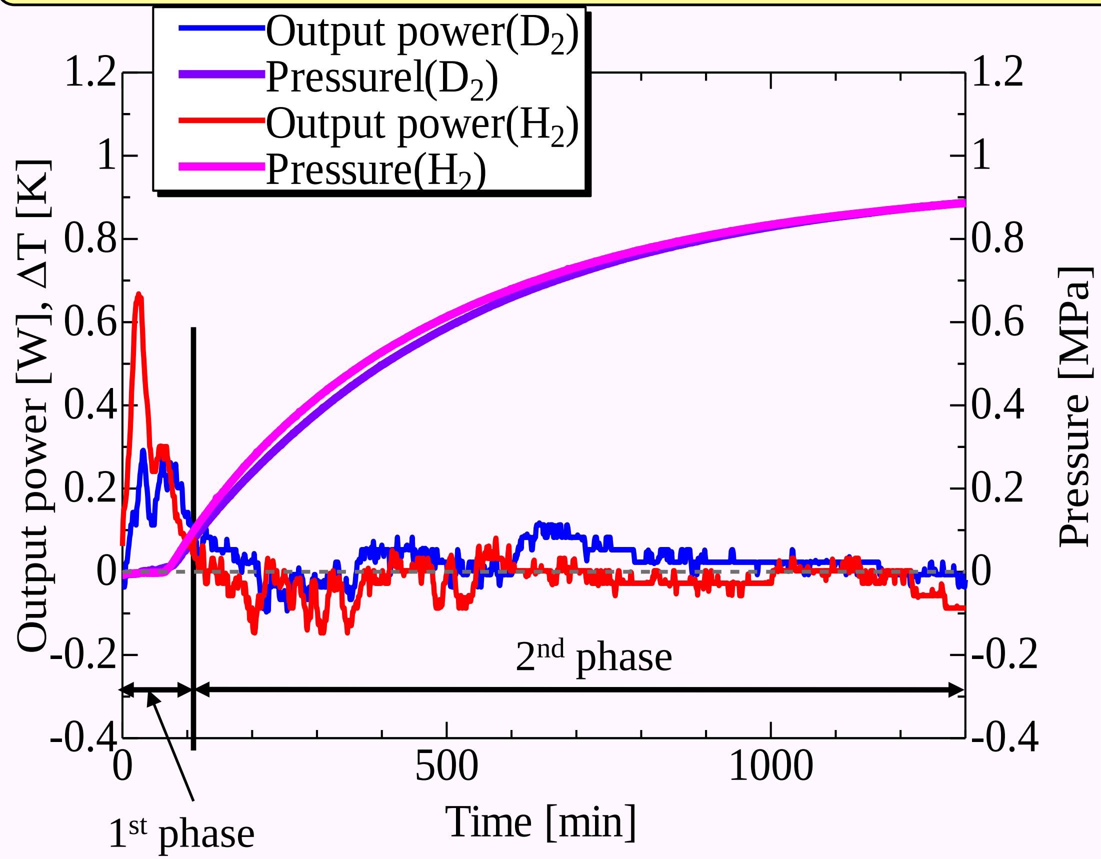
Pd powders (ϕ0.1μm, 99.5%) – results

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.



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)

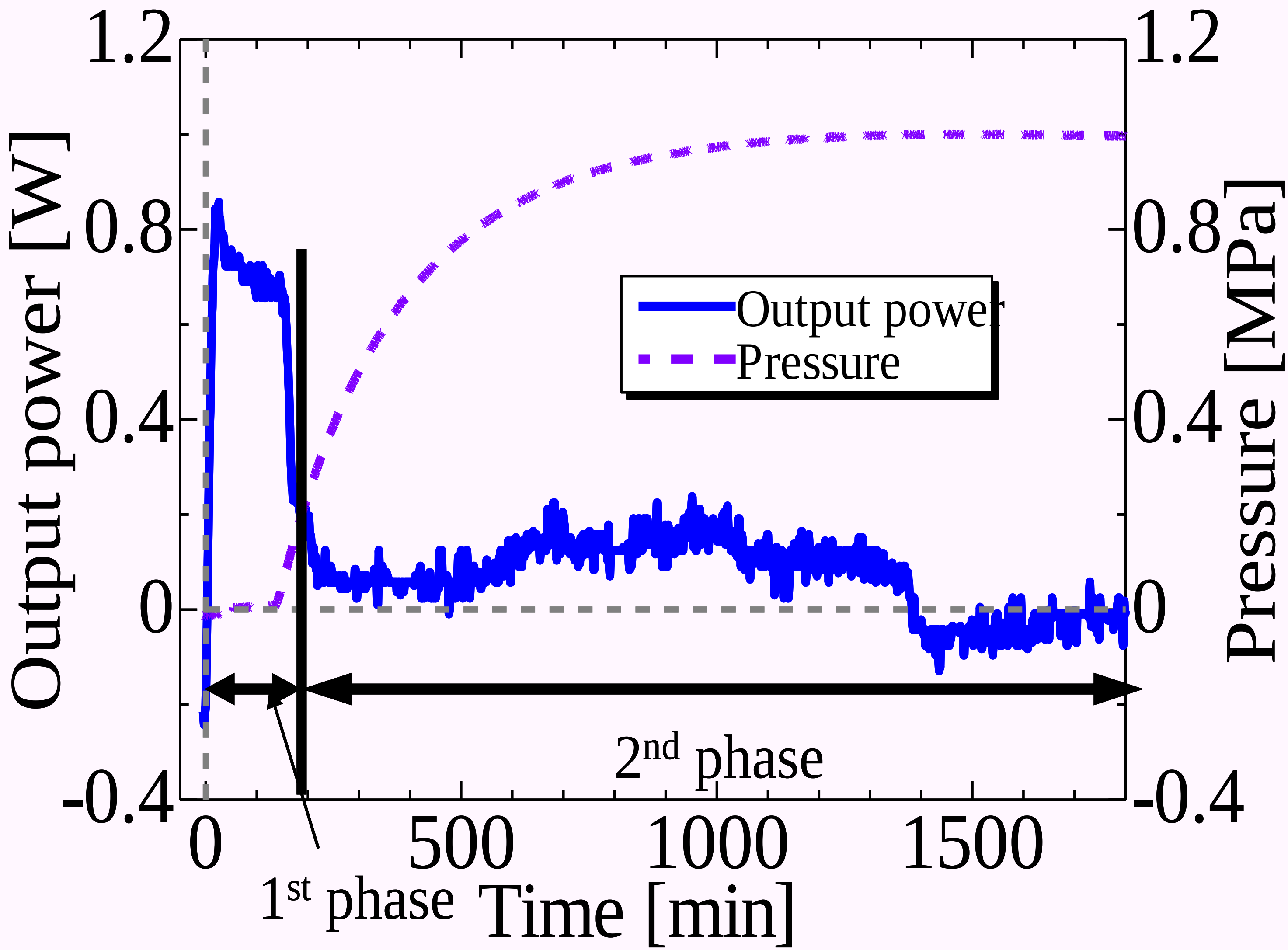
・On the contrary, the output energy in the 2nd phase appears to be larger for D_2 than H_2.

Experiments with Pd/PdO/ZrO_2 Dispersed Samples

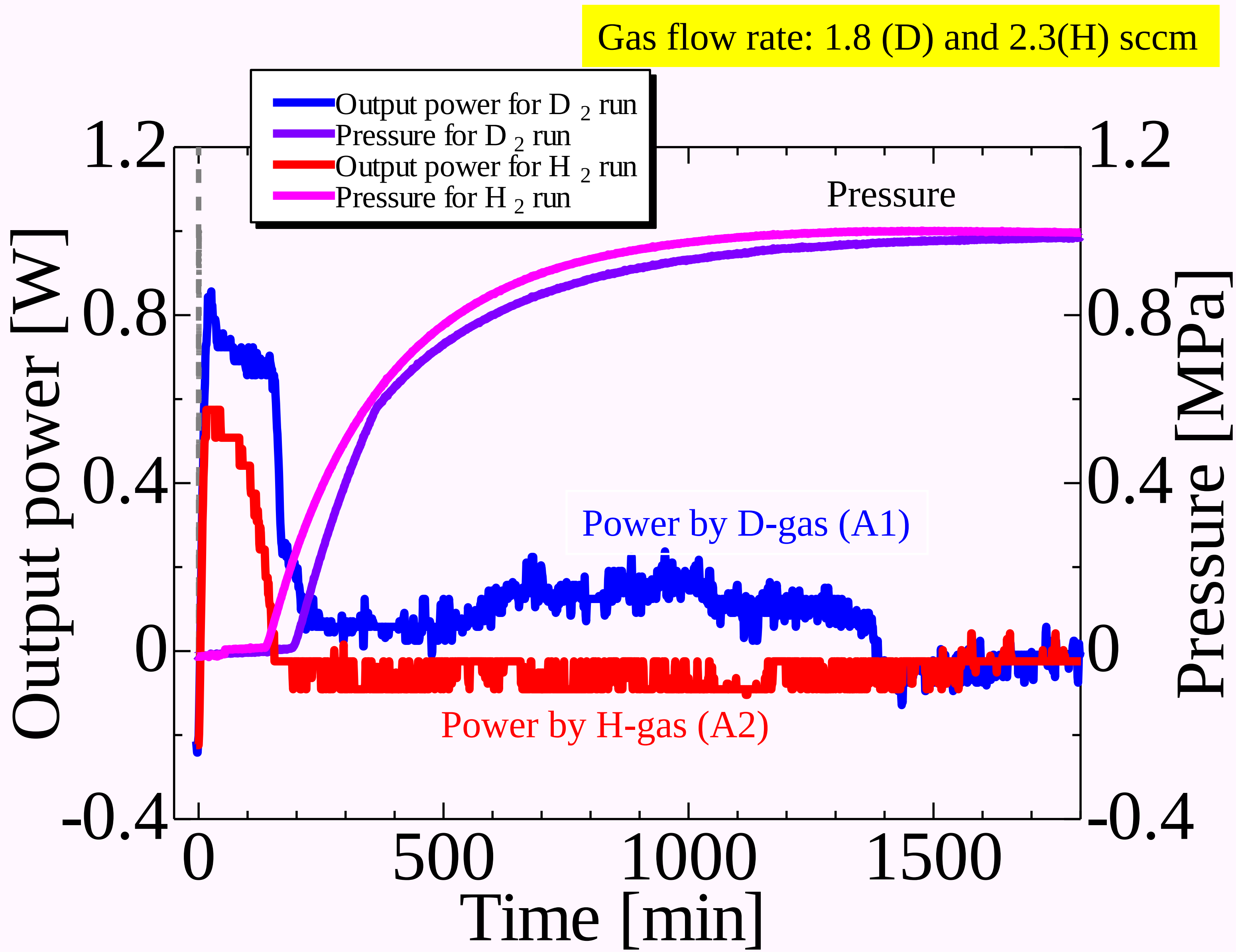
10g (Net Pd weight : **3 g**): Three trials for Santoku 1, Santoku 2 and Santoku 3 samples, #1 and #2 runs for each sample

- 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 10nm in averaged diameter.
- 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

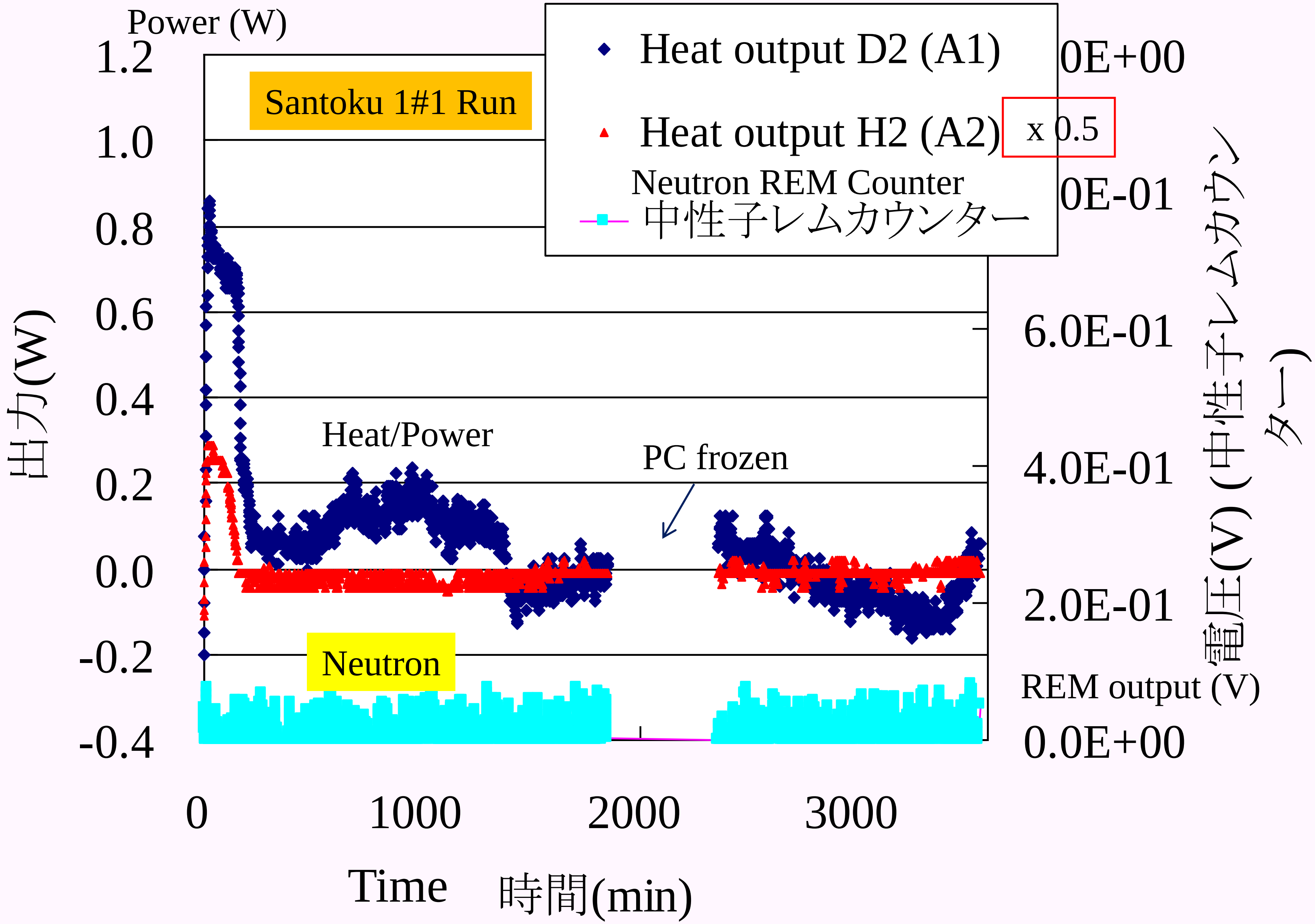
Definition of Phase-I and Phase-II



D-PZ1#1 and H-PZ2#1; Results of Heat Evolution

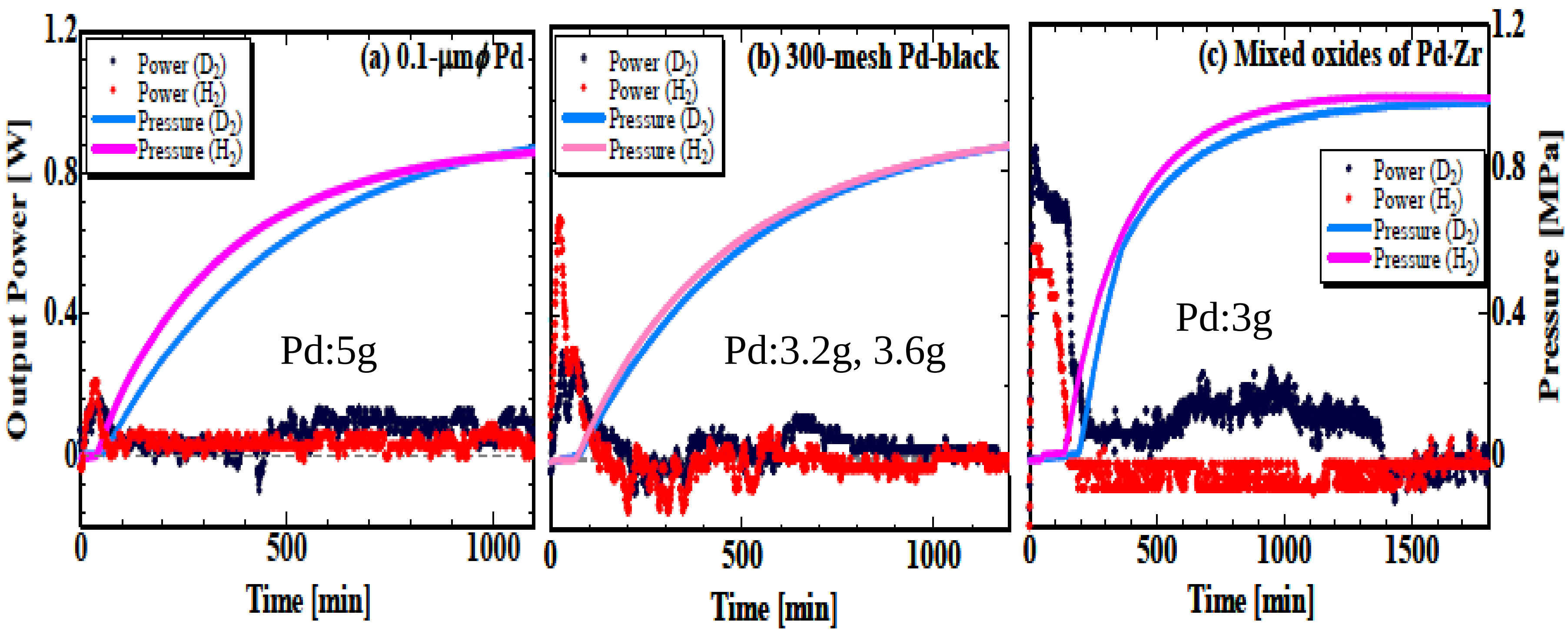


No increase of neutron count rate by REM counter was seen, gamma-ray either.



Comparison of heat-power evolutions for 100nm Pd, Pd-black and 10nmPd/PdO/ZrO_2 samples:

Blue by D-charge cf. Red by H-charge



a) Bulk Character

b) Near-Nano Character

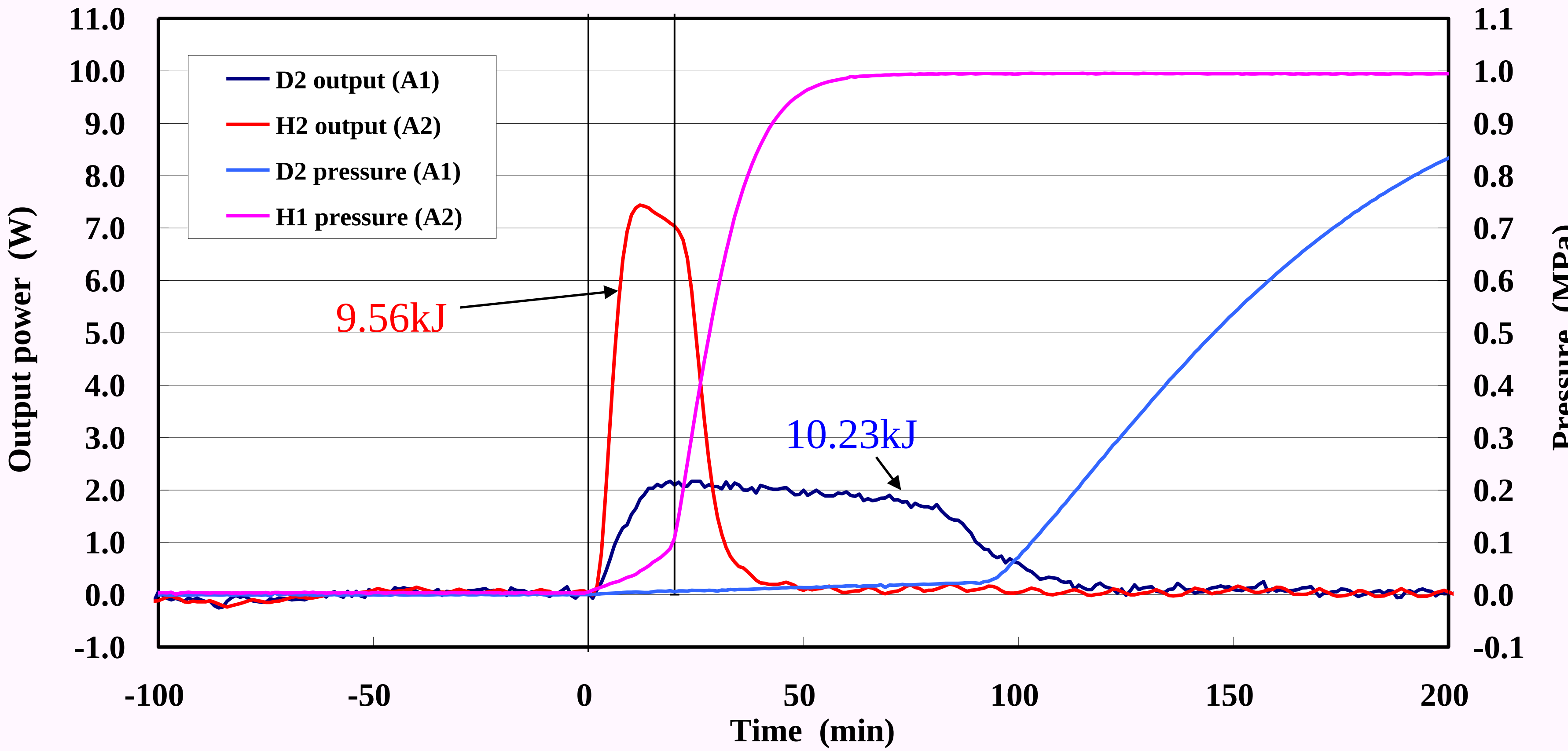
c) Mesoscopic Character

D-PZ9#1 vs. H-PZ10#1 :-100~300min

Flow Rates: 6.42 (D), 20.5 (H) :sccm

E1st: 1.87eV/D, 2.53eV/H

Sample net Pd weight: 4.2g (Pd particle size : about 8 nm)



Summary table of integrated data for phase-1 and phase-2

Run #	weight of Pd [g]	Flow rate [sccm]	Output energy [kJ] 1st phase	Output energy [kJ] 2nd phase	Specific output energy [kJ/g] 1st phase	Specific output energy [kJ/g] 2nd phase	D/Pd or H/Pd (1st ph.)	E1st [eV/D(H)]
D-PP1#1	5.0	2.7	0.5±0.4	2.5±4.1	0.10±0.07	0.52±0.83	0.43	0.26±0.14
D-PP1#2	5.0	3.8	0.5±0.2	4.0±4.4	0.10±0.05	0.79±0.88	0.44	0.25±0.09
H-PP2#1	5.0	5.4	0.4±0.2	2.6±3.9	0.08±0.03	0.53±0.80	0.44	0.20±0.07
D-PB1#1	3.2	3.6	1.7±0.3	8.3±4.5	0.54±0.10	2.60±1.40	0.88	0.67±0.12
H-PB2#1	3.6	4.2	1.6±0.3	(-2.2±4.6)	0.45±0.08	(-0.62±1.30)	0.79	0.62±0.11
D-PB3#1	20.0	2.9	9.3±1.1	1.1±0.5	0.47±0.06	0.06±0.02	0.79	0.65±0.08
D-PB3#2	20.0	0.9	3.3±0.5	3.4±2.6	0.17±0.03	0.17±0.13	0.23	0.79±0.05
H-PB3#3	20.0	2.1	3.2±0.2	14±4.6	0.16±0.01	0.68±0.24	0.24	0.74±0.05
D-PZ1#1	3.0	1.8	7.0±0.2	6.8±1.3	2.33±0.05	2.27±0.43	1.08	2.4±0.05
H-PZ2#1	3.0	2.3	3.6±0.1	(-5.1±1.4)	1.20±0.02	(-1.70±0.47)	1.00	1.3±0.02
D-PZ3#1	3.0	1.9	6.4±0.2	6.2±1.4	2.13±0.05	2.07±0.47	1.08	2.2±0.05
H-PZ4#1	3.0	3.6	4.8±0.1	1.9±1.4	1.60±0.02	0.63±0.47	0.86	2.1±0.03
D-PZ5#1	3.0	2.0	7.1±0.2	1.3±1.4	2.38±0.03	0.42±0.45	1.04	2.5±0.03
H-PZ6#1	3.0	5.9	7.1±0.1	(-0.2±1.4)	2.36±0.02	(-0.08±0.48)	1.34	1.9±0.02
Average for PZ		(D)	6.9±0.4	4.8±3.0	2.3±0.1	1.6±1.0	1.1±0.0	2.4±0.2
		(H)	5.2±1.8	(-1.1±3.6)	1.7±0.6	(-0.4±1.2)	1.1±0.3	1.8±0.4

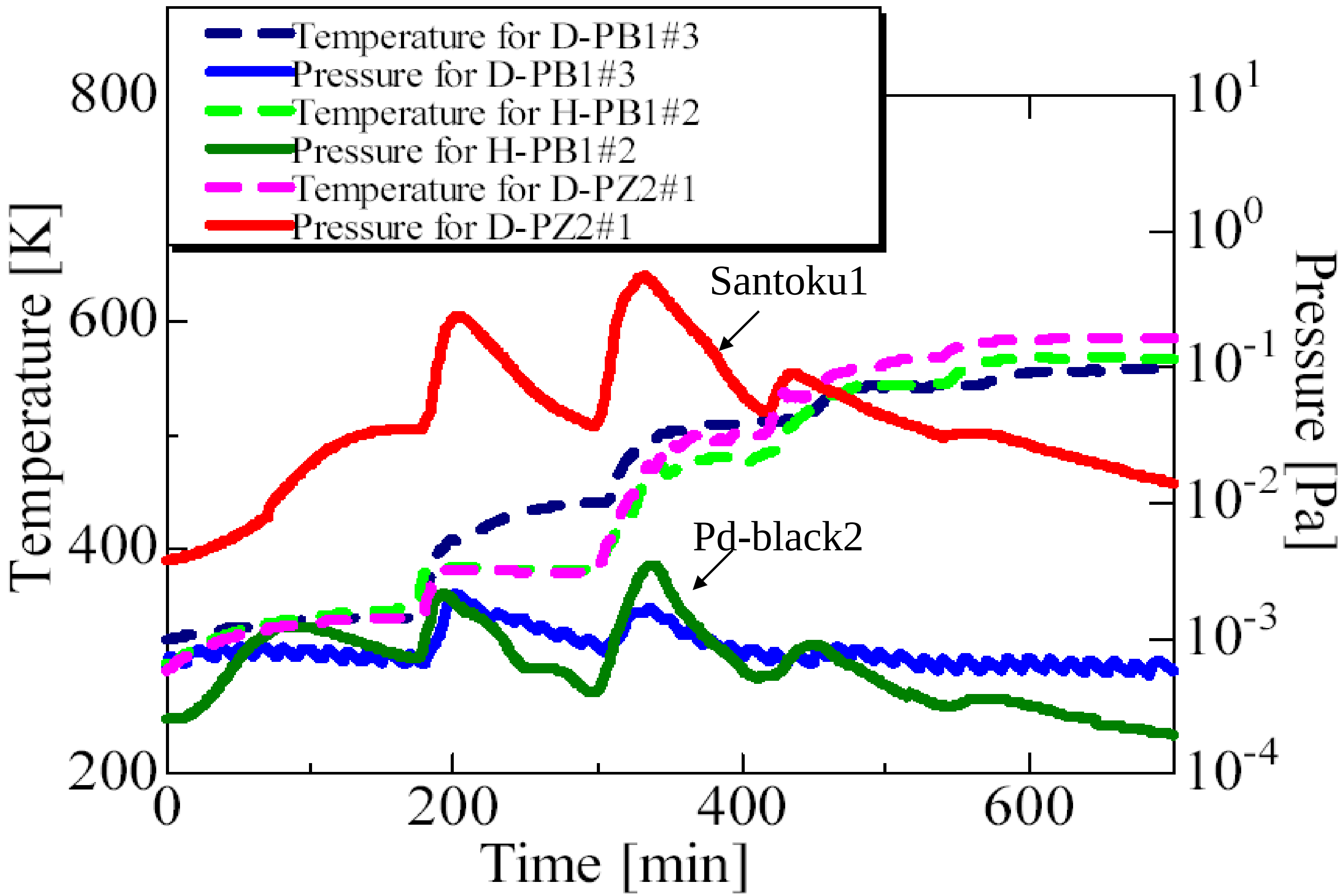
Discussions for the 1st Phase

- Pd 0.1 micron: $(Heat/D)_{av}$ = 0.25 (±0.1) eV
  $(Heat/H)_{av}$ = 0.20 (±0.1) eV
- Pd-black: $(Heat/D)_{av}$ = 0.70 (±0.15) eV
  $(Heat/H)_{av}$ = 0.69 (±0.1) eV
- Santoku1-3: $(Heat/D)_{av}$ = **2.4** (±0.2) eV
  (Pd/ZrO_2) $(Heat/H)_{av}$ = **1.8** (±0.4) eV

- 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 is visible. Flow rate dep.
- 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.

TEM Image of Pd/ZrO_2 Sample

(Courtesy of the Nuclear Science and Engineering Institute and Particulate Systems Research Center at the University of Missouri-Colombia; by R. Duncan)

TEM images of Palladium nanoparticles from Japan (sample # 2)

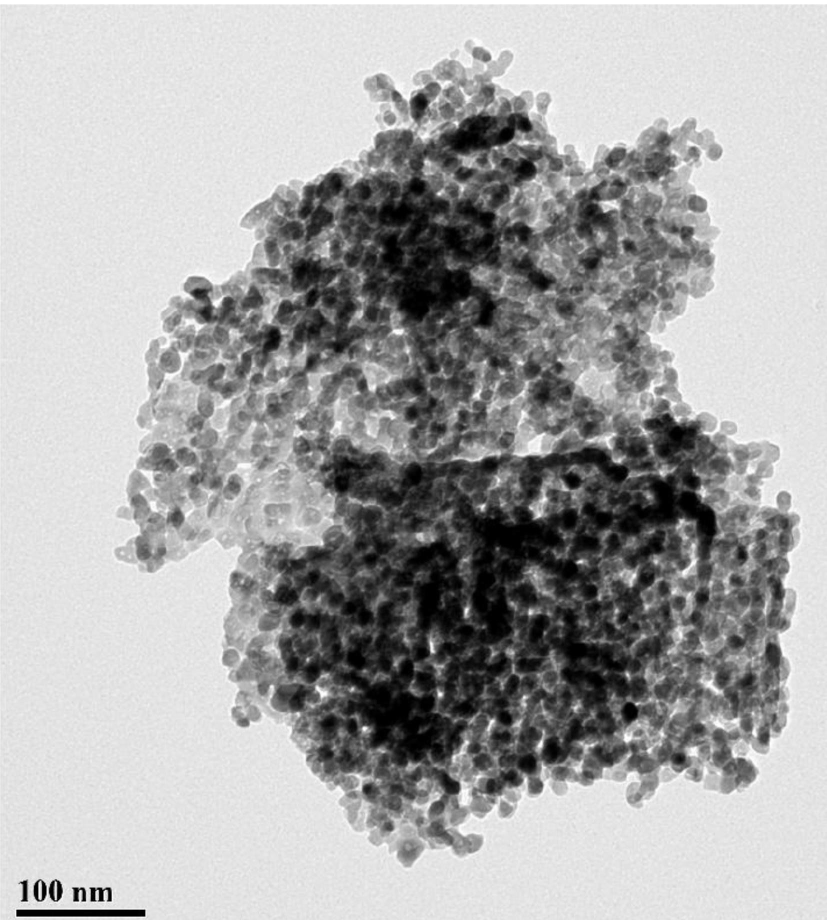
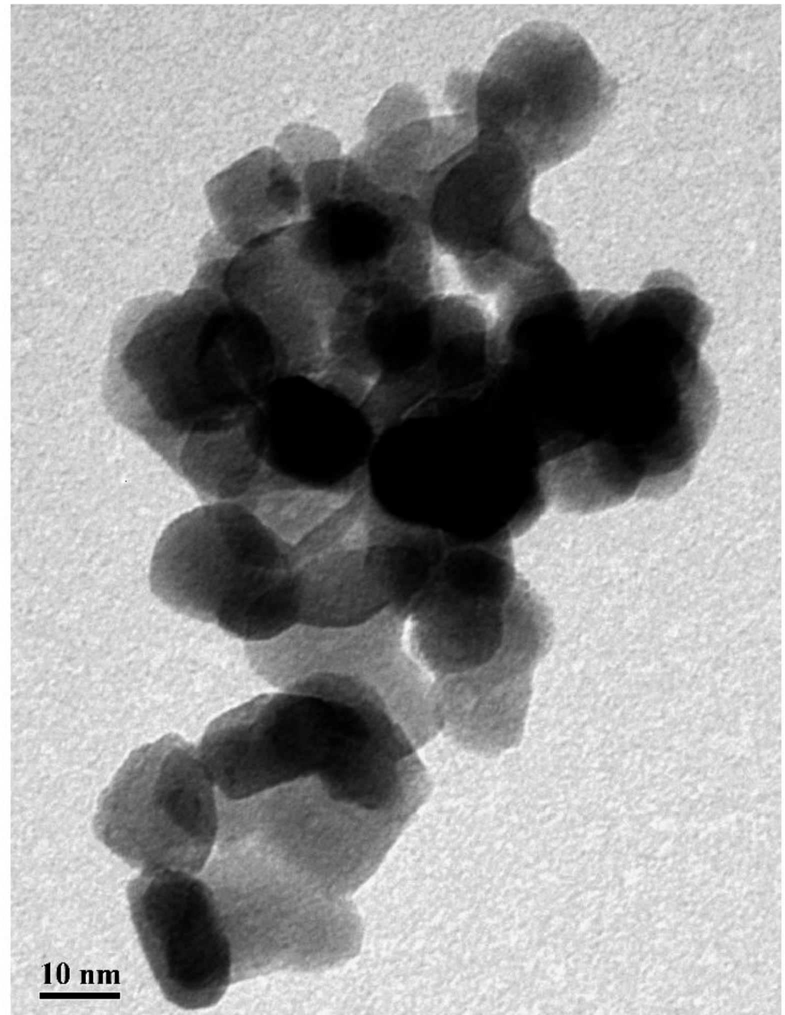
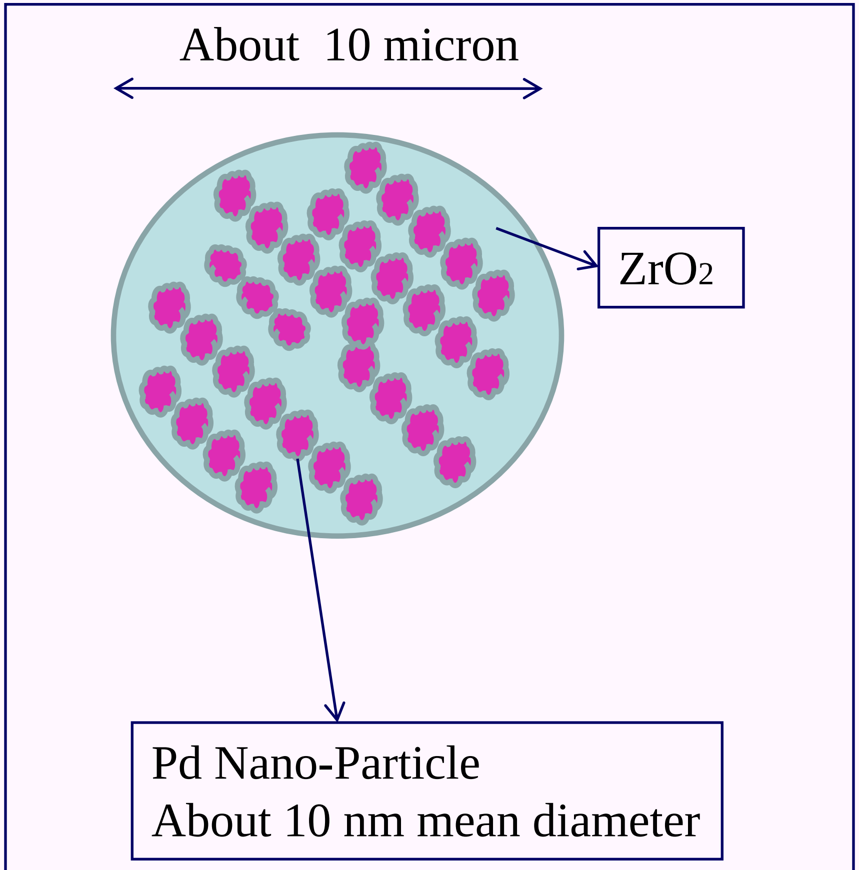


Image at 25000X magnification



Metal-Oxide-Nano-Pd Composite



- PdDx
- **X=1.0** by Arachi et al.;

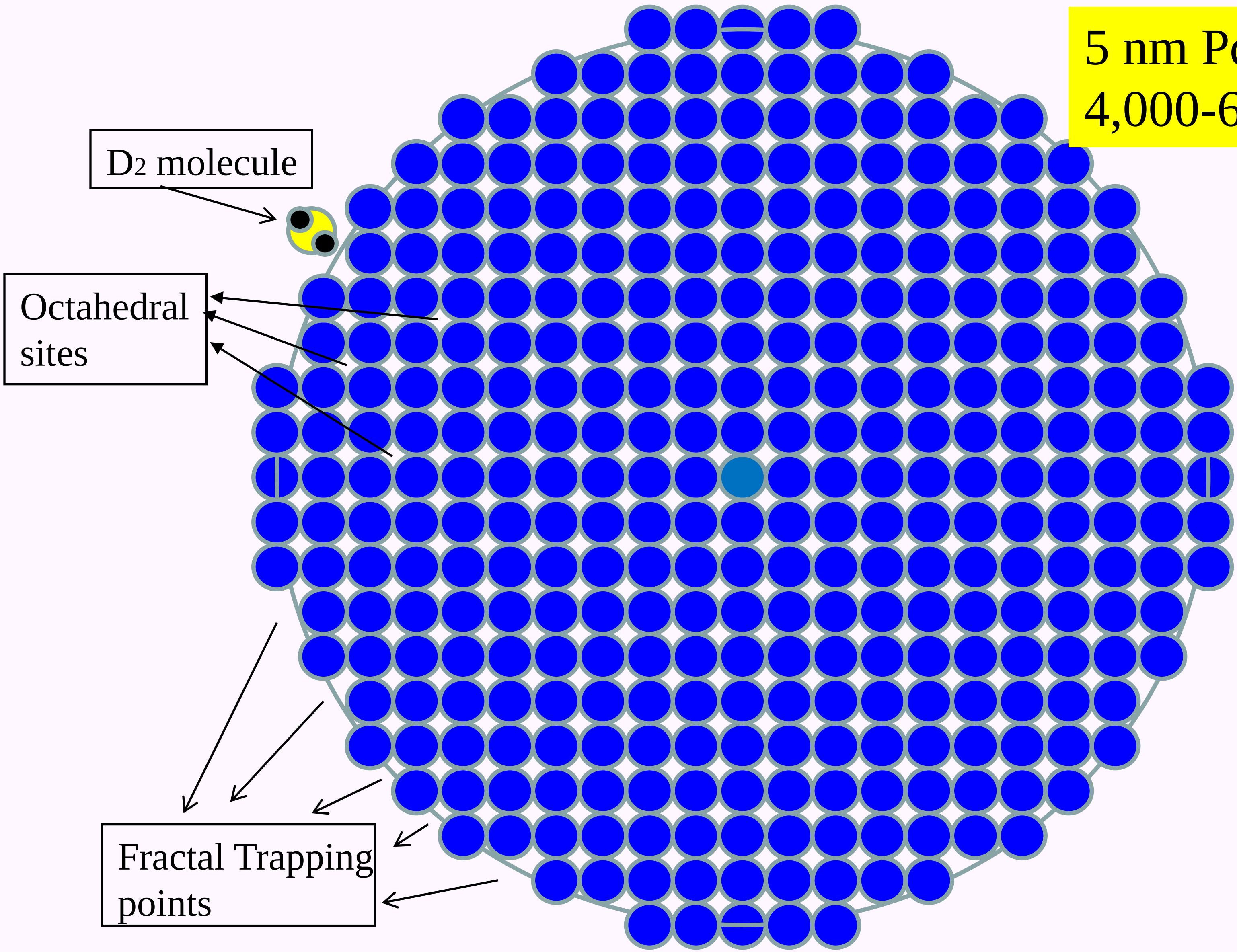
  D-Absorption in O-sites of Pd-Lattice

(We support this data)

- X=2.0 by Yamaura et al; deuterons at Pd-ZrO_2 interface (Voids?)
- Arata claimed: **x=2.5**

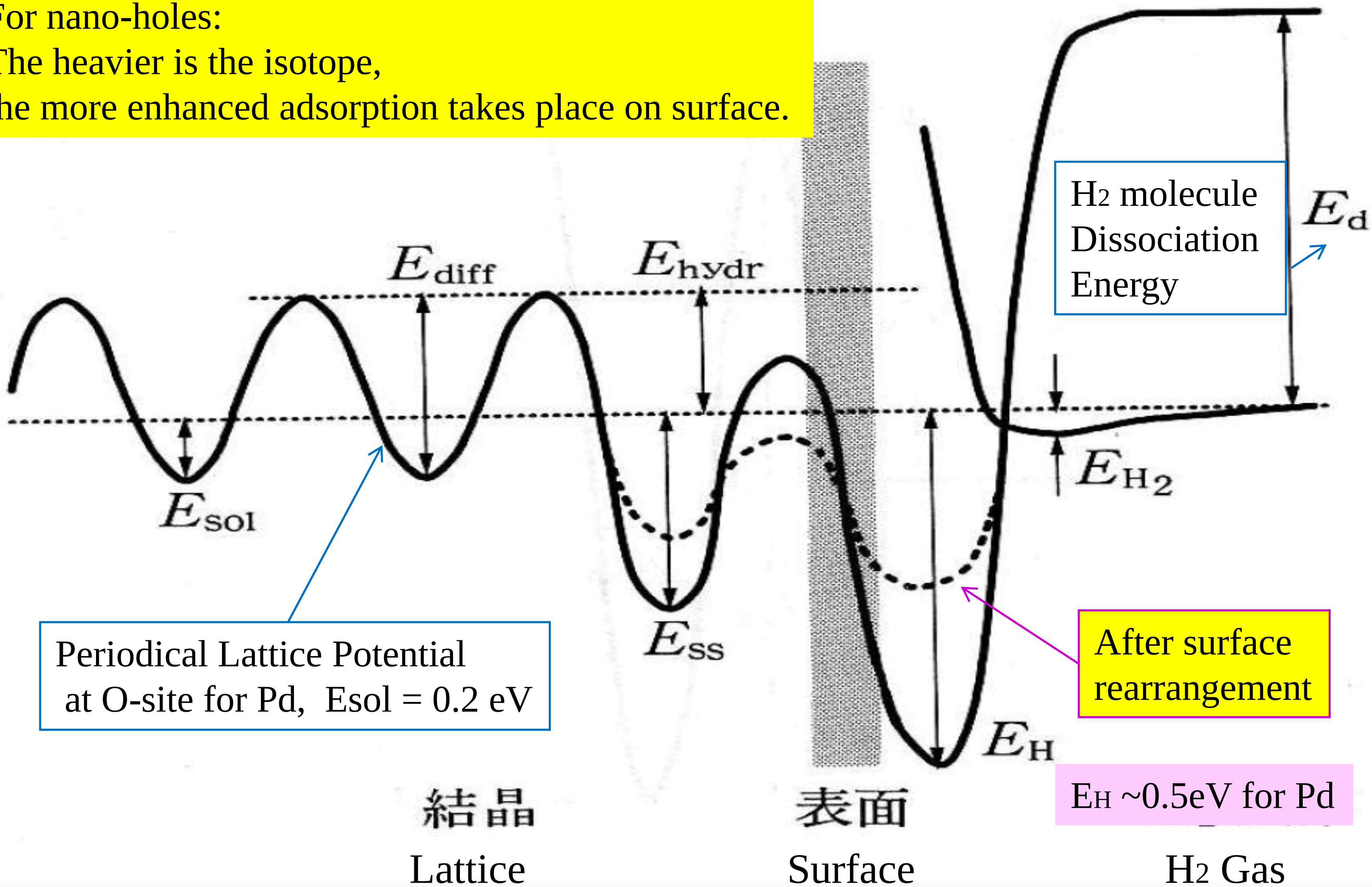
Irregular and Fractal Sites should form on surface of nano-particle

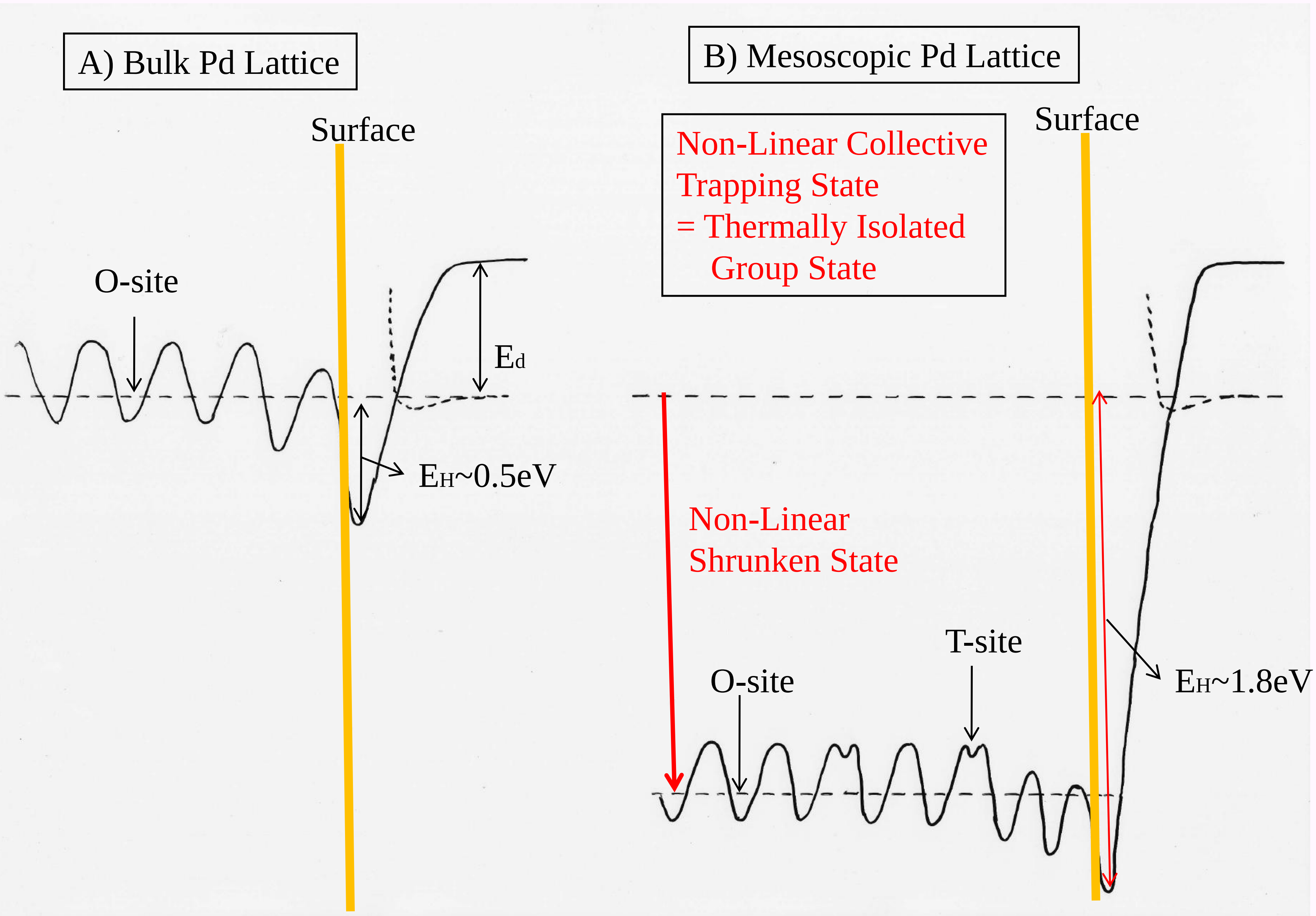
5 nm Pd particle:
4,000-6,000 atoms

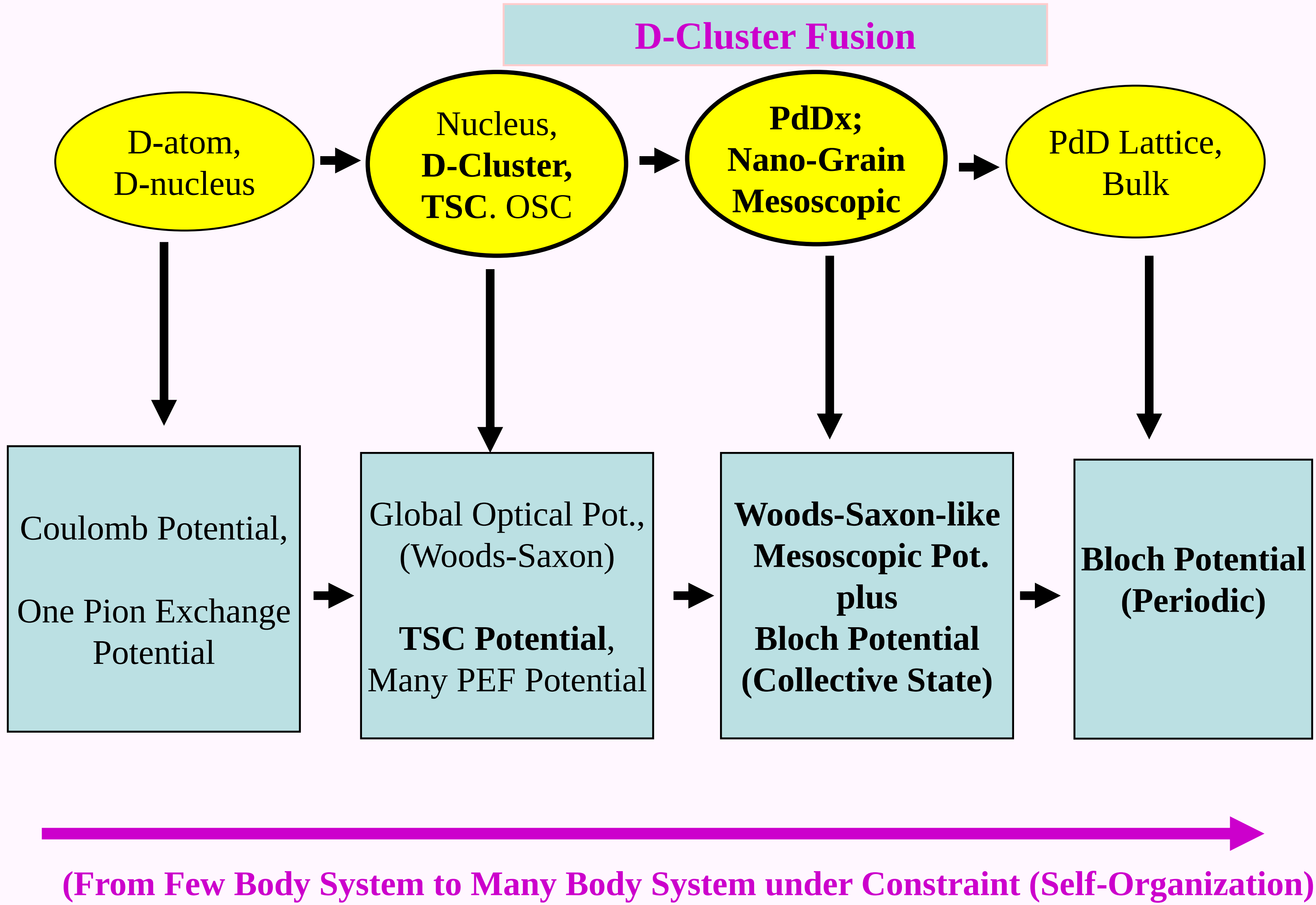


Potential form of hydrogen adsorption and absorption near surface

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




A) Bulk Pd Lattice
Surface
O-site
Ed
EH~0.5eV
B) Mesoscopic Pd Lattice
Non-Linear Collective
Trapping State
= Thermally Isolated
Group State
Surface
Non-Linear
Shrunken State
T-site
O-site
EH~1.8eV


D-Cluster Fusion
D-atom, D-nucleus
Nucleus, D-Cluster, TSC. OSC
PdDx; Nano-Grain Mesoscopic
PdD Lattice, Bulk
Coulomb Potential,
One Pion Exchange Potential
Global Optical Pot., (Woods-Saxon)
TSC Potential, Many PEF Potential
Woods-Saxon-like Mesoscopic Pot. plus Bloch Potential (Collective State)
Bloch Potential (Periodic)
(From Few Body System to Many Body System under Constraint (Self-Organization))

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 3 kJ/g-Pd) for D-gas charge**, while zero level for H-gas charge. (0.4 kJ/g-Li for lithium-ion battery)

- No increase of neutron counts was seen.
- D(H)/Pd ratio in the end of 1st phase was >1.0 (x=1.1 in average) Flow rate dependence.
- The Clumping-Together Effect can be depressed by the Pd/ZrO_2 dispersed sample.

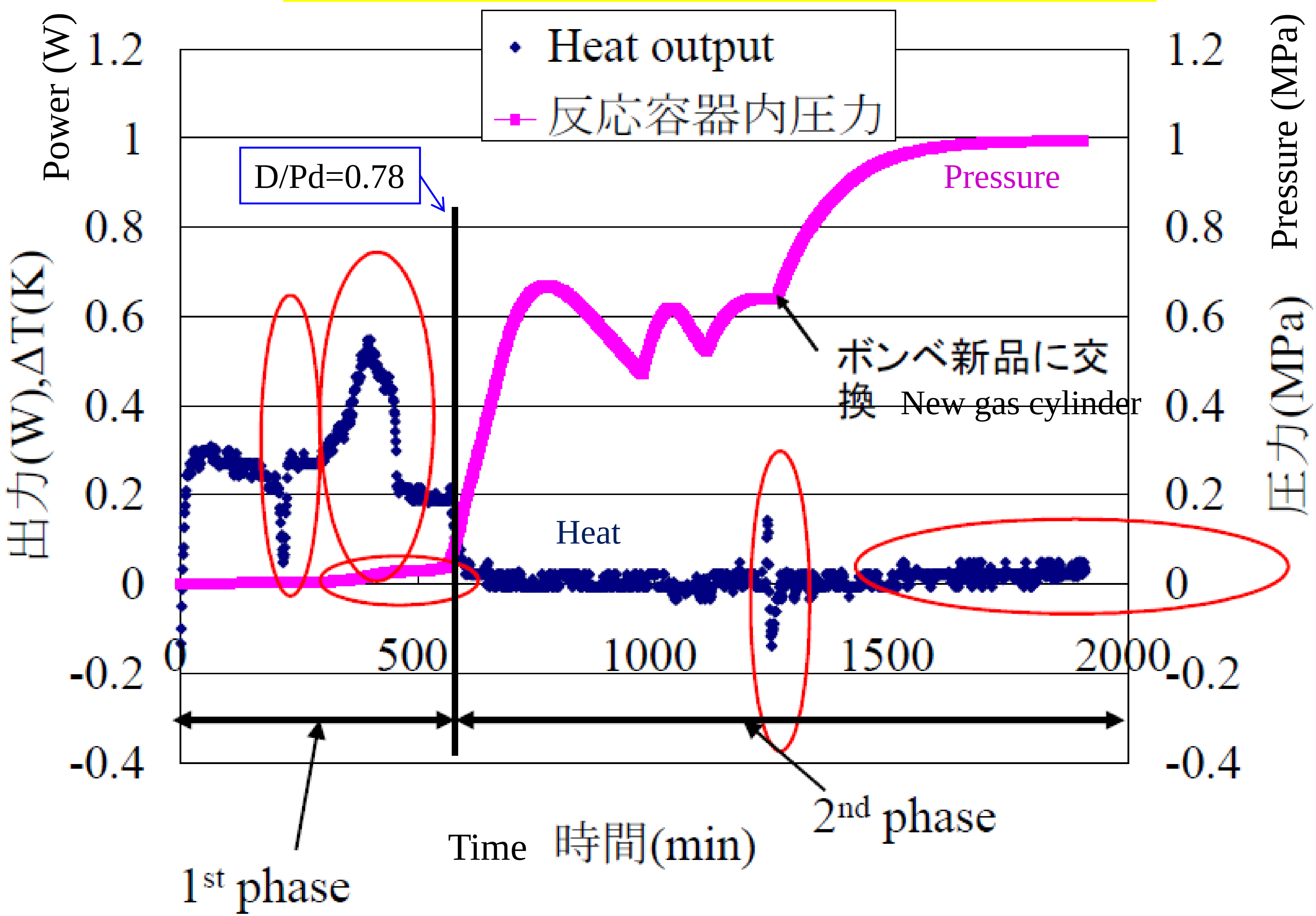
Conclusions-2

- 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; **deep well plus Bloch potential** for collective state: probably makes **deep D(H) trapping potentials (1.8-2.5eV).**
- We need study for D(H)-gas flow-rate dependence and Pd-particle size dependence.
- **Heat of Pd/ZrO_2 in Phase-I was about 10 times of bulk Pd. Peak power increases with flow rate increase.**
- Replication by other groups is important.

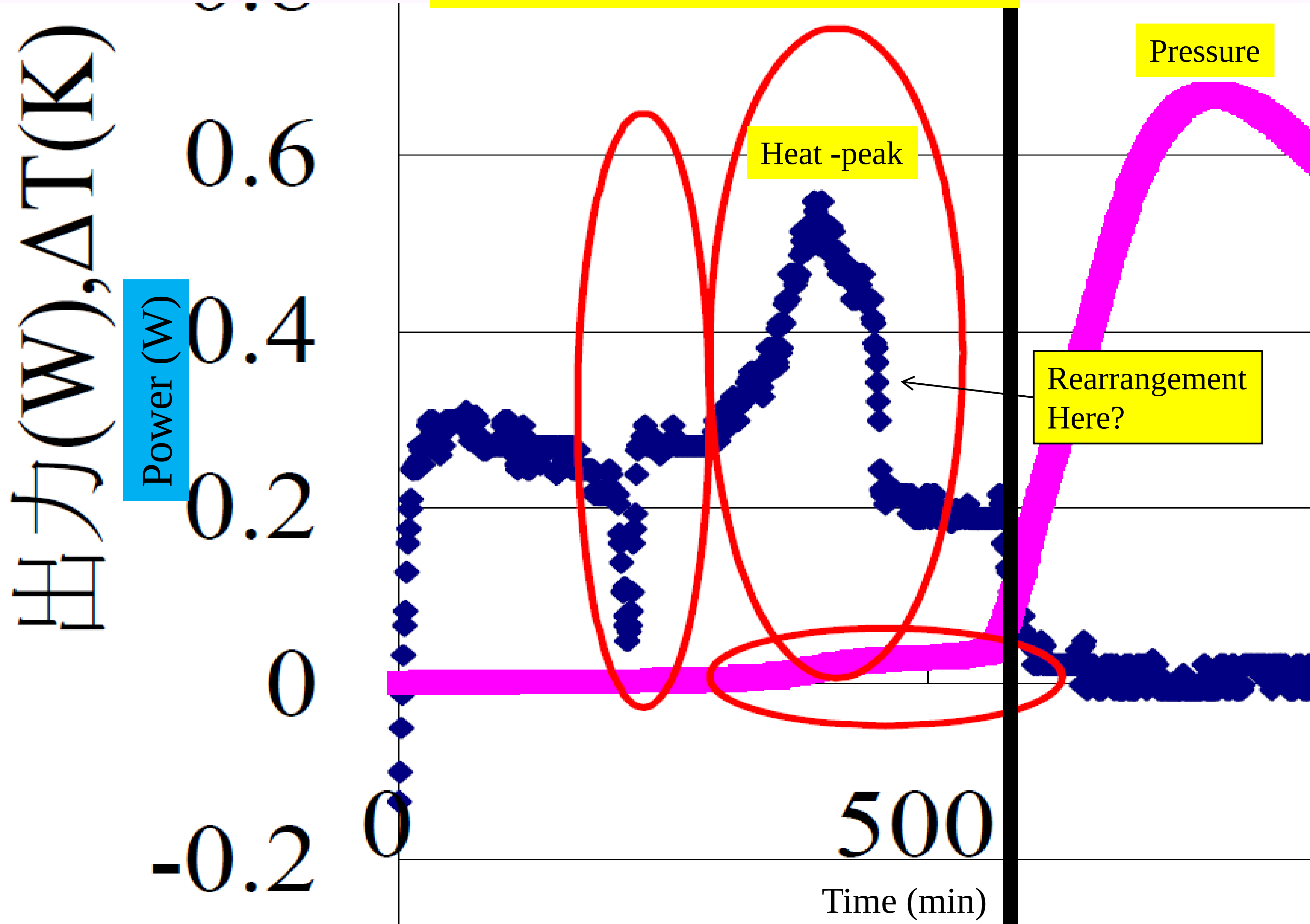
Supplement Data-1

- Pb Black data
- Clumping-together Effect
- SEM Images

Pd-black (20g) / D-gas charge #1: Nov. 2008

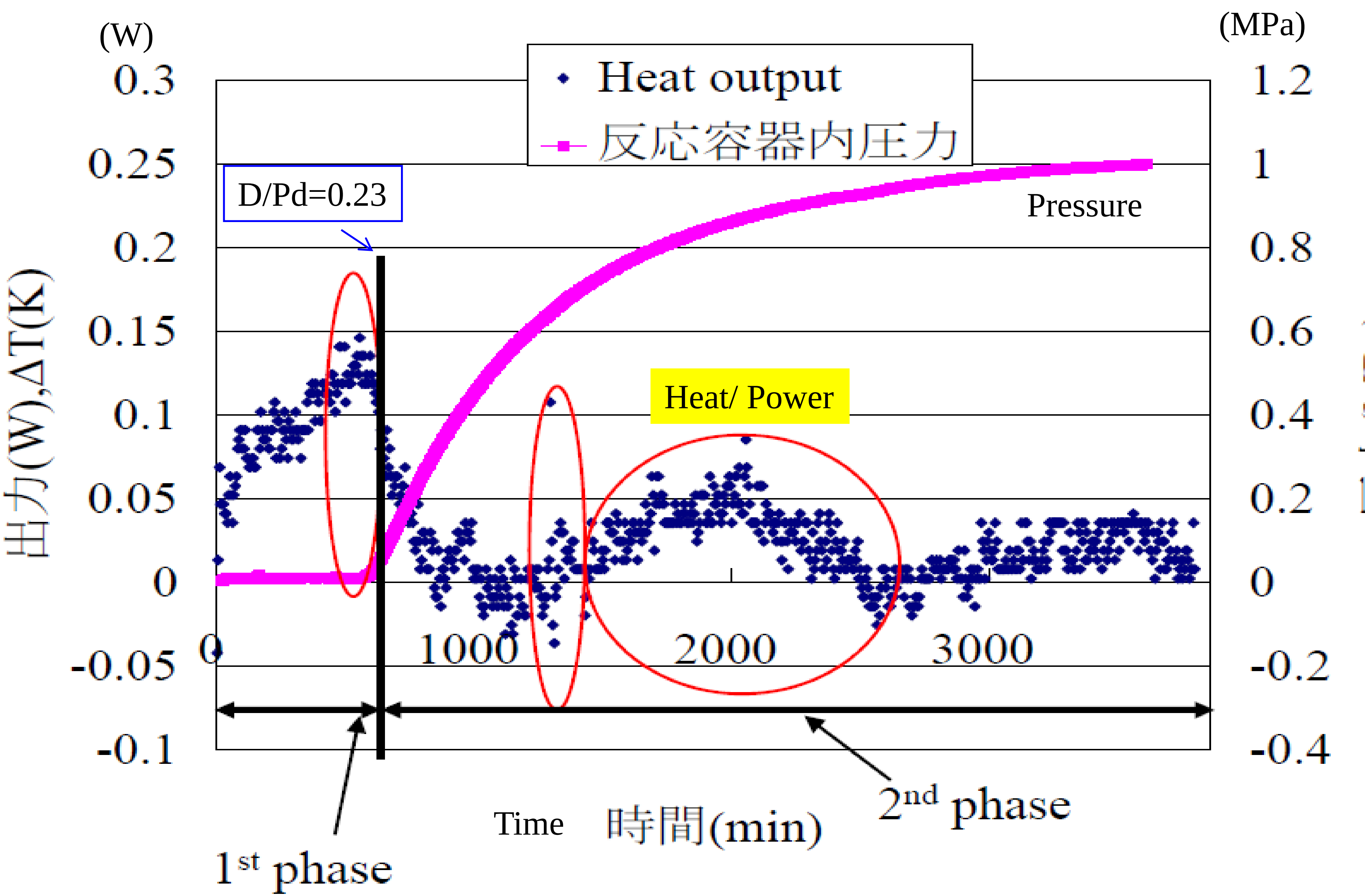


Pd-black / D-gas charge #1 data

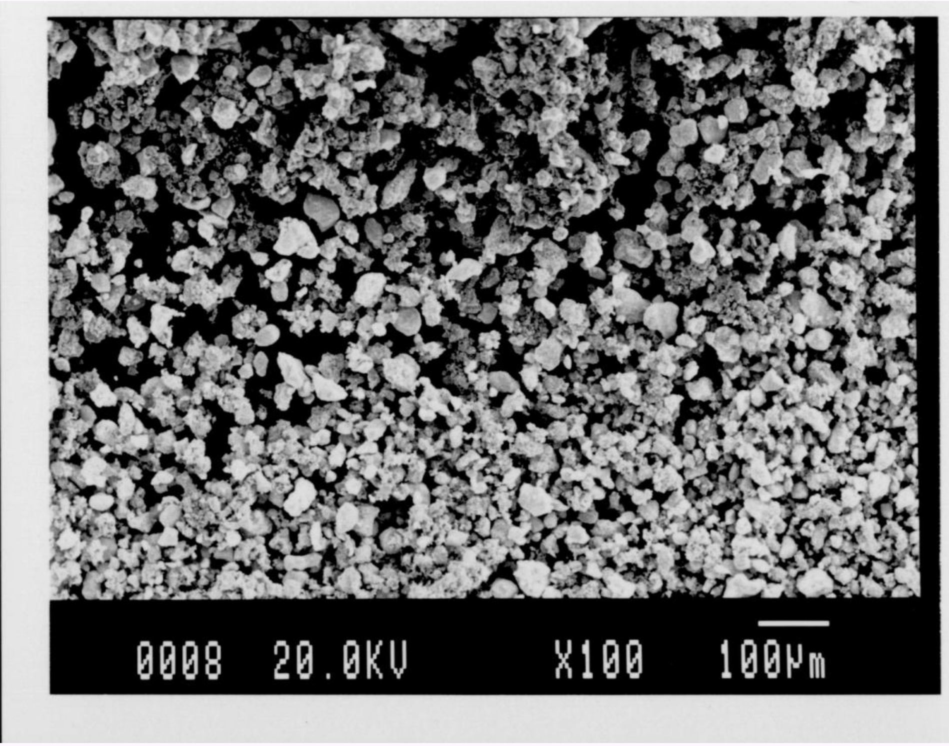


Decreased absorption and heat level for #2

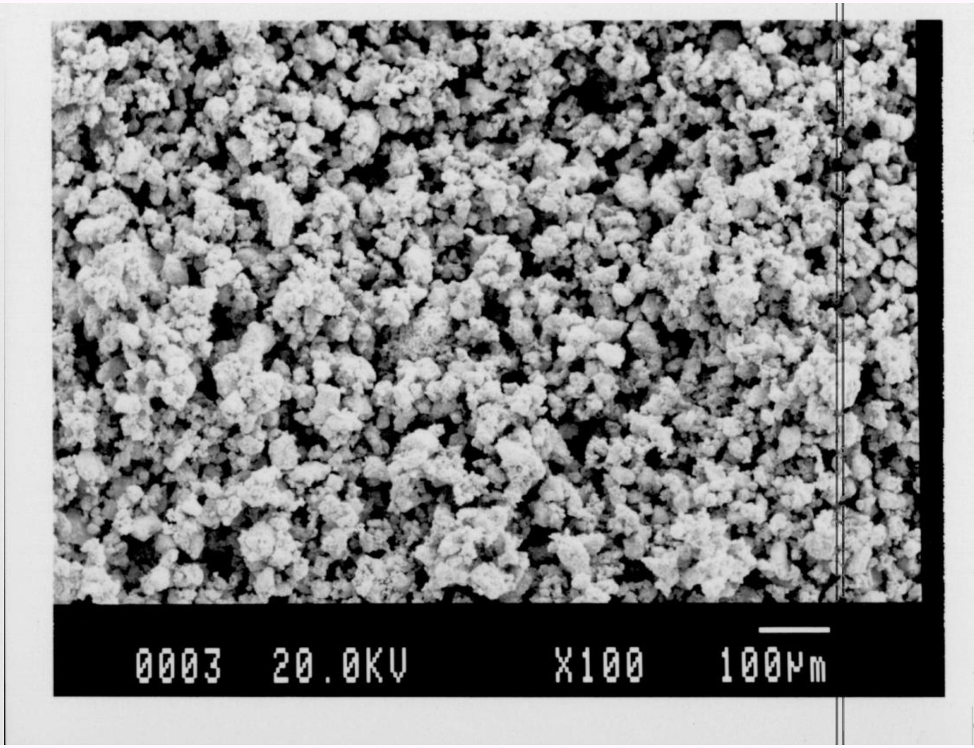
Pd-black (20g)/ D-gas #2



Before Runs



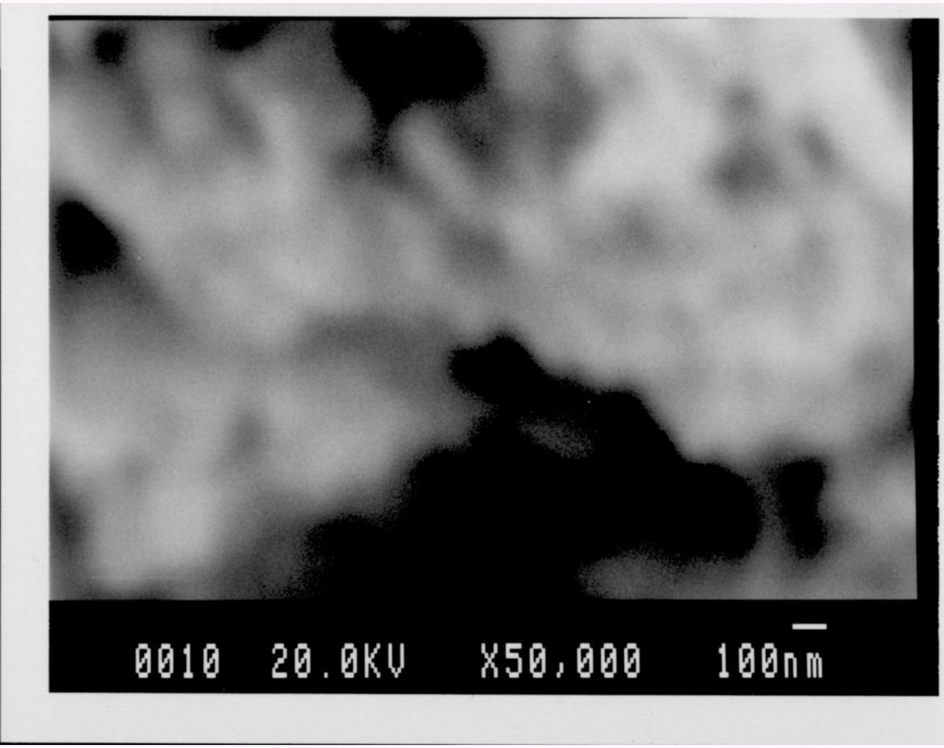
After Runs



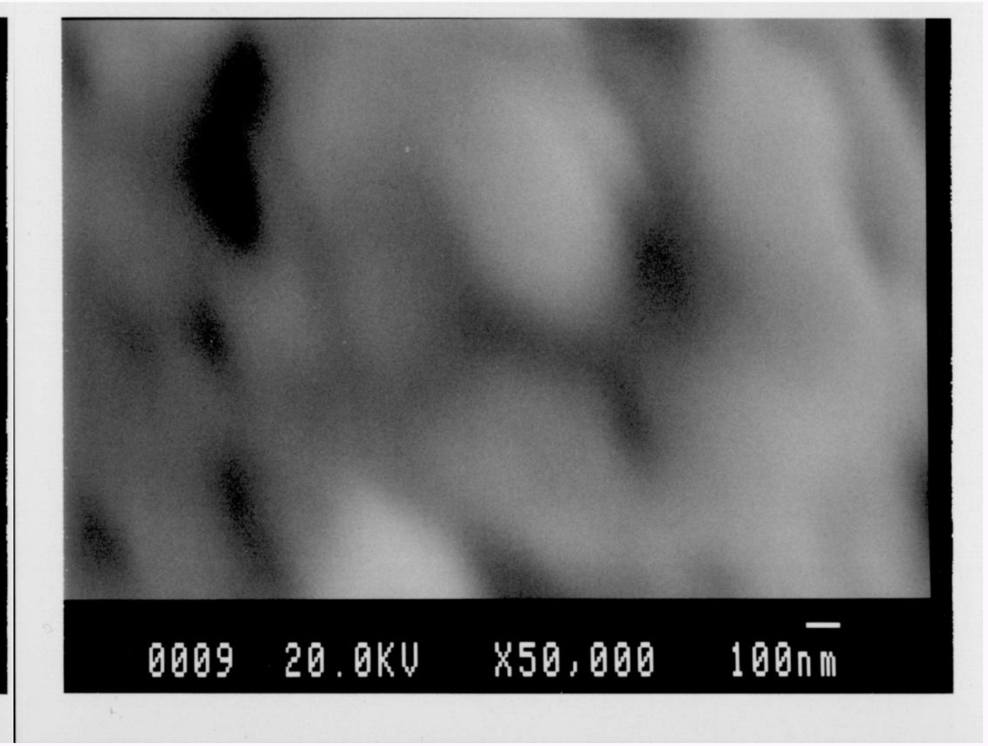
Magnification: ×100 SEM Image

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

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

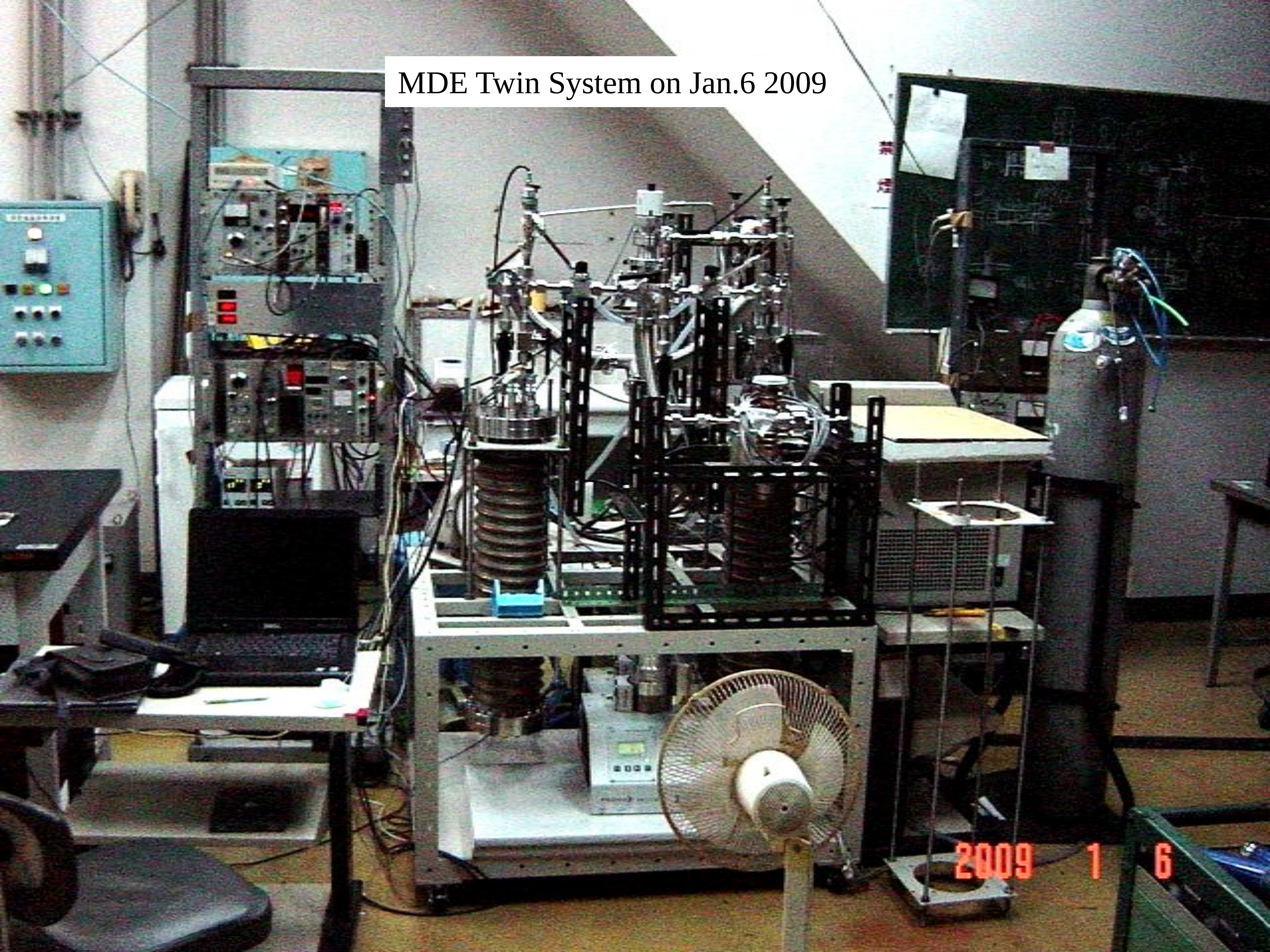
Summary for Pd-black

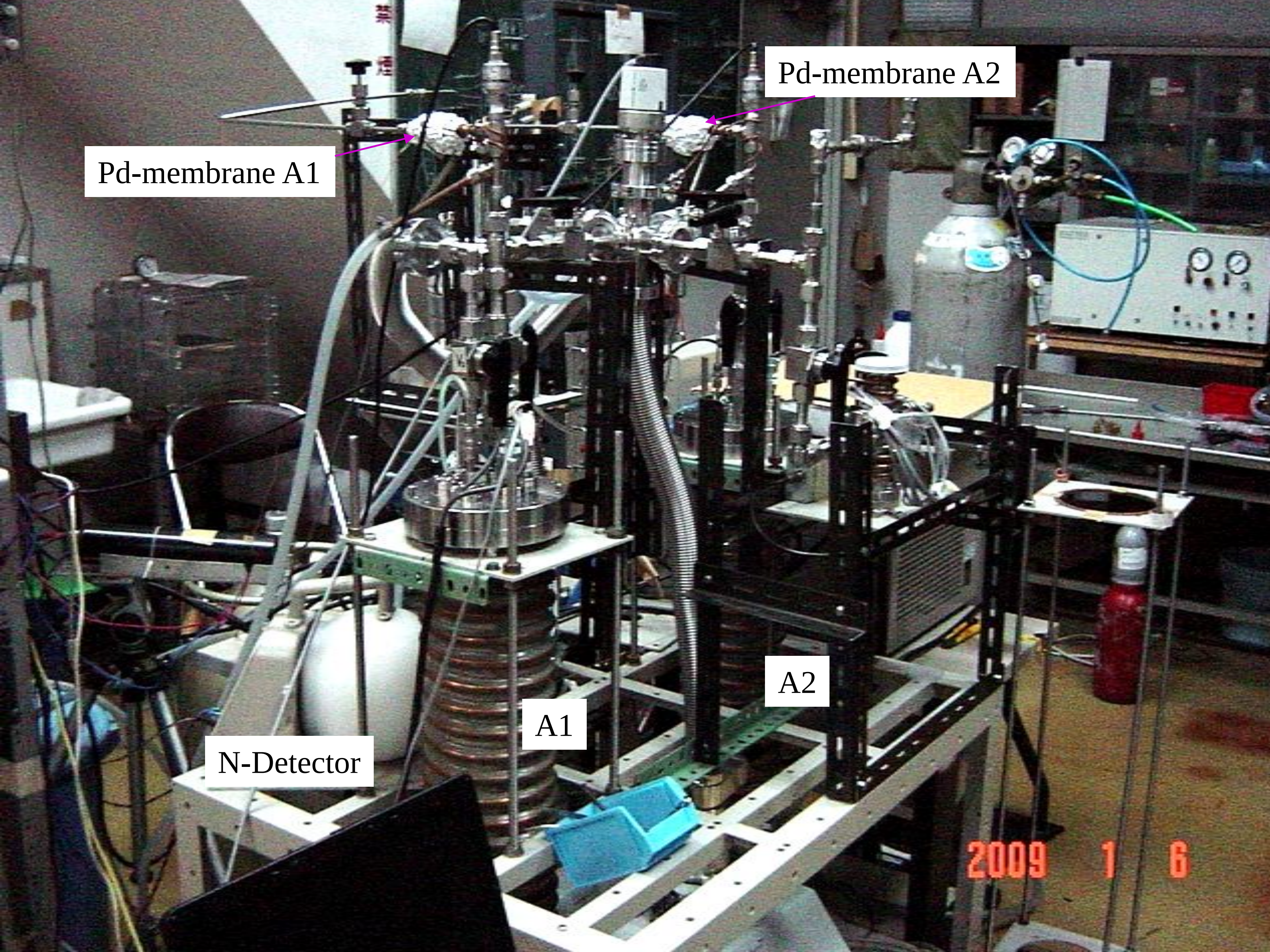
- There were seen excess heat in the 1st and 2nd phases, but smaller than those by Pd/ZrO_2
- Pd-black powders stuck to be bigger sizes (about 10 times diameter by SEM observation), after the #1 run.
- This is the Clumping-Together-Effect of nano-powders.
- In the #2 run and following runs, no significant 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.

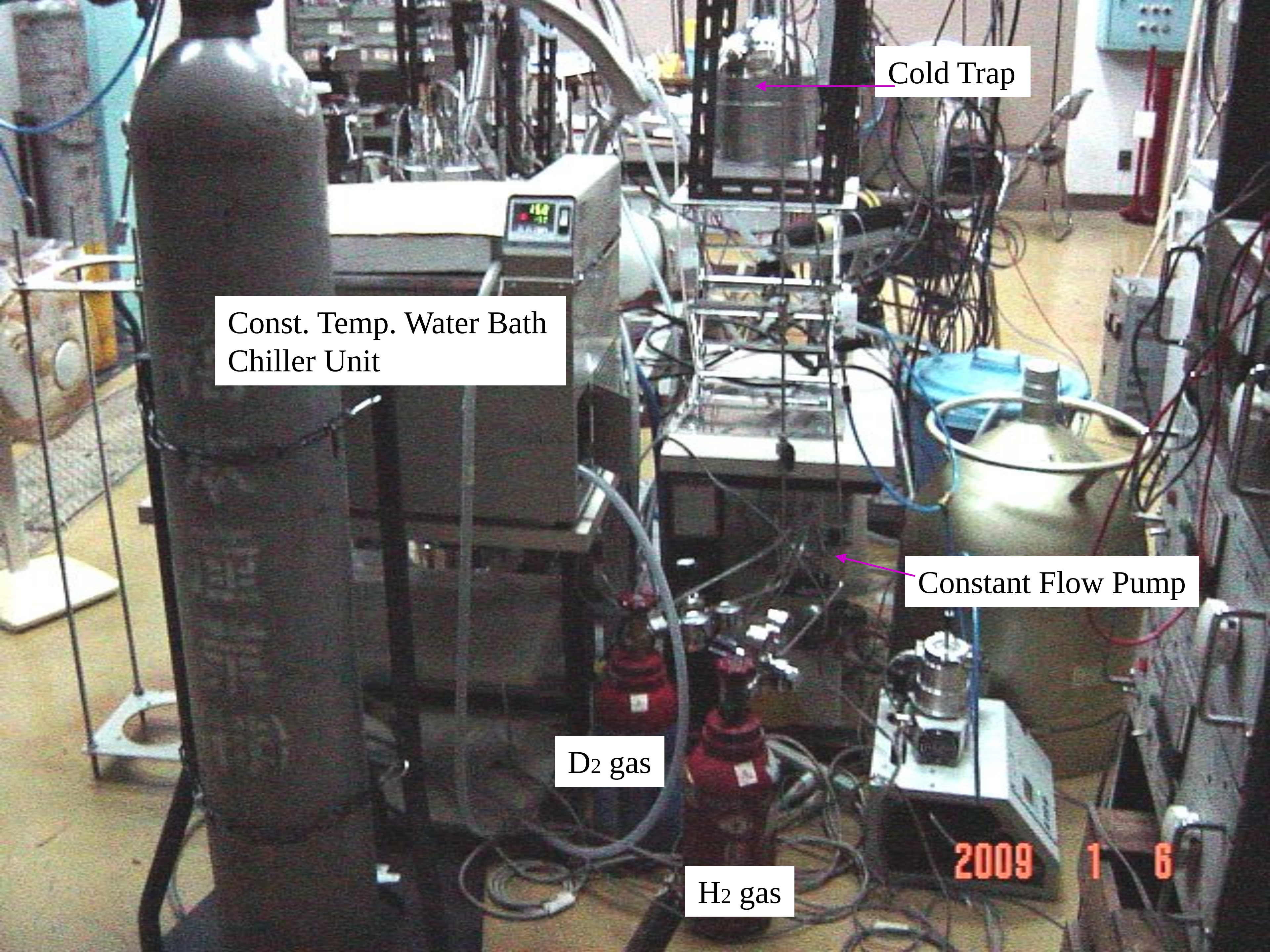
Supplement Data 2

- Photographs of experimental systems
- A_0 System
- A_1 and A_2 Twin system

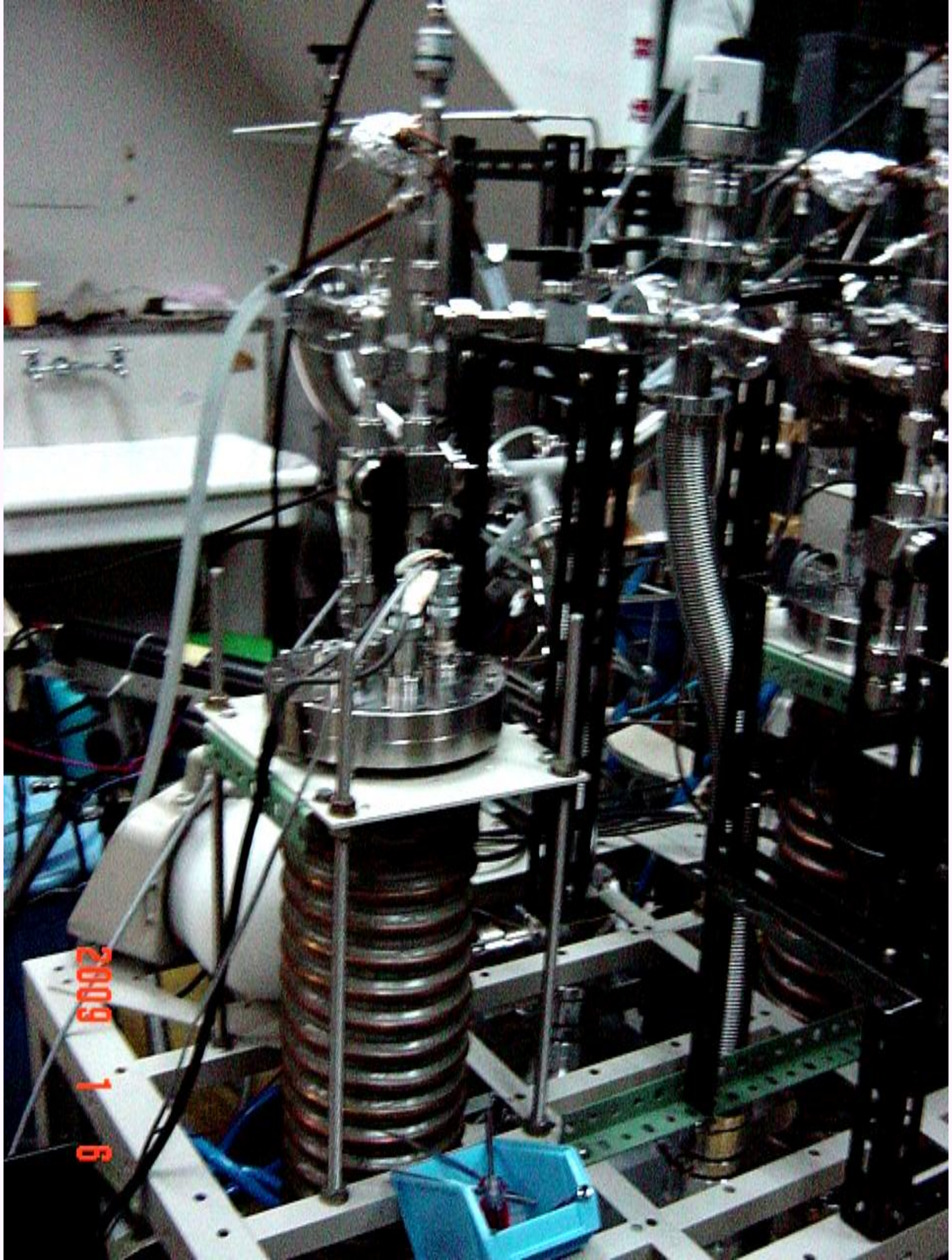
MDE Twin System on Jan.6 2009




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

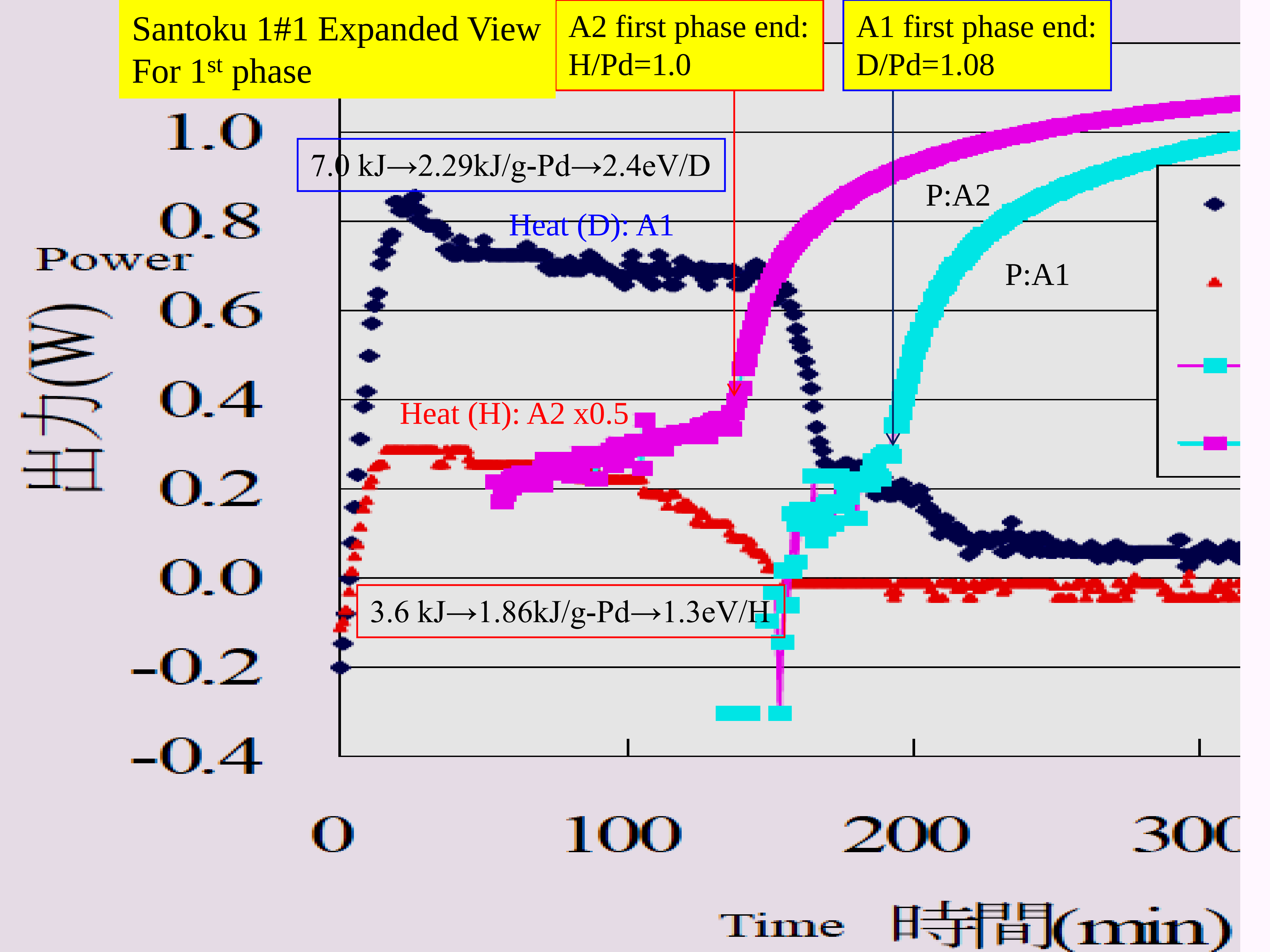


B System
Under
Construction

Supplement Data 3

- Detail data for PZ-series runs
  (PZ=$PdZrO_2$ nano-composite powder)

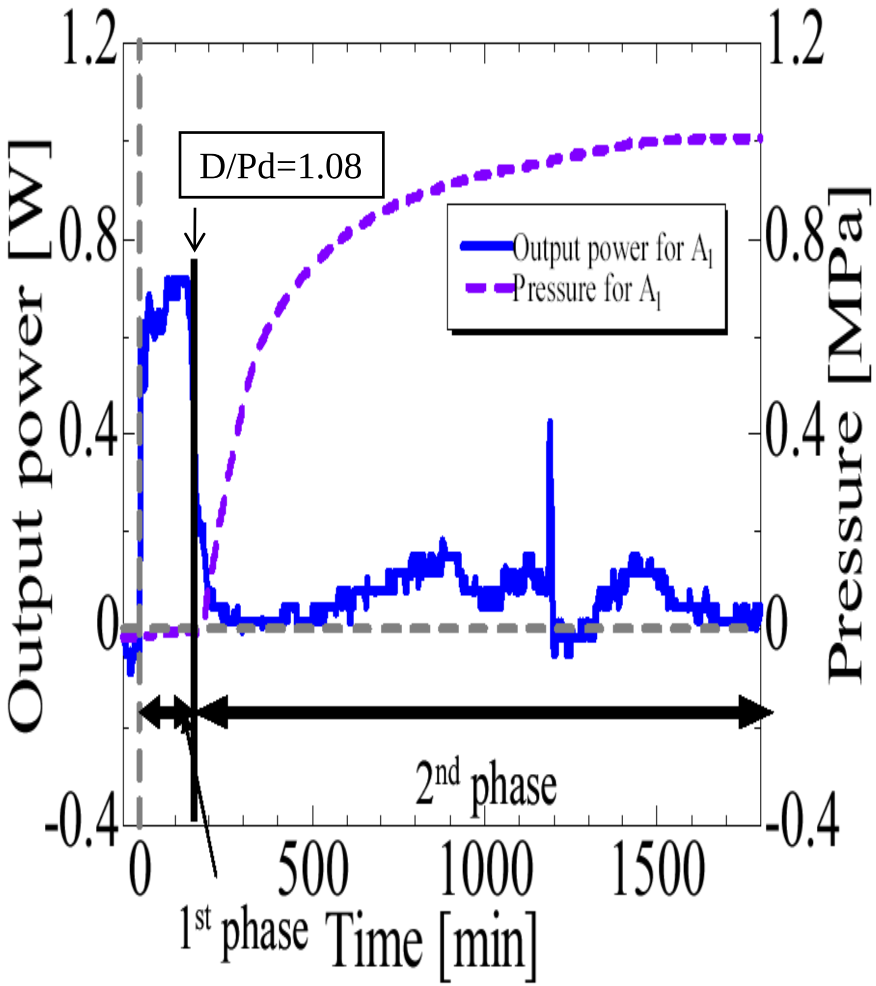
- Reproducibility of Pase-1 and Phase-2 Data
- Comparison with Arata-Zhang Data



Santoku 1#1 Expanded View
For 1st phase
A2 first phase end:
H/Pd=1.0
A1 first phase end:
D/Pd=1.08
7.0 kJ→2.29kJ/g-Pd→2.4eV/D
Heat (D): A1
P:A2
P:A1
Heat (H): A2 x0.5
3.6 kJ→1.86kJ/g-Pd→1.3eV/H
Power
出力(W)
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
0
100
200
Time 時間(min)

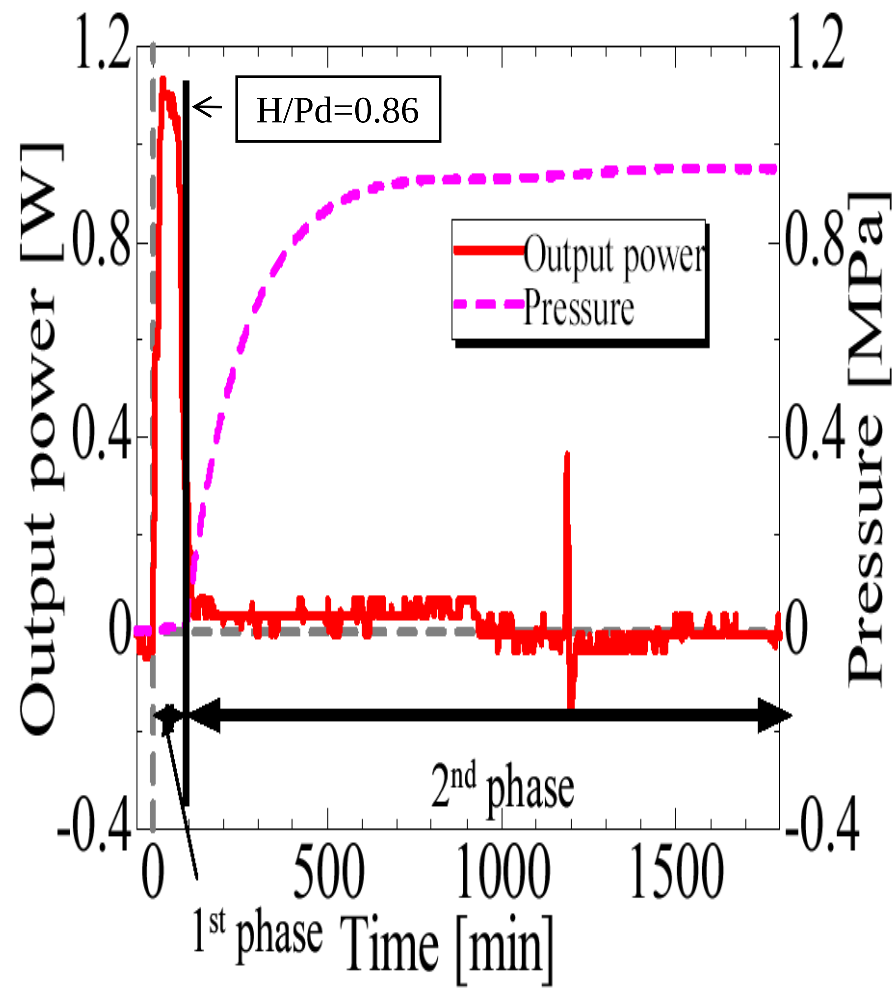
Results of Santoku2#1 run

A1: D-gas Charge with 1.9 sccm



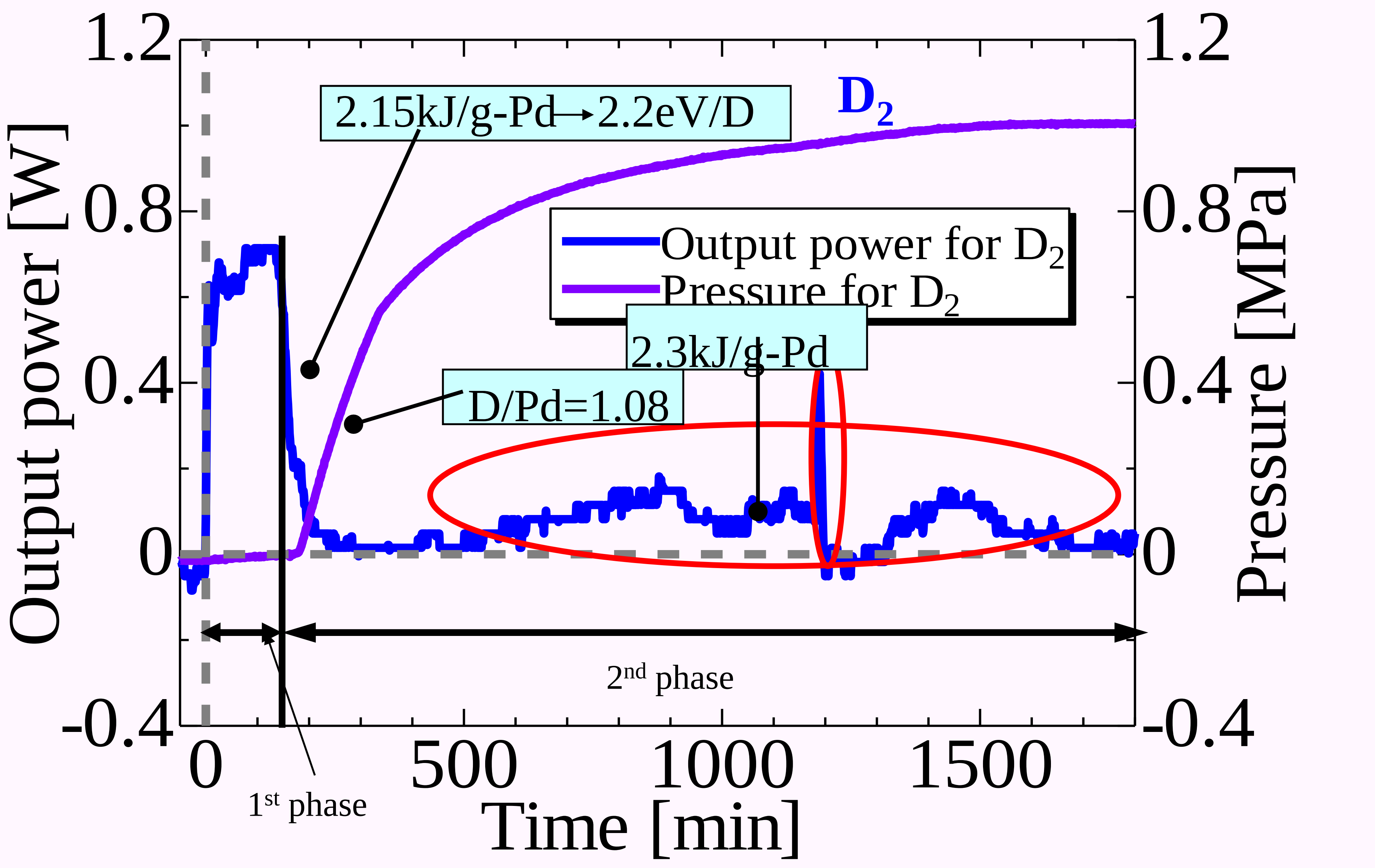
D-gas Charging to Santoku2#1

A2: H-gas Charge with 3.6sccm

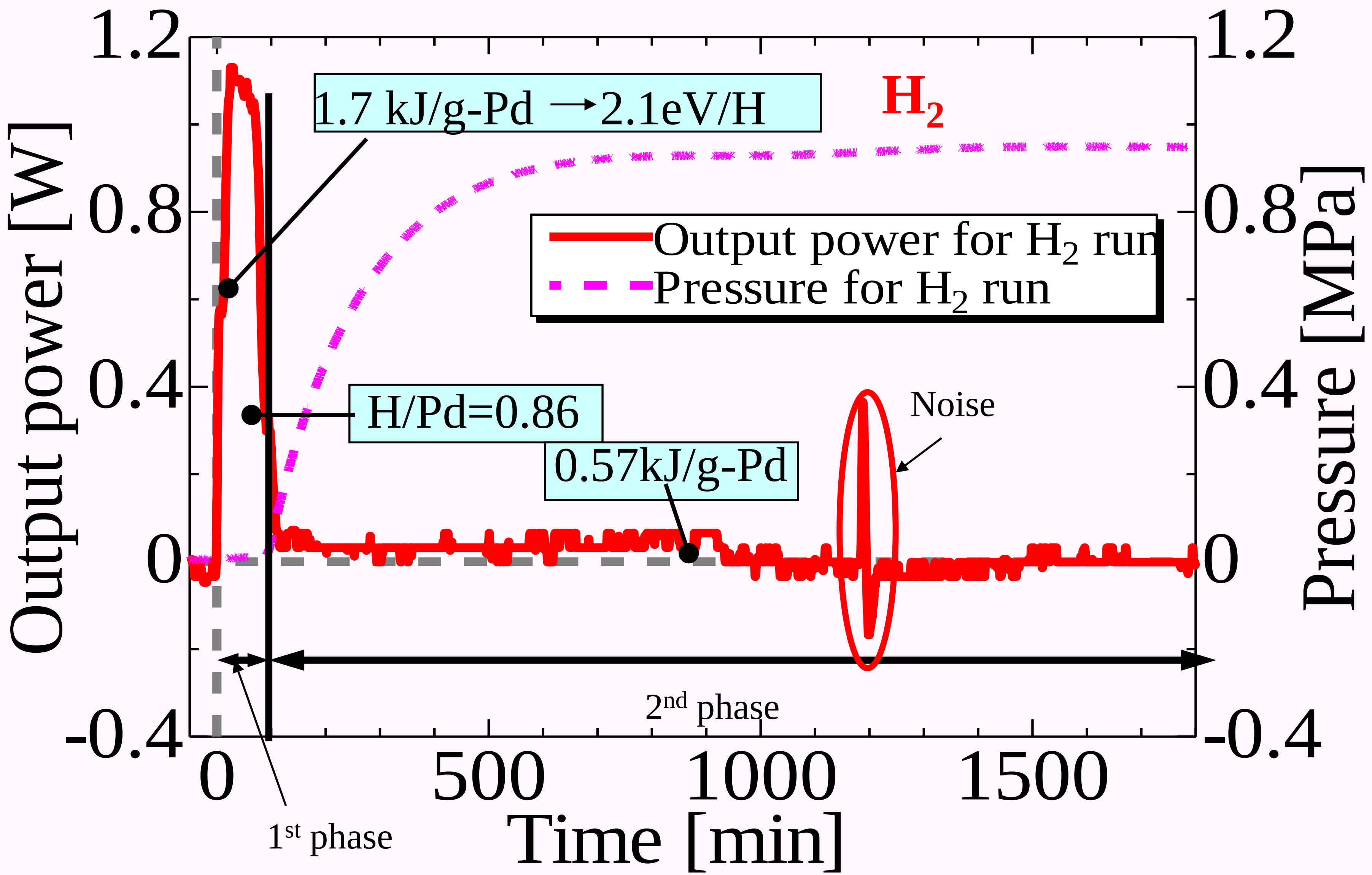


H-gas Charging to Santoku2#1

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

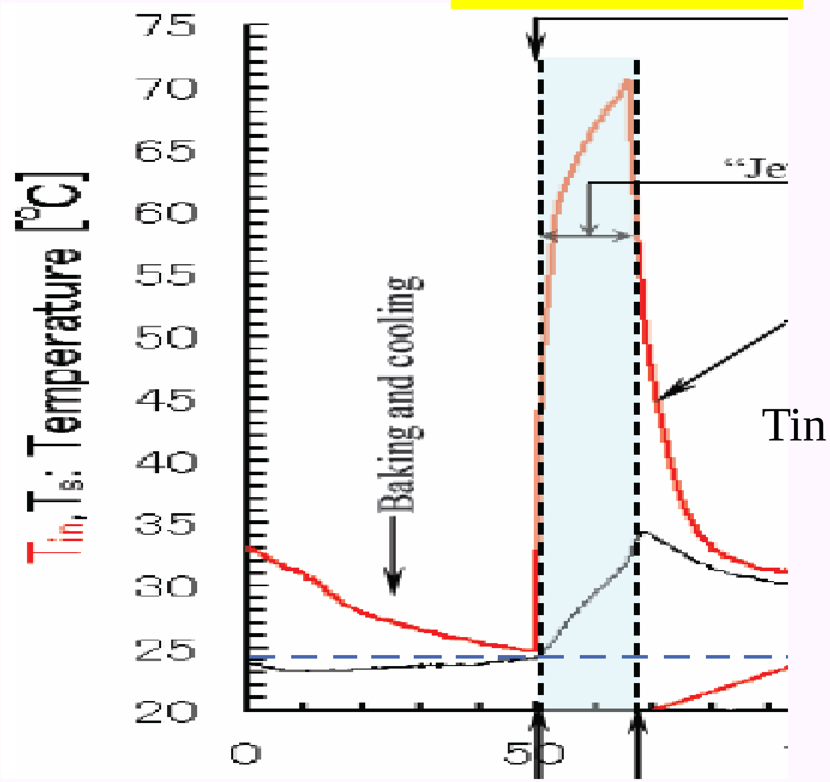


Pd·ZrO2 Santoku 2 #1 Run (A2) for H-gas Charge

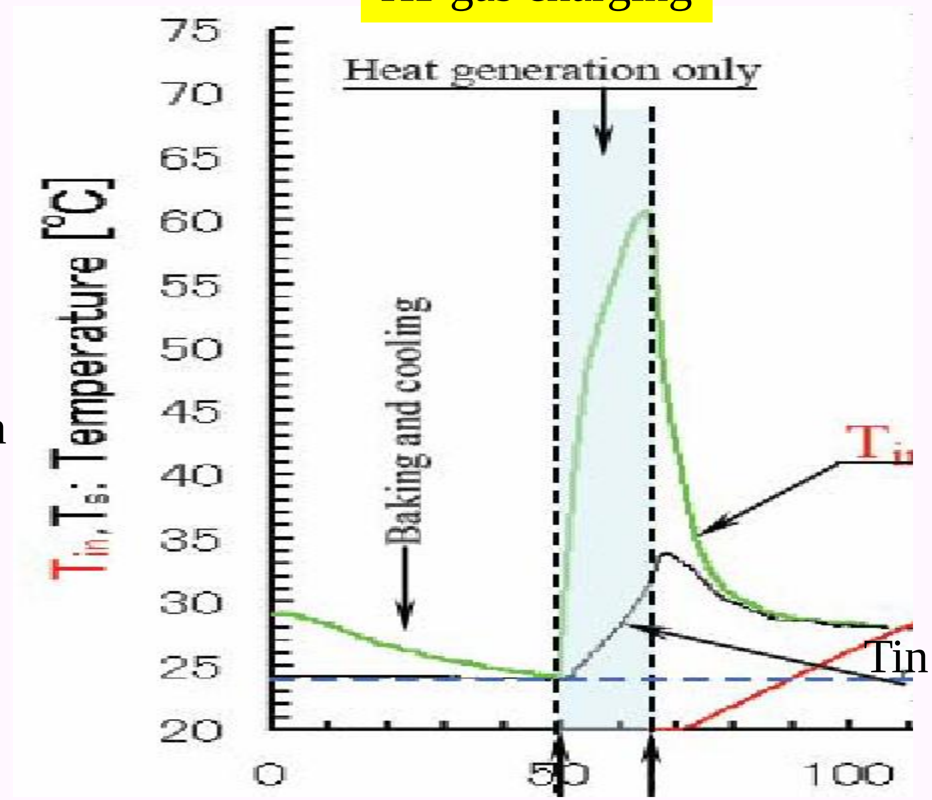


Arata-Zhang's 1st Phase Data for Pd/ZrO2 (7g)

D2-gas charging



H2-gas charging



Time (min)

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**

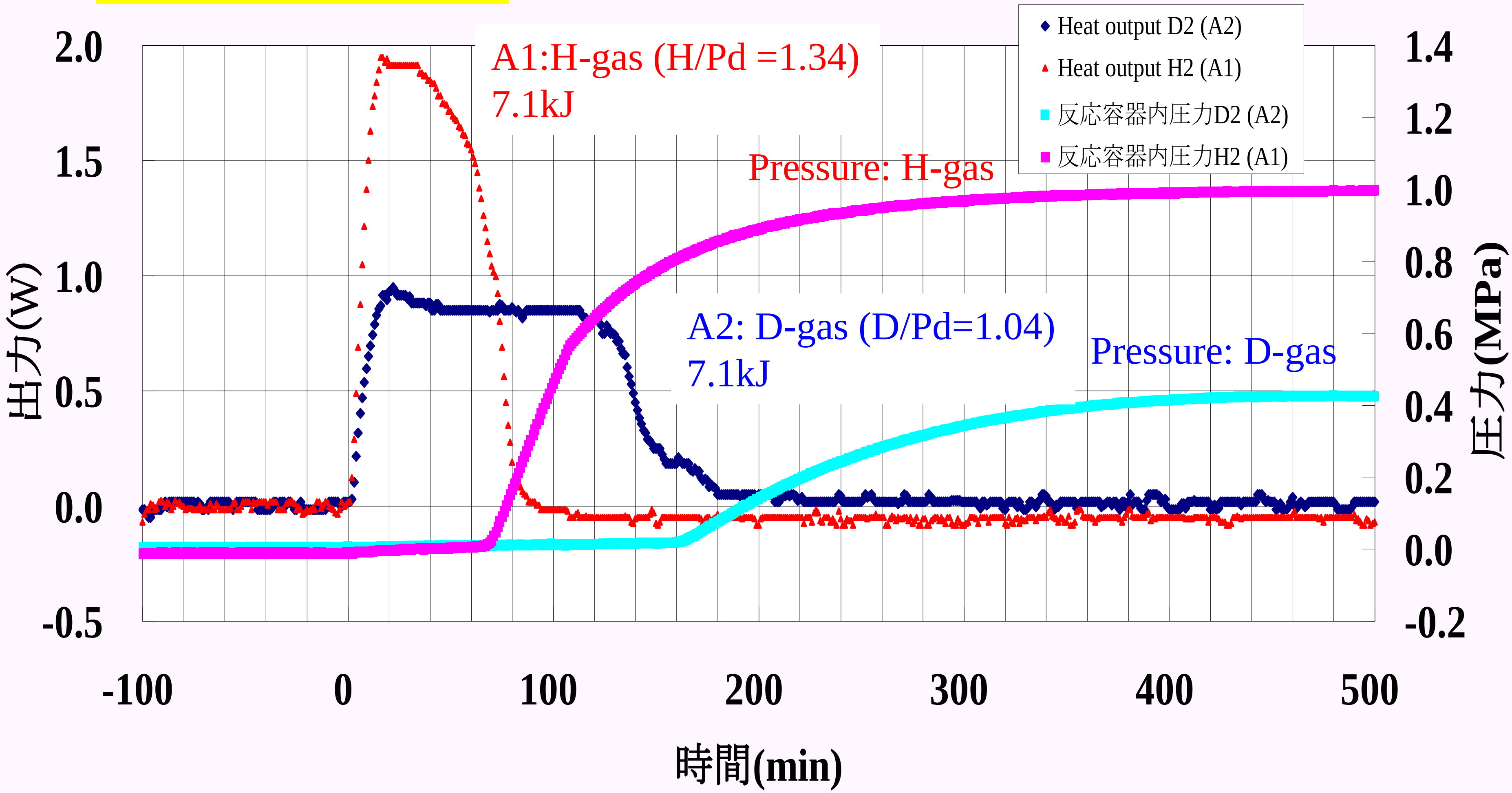
Our Exp. Santoku2: [Heat(D)/Heat(H)] = (6.4kJ)/(5.1kJ) = **1.26**

Agreed!

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

Santoku **3#1** Run

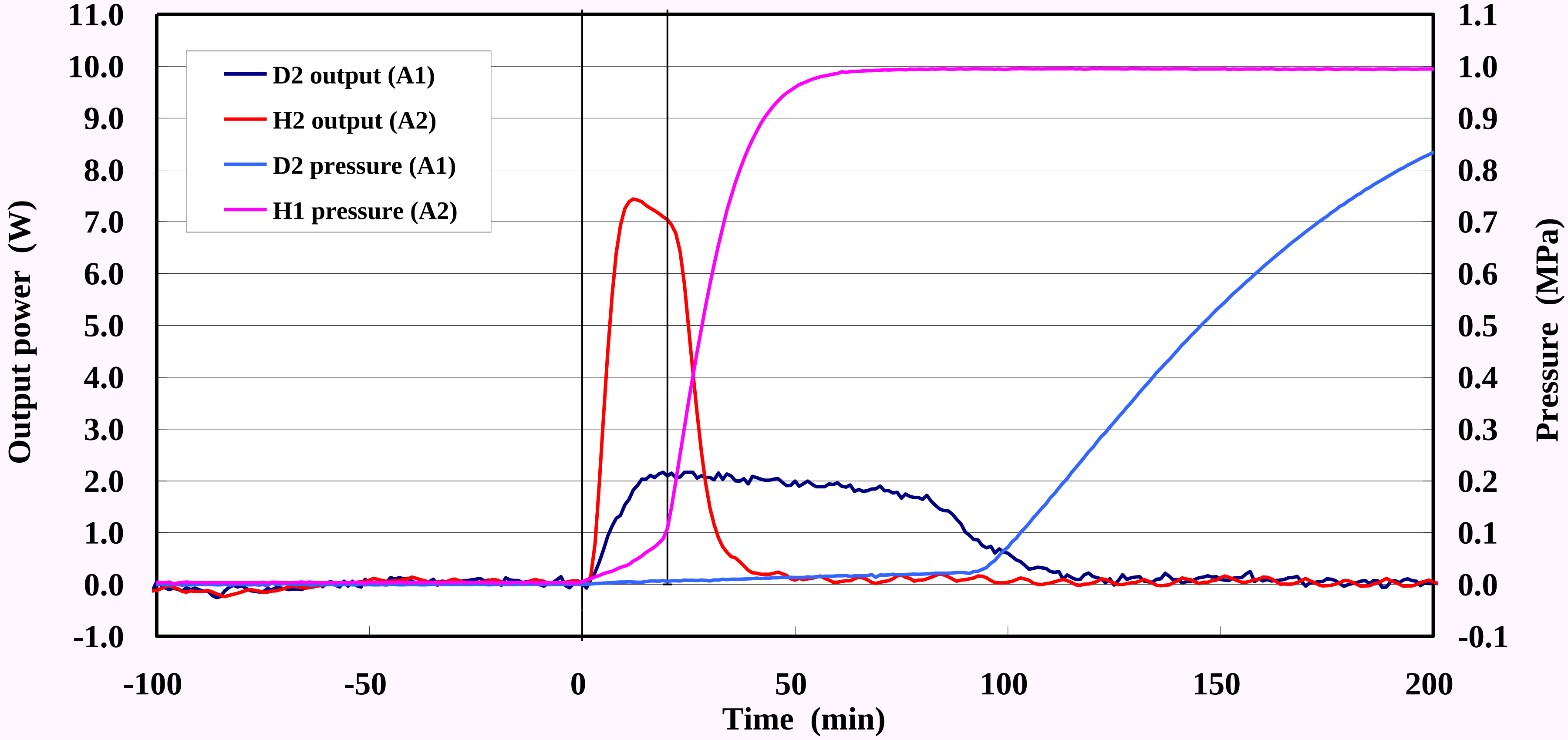
A1: H-gas, Flow Rate = 5.9 sccm
A2: D-gas, Flow Rate = **2.0** sccm



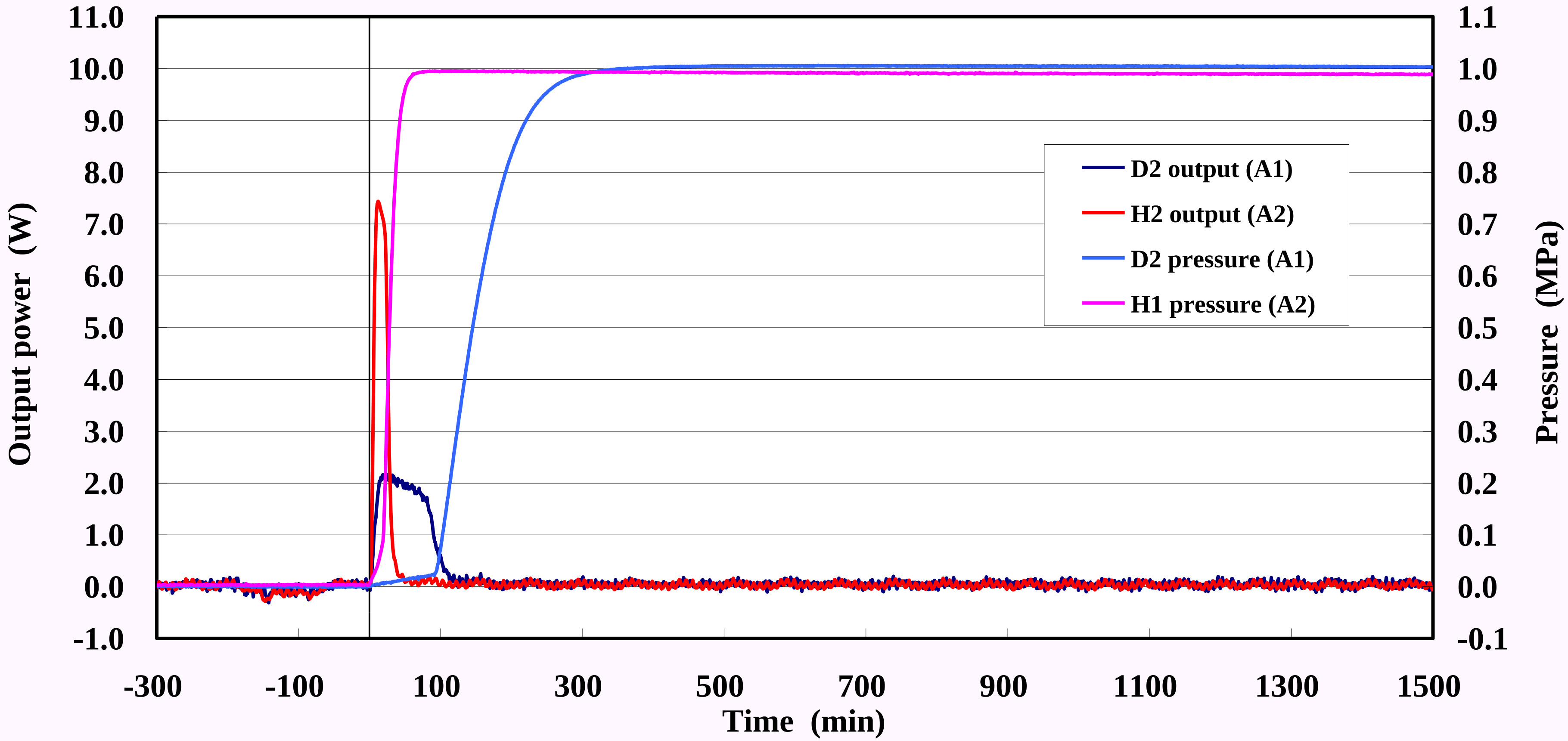
D-PZ9#1 vs. H-PZ10#1 :-100~300min

Flow Rates: 6.42 (D), 20.5 (H) sccm

Sample net Pd weight: 4.2g



D-PZ9#1 vs. H-PZ10#1



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/ZrO_2 sample

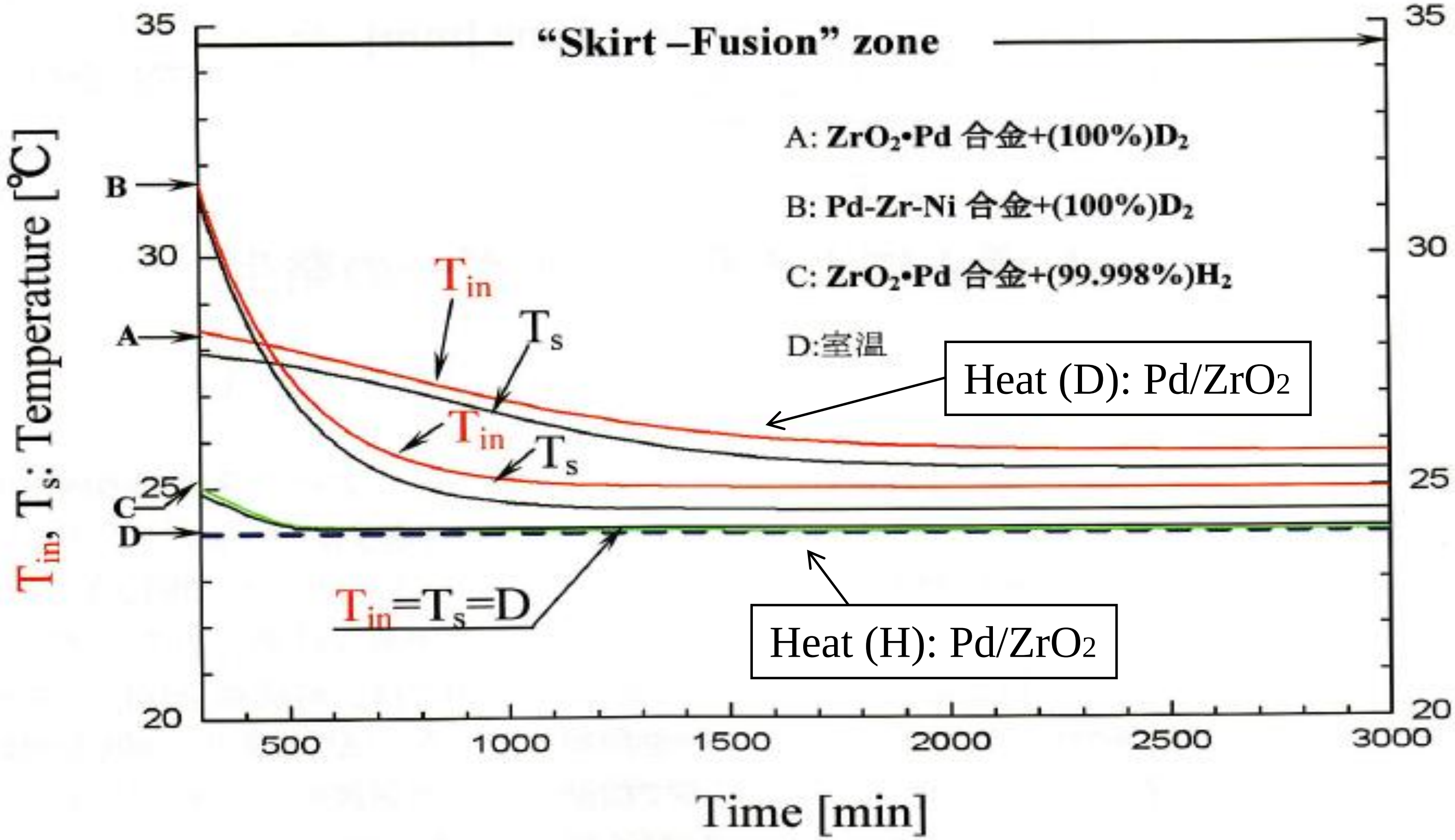
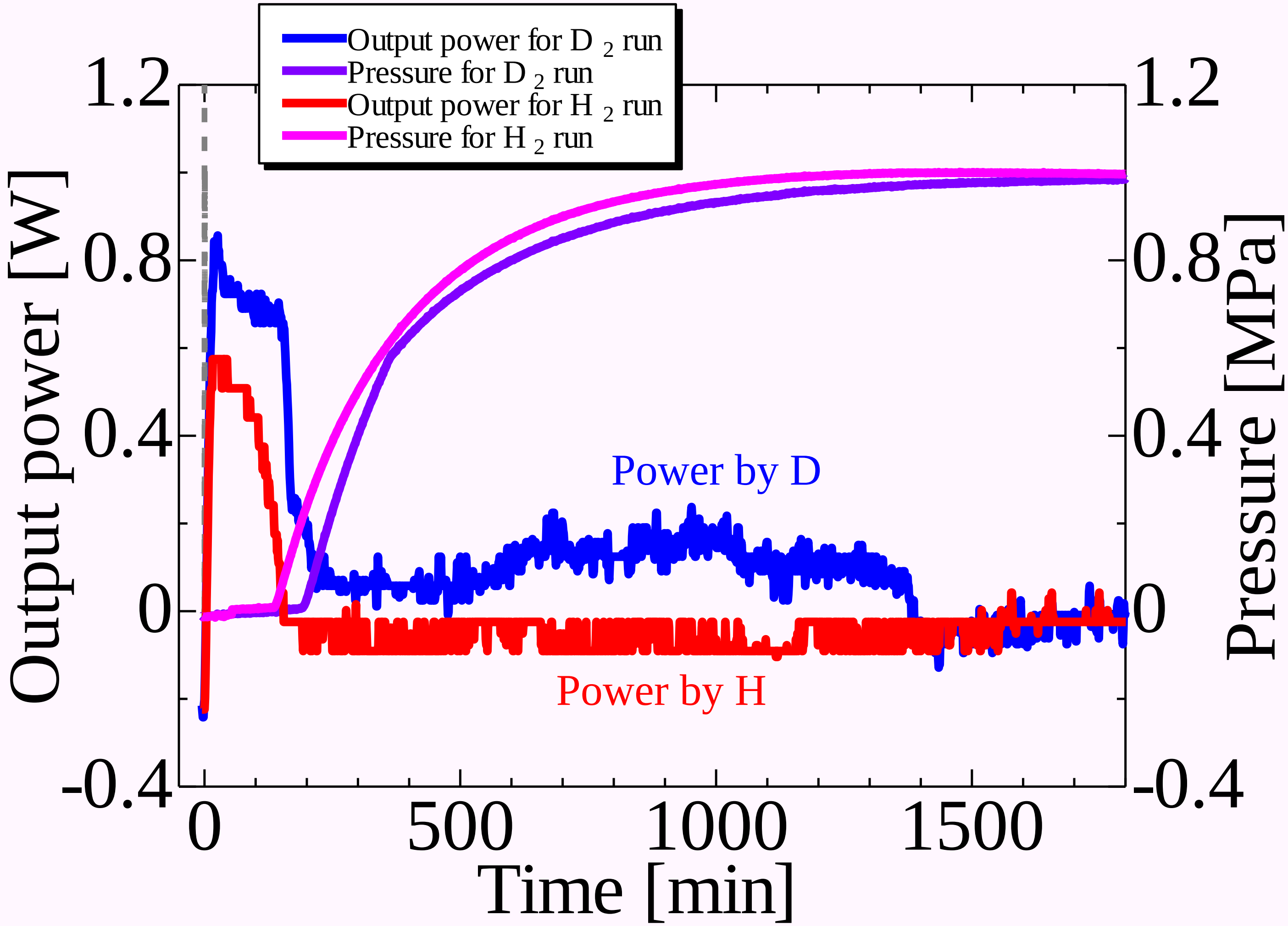


Fig.5B “Skirt-Fusion” zone における各燃料にたいする Nuclear fusion の発生特性の比較(after 300min)

Santoku 1#1

For 1st phase: 7.0 kJ by D and 3.6kJ by H; 3.4KJ net excess heat
For 2nd phase: 6.8kJ by D
Total Excess Heat = 10.2kJ → 3.4kJ/g-Pd



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: 7.7 g
- Observed Excess Heat

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

  3.79 (kJ/g-Pd)

(Anomalous heat by H

about 1 kJ/g inclusive)

→ Net Value ~ 2.8（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: 3.78 ± 0.30 (kJ/g-Pd)

S2: 2.77 ± 0.30

TEM Image of Used Pd/ZrO2 Sample

taken by R. Duncan 2009

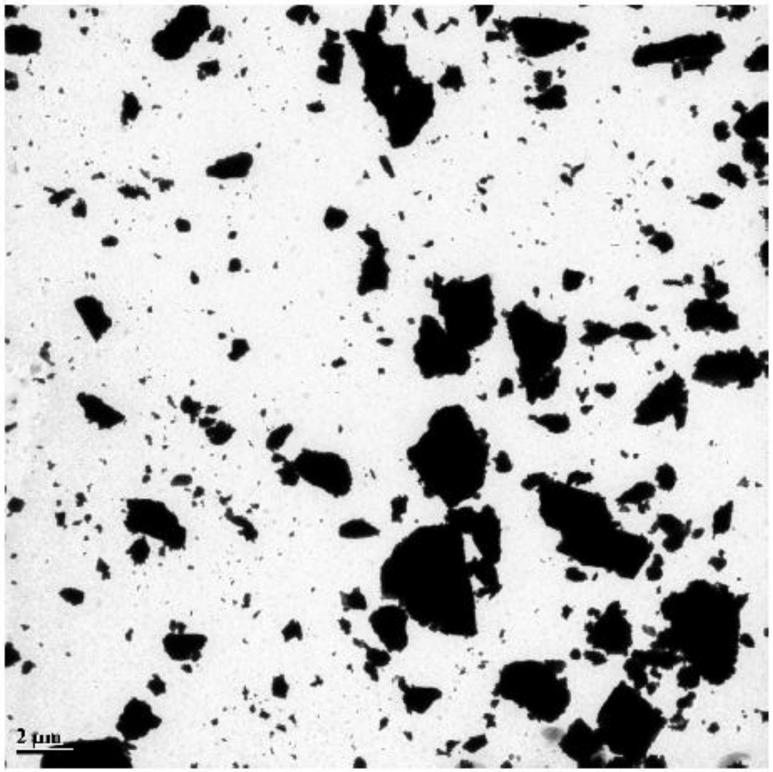


Image at 800 X magnification (scale size 2 µm)

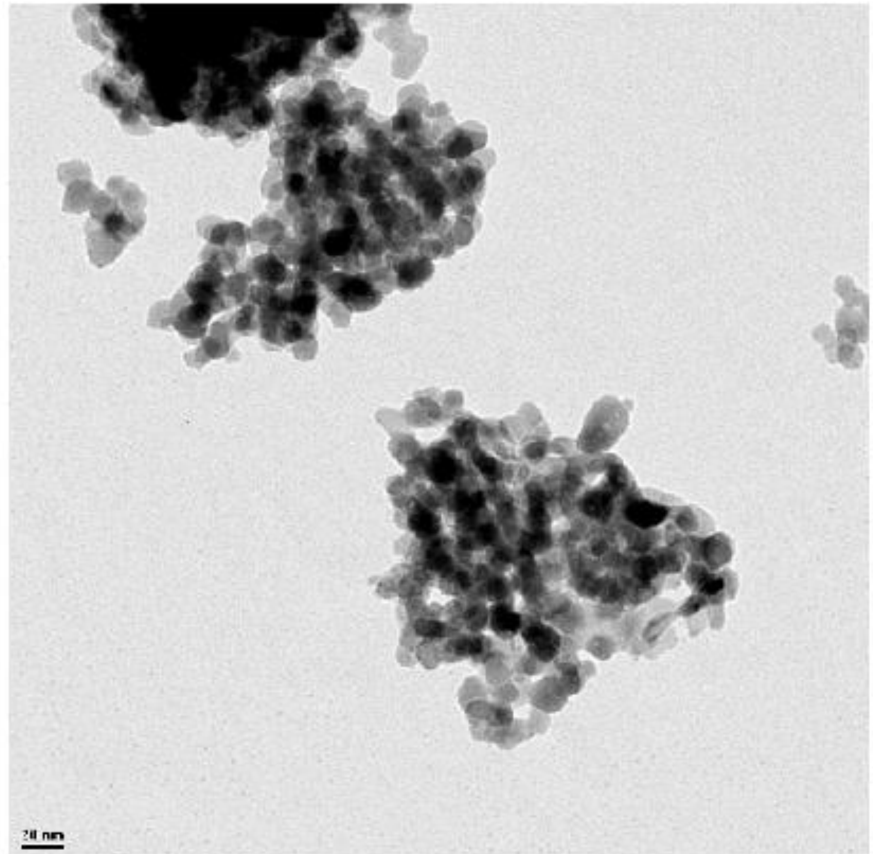
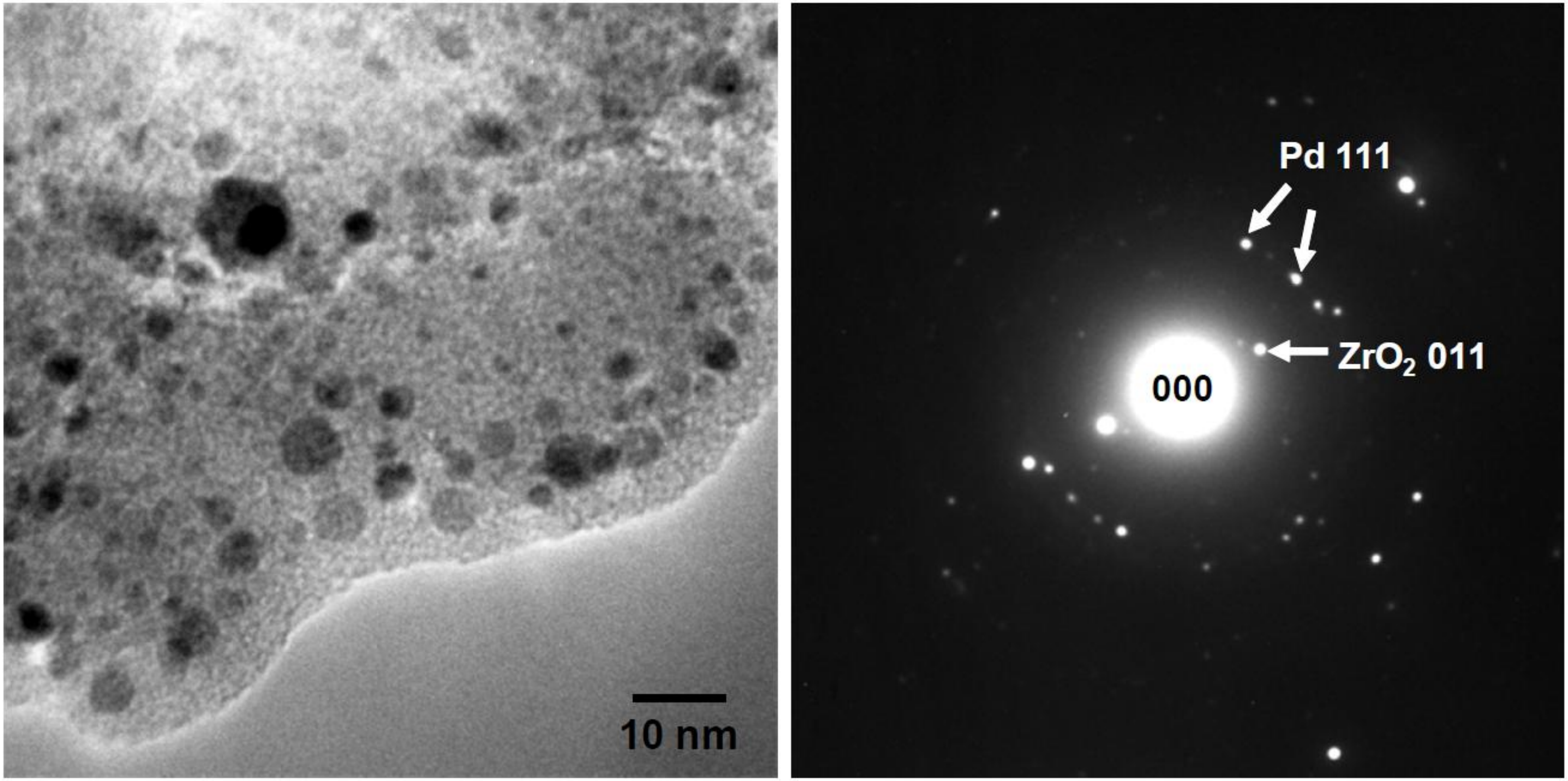


Image at 50000 X magnification (scale size 20 nm)

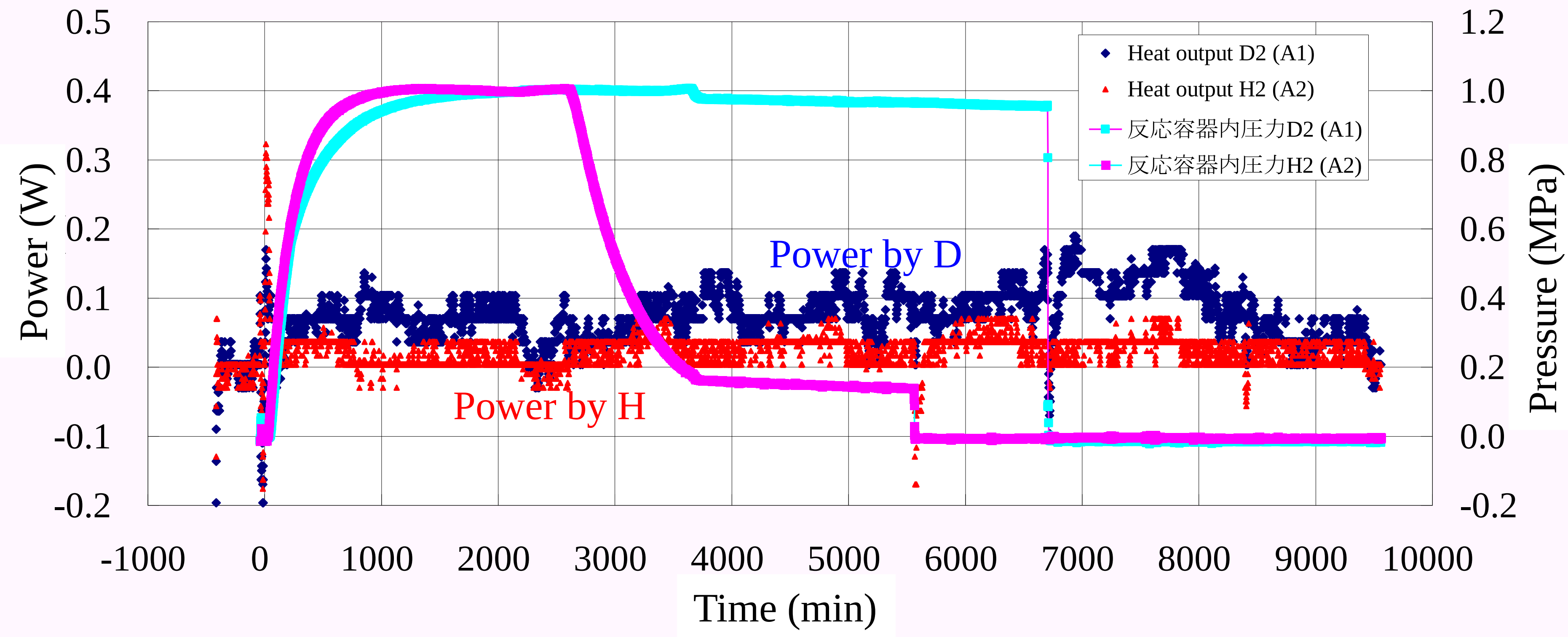
TEM Image of Pd/ZrO_2 Sample



Supplement Data 4 :Reuse of PZ Samples

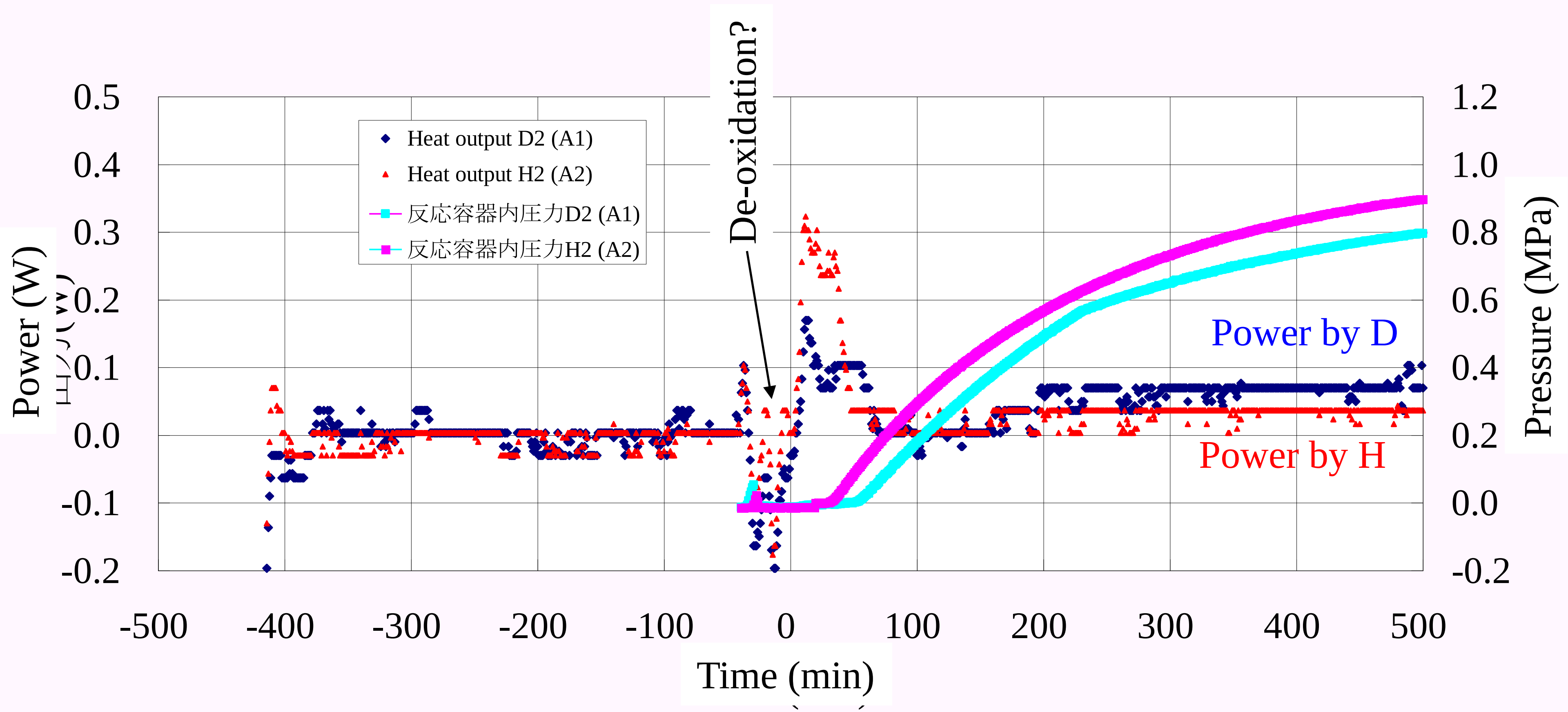
- #2, #3 Runs
- “Heat after Death?”

Reuse of Sample: Long Time Lasting Excess Heat by Run: Santoku **2#2**

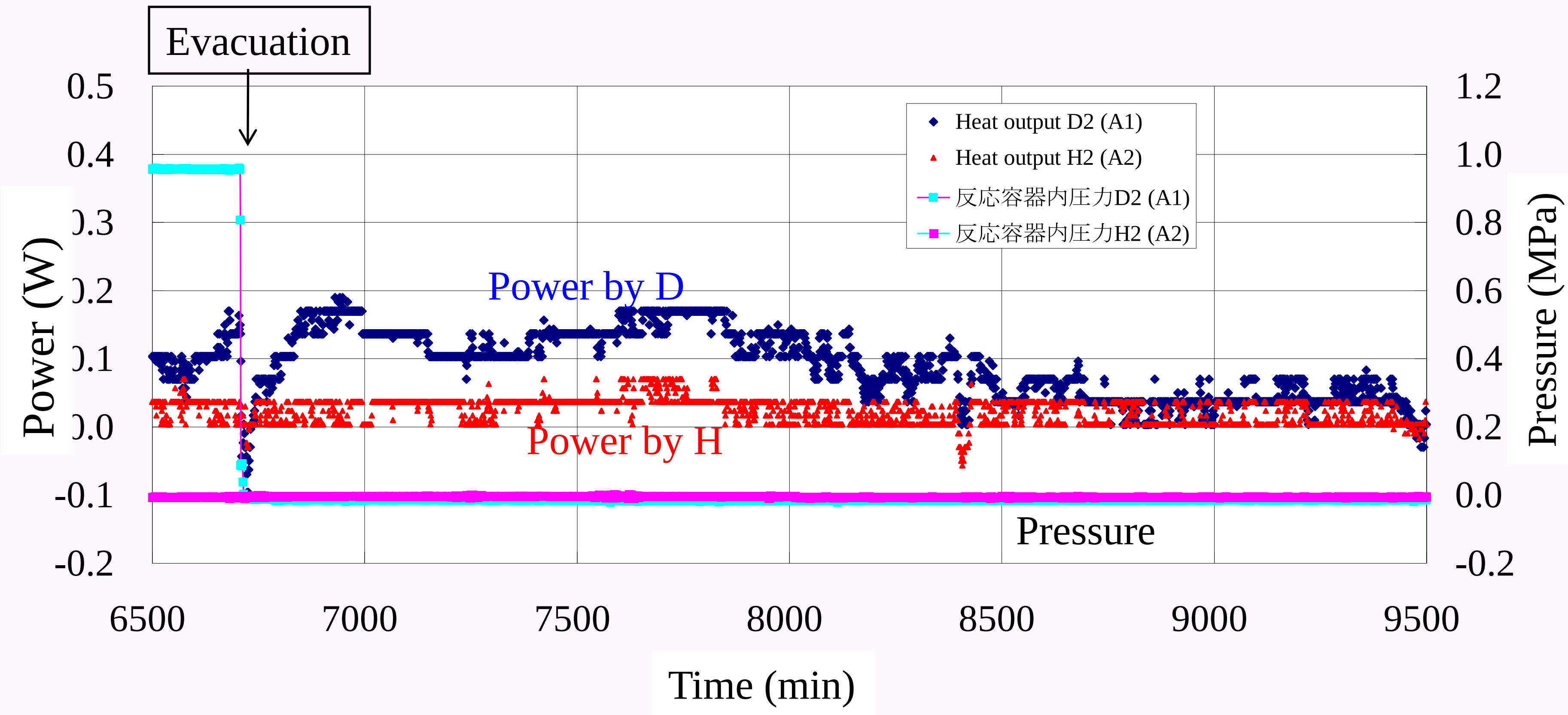


run	Gas	Measured flow rate [sccm]	1st phase [kJ]	2nd phase [kJ]	1st phase [J/g]	2nd phase [J/g]	D/Pd or H/Pd
D_2-2-2	D	3.87	0.17±0.03	9.89±1.48	40±7.0	2300±345	0.47
H_2-2-2	H	3.62	0.58±0.05	1.68±1.46	136±10.9	391±341	0.28

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



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

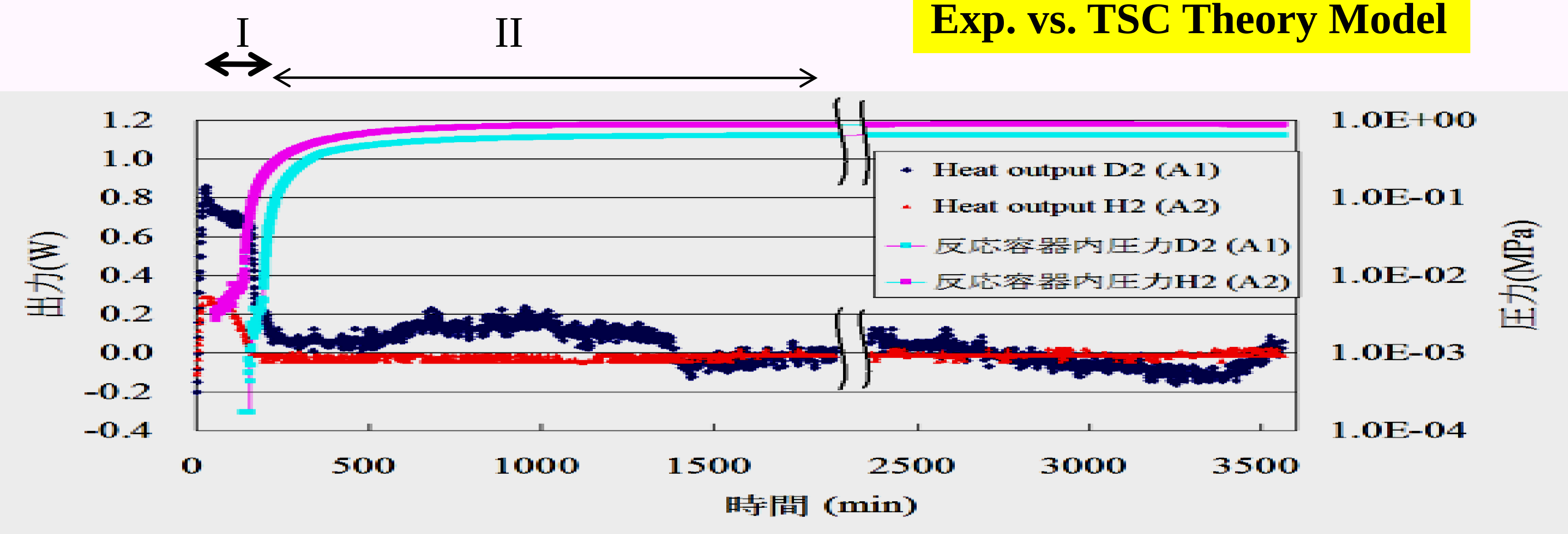


Is Evacuation STIMULUS?

Theoretical View

- Tetrahedral Symmetric Condensate
- 4D Fusion and Products

Exp. vs. TSC Theory Model



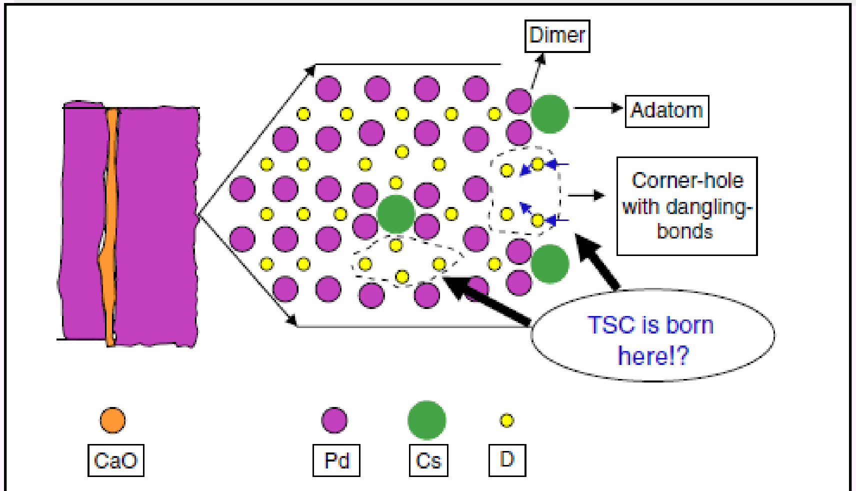
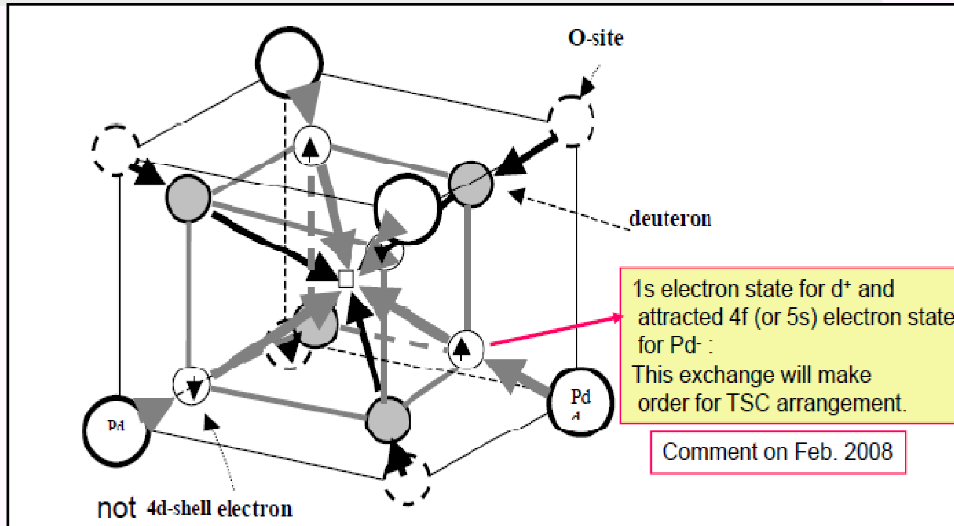


Figure 2. Image of Pd-complex surface.

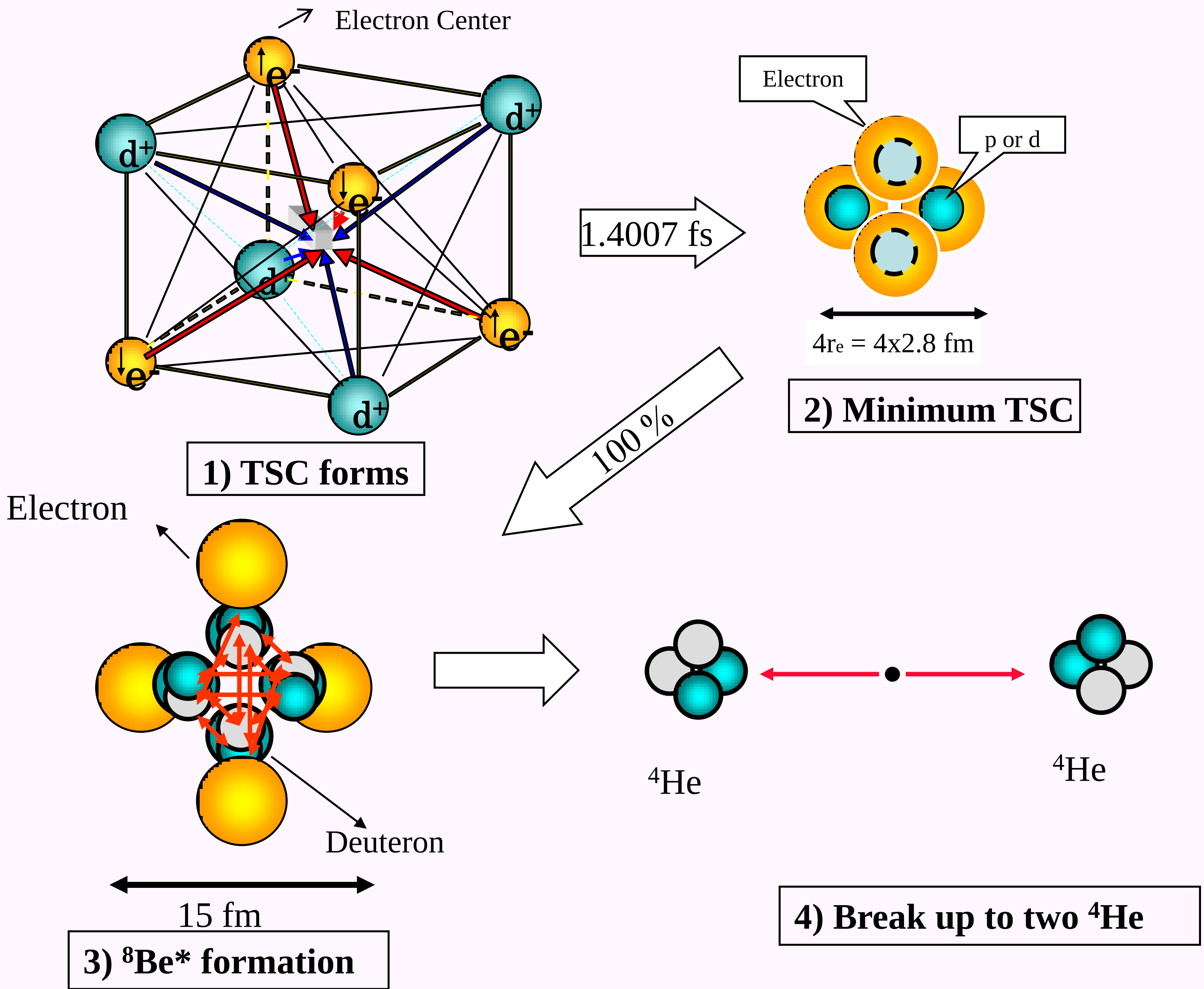


Model b) may correspond to **I.**

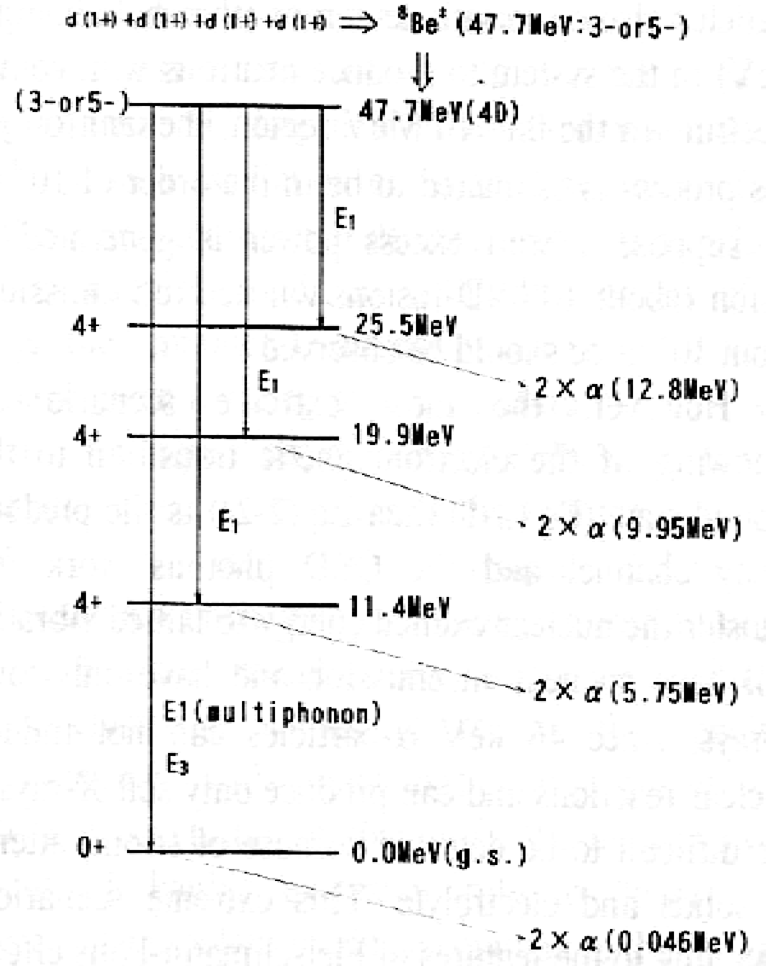
Model a) may correspond to **II.**

4D/TSC → ^{4}He + ^{4}He + 47.6MeV

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



After A. Takahashi, Trans. Fusion Technology 1994



.1: Typical decay channels of 4D fusion; E_1 transition may be induced with electromagnetic energy transfer via QED photons to lattice plasma oscillation. Major nuclear products are ^{4}He with specified kinetic energies.

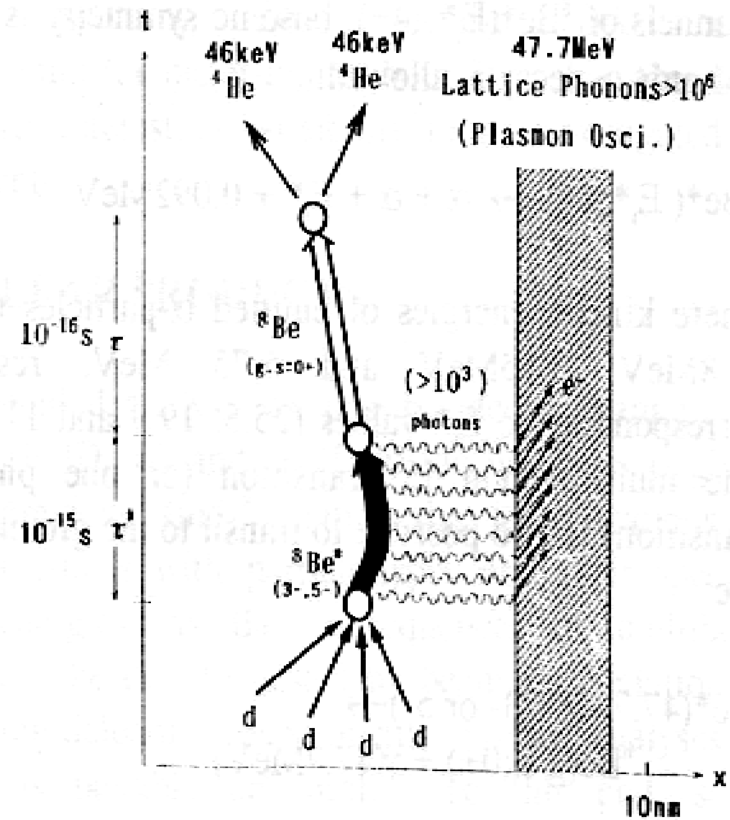


Fig.2: Illustration of extreme scenario of decay channel for 4D fusion; final nuclear products are 46 keV α-particles and most energy (47.7MeV) is transferred to lattice vibration via QED photons.

Channels for CP Generation by 4D

I. Symmetric Fragmentation

1) $4D \rightarrow {}^{8}Be^*(47.6MeV;0^+,0) \rightarrow$
${}^{4}He^*(Ex) + {}^{4}He^*(Ex) + 47.6MeV\text{-}2Ex$

- 1-1) Ex=0;

  ${}^{4}He^*(gs;0^+,0)$: $4D \rightarrow \alpha+\alpha+47.6MeV$; **$E_\alpha$=23.8MeV**

- 1-2) Ex=20.21MeV (1^{st} excited state of ${}^{4}He$);

  ${}^{4}He^*(20.21MeV;0^+,0)$ $\rightarrow$p(0.6-2.2MeV)+**t(1.8-3.4MeV)**

  + (Ex-19.815=0.4MeV) + (3.6MeV; moving ${}^{4}He^*$)

  ; this **triton** makes secondary d+t reaction to **emit 10-17MeV neutrons**

2) 4D $\rightarrow {}^{8}Be^{*} \rightarrow {}^{6}Li(E_x)$+d+(25.3MeV-$E_x$)

- Even parity states: Ex= 2.186MeV(3+,0), 3.563MeV(0+,1), 4.31MeV(2+,0), 5.31MeV(2+,1), 5.65MeV(1+,0), 15.8MeV(3+,0)

- 2-1) 4D$\rightarrow {}^{6}$Li(2.186)+d+23.11MeV

KE=5.77 KE=17.3

^{6}Li(2.186MeV):KE=5.77MeV:

$\rightarrow {}^{4}$He(3.6-4.1MeV) + d(1.6-2.4MeV)

CP Spectra by 4D/TSC; Predicted

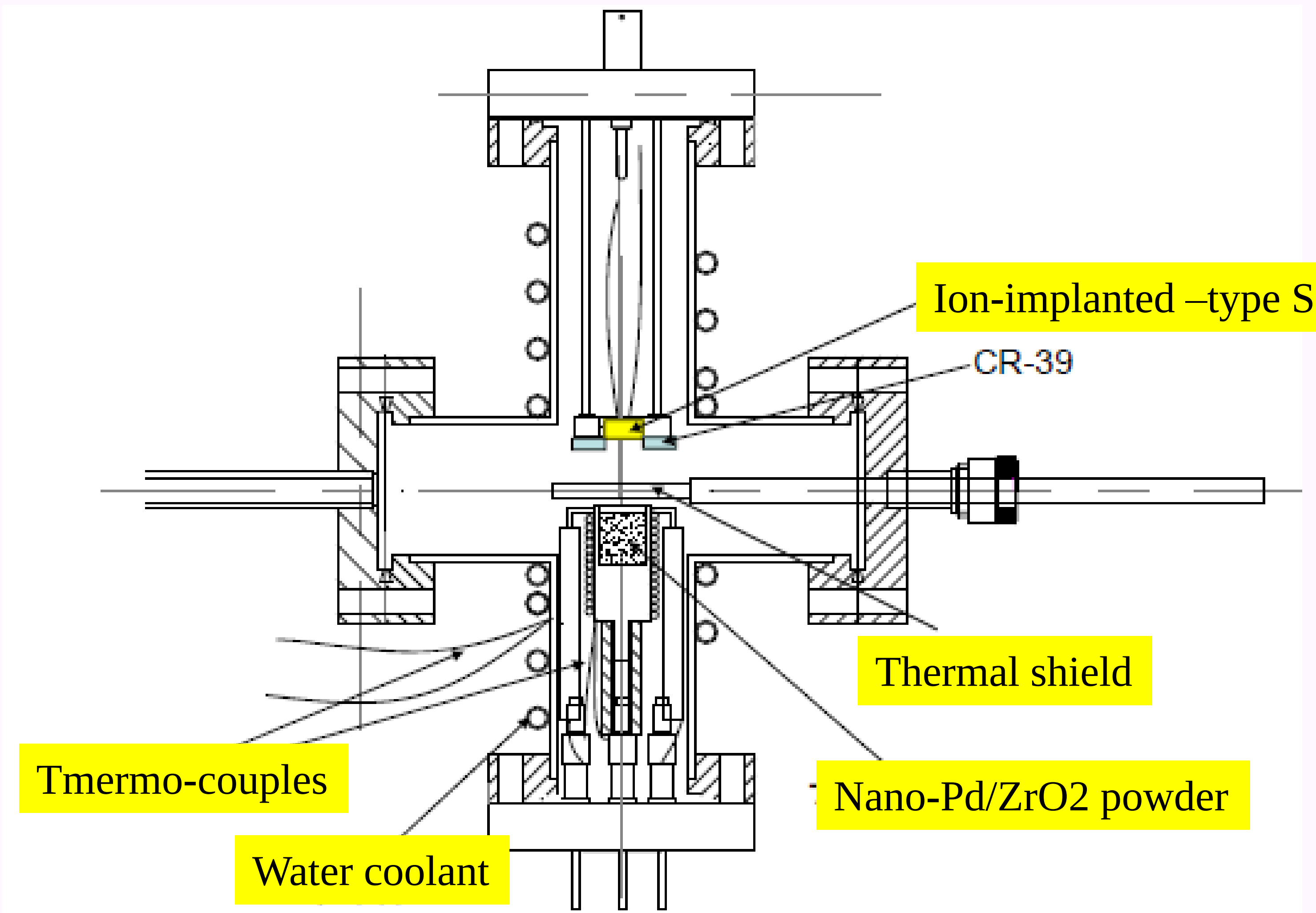
- ^{4}**He**: **0.046**, 1.52, **3.6-4.1, 2.9-4.3, 2.6-4.5, 2.1-4.6, 1.9-4.7, 4.0-5.6**, 5.75, **7.9**, 9.95, **11.9**, 12.8, **13.69, 23.8** (MeV)
- **Triton**: **1.8-3.4, 10.2-10.6** (MeV)
- **Deuteron**: **0.9, 1.6-2.4, 0.2-2.6, 1.9-3.6, 0.9-4.2, 1.1-4.4, 5.95, 8.0-11.1,15.9** (MeV)
- **Proton**: **0.6-2.2, 3.5-3.9** (MeV)

Purple values are by odd spin-parity of

^{8}Be*(Ex=47.6MeV)

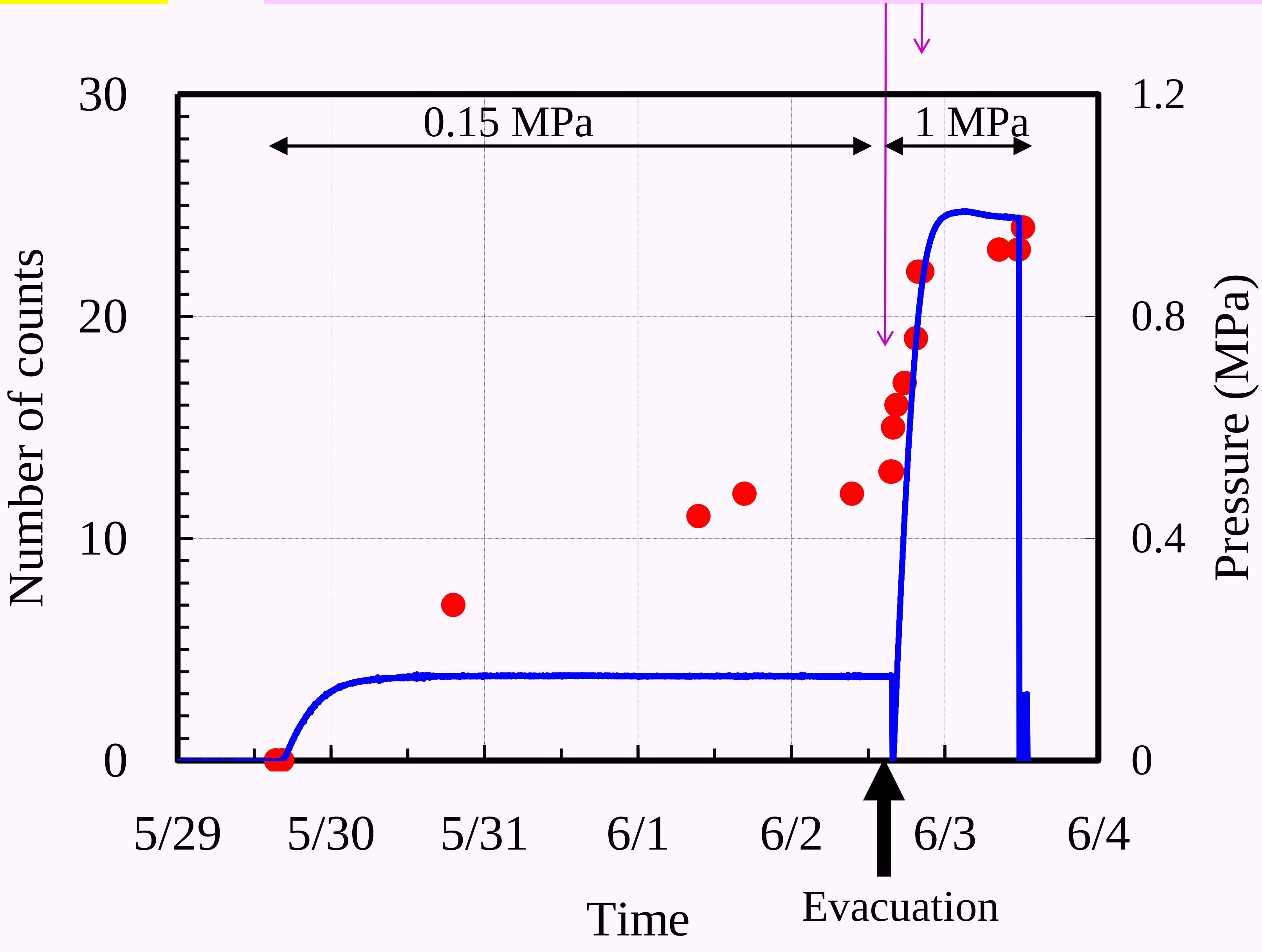
Others are S-wave Transitions

System-B Experiment
for Charged Particle Spectroscopy



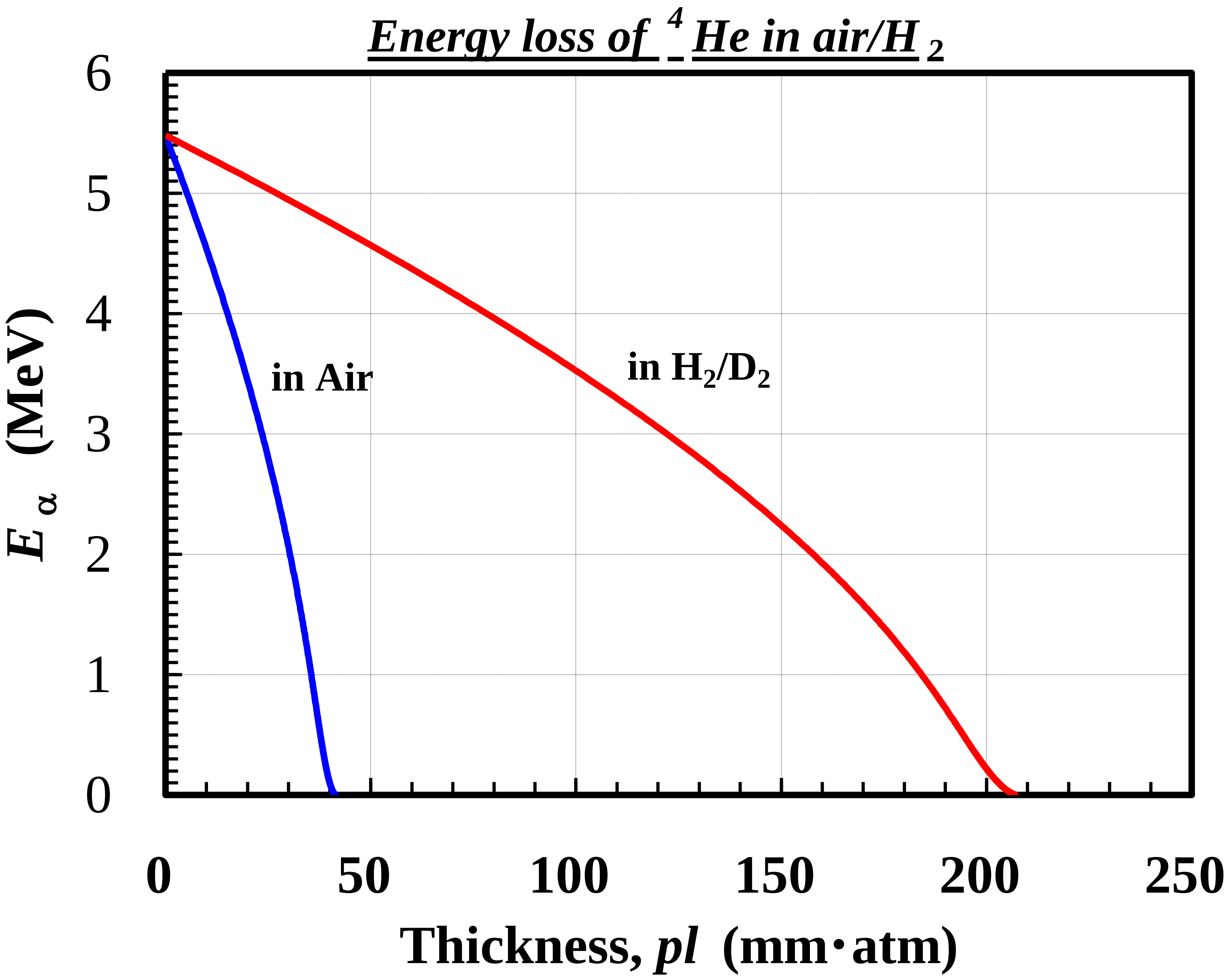
D-PZ1#3B Run1

Alphas of 5.75, 9.95, 12.8 MeV by minor branch of 4D fusion ?



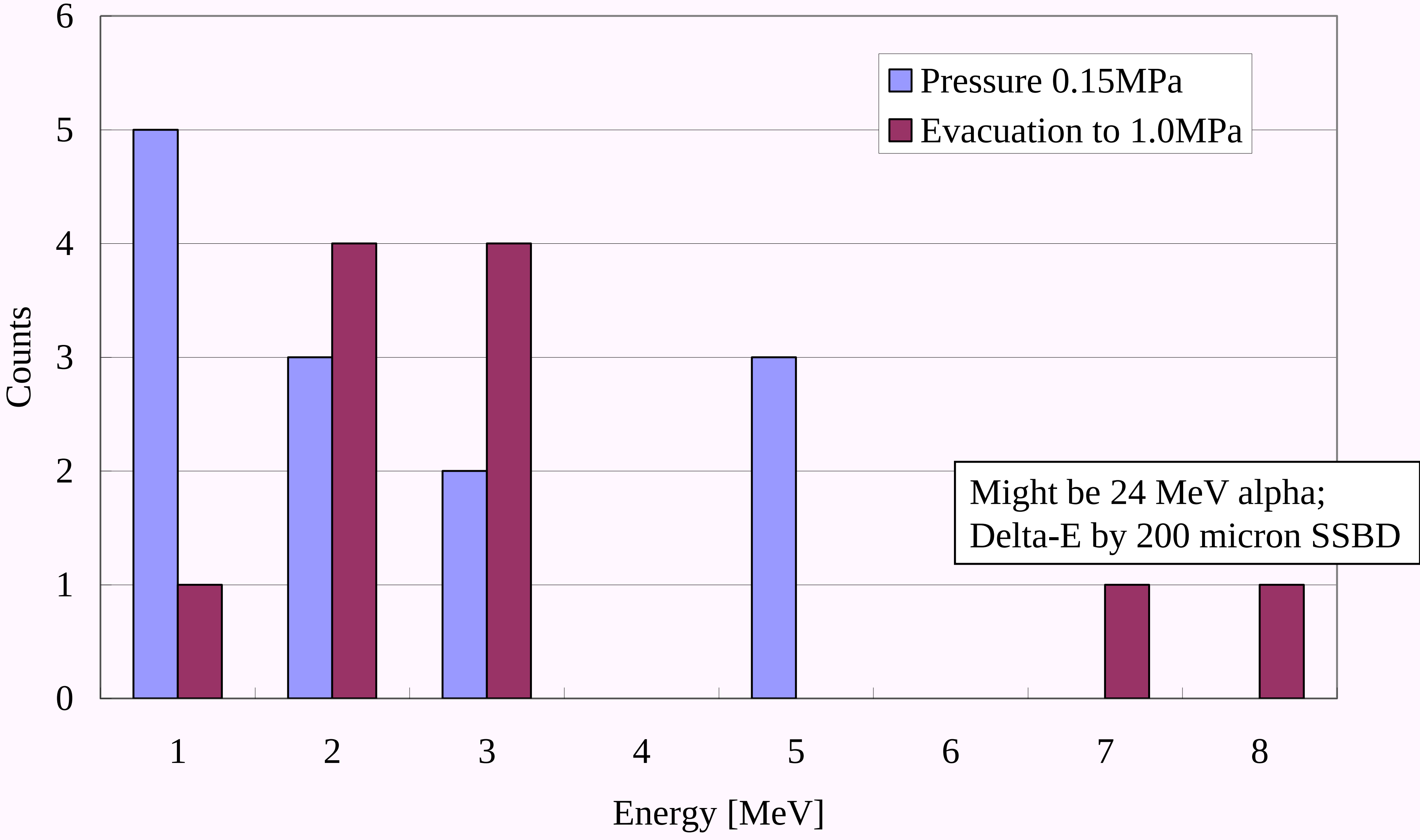
Evolution of total counts in “1-12 MeV “range of SSD detector, 5mm from sample

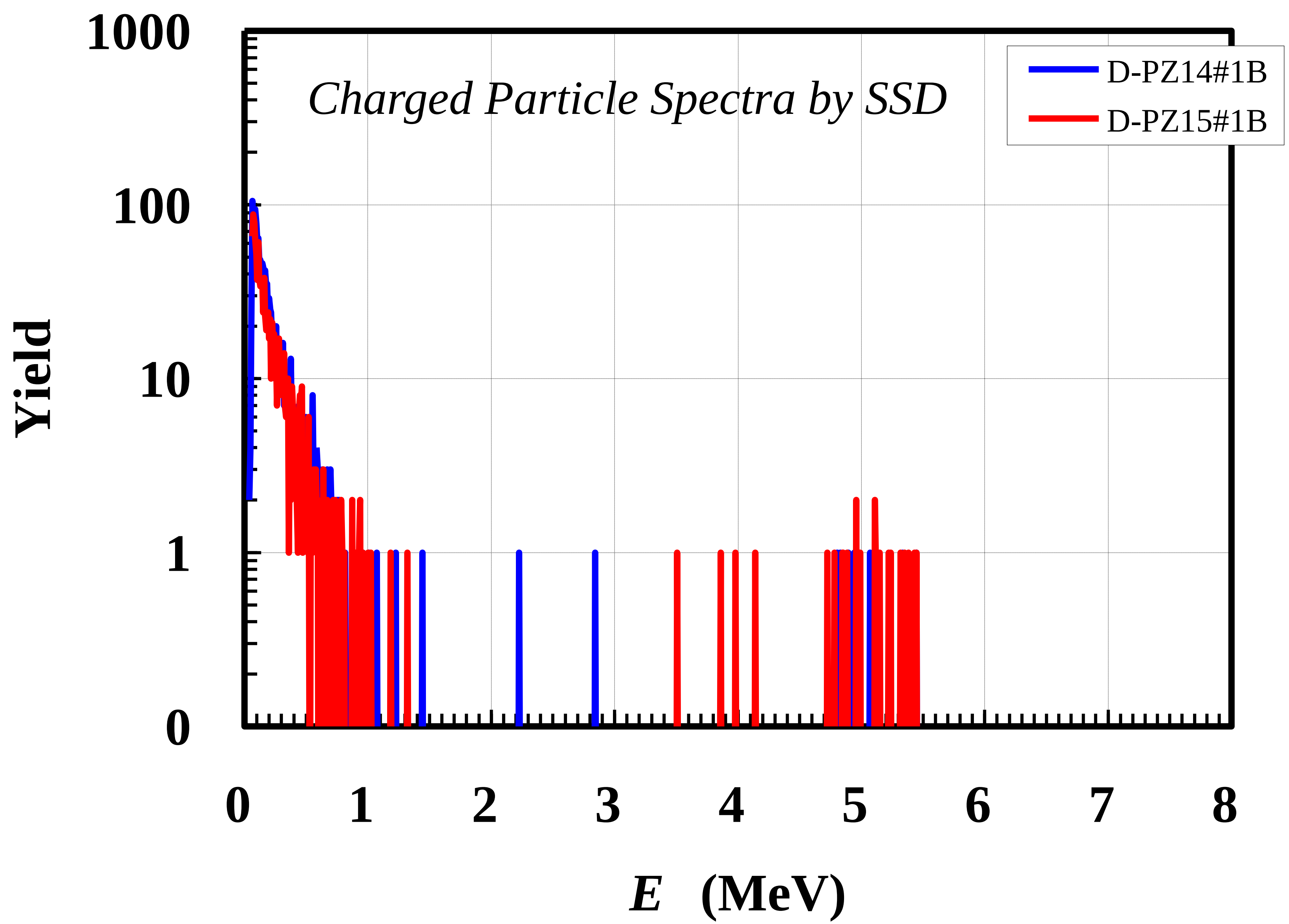
ICCF15



Energy loss of ^4He in air/H_2
E_α (MeV)
6
5
4
3
2
1
0
in Air
in H_2/D_2
0
50
100
150
200
250
Thickness, *pl* (mm·atm)

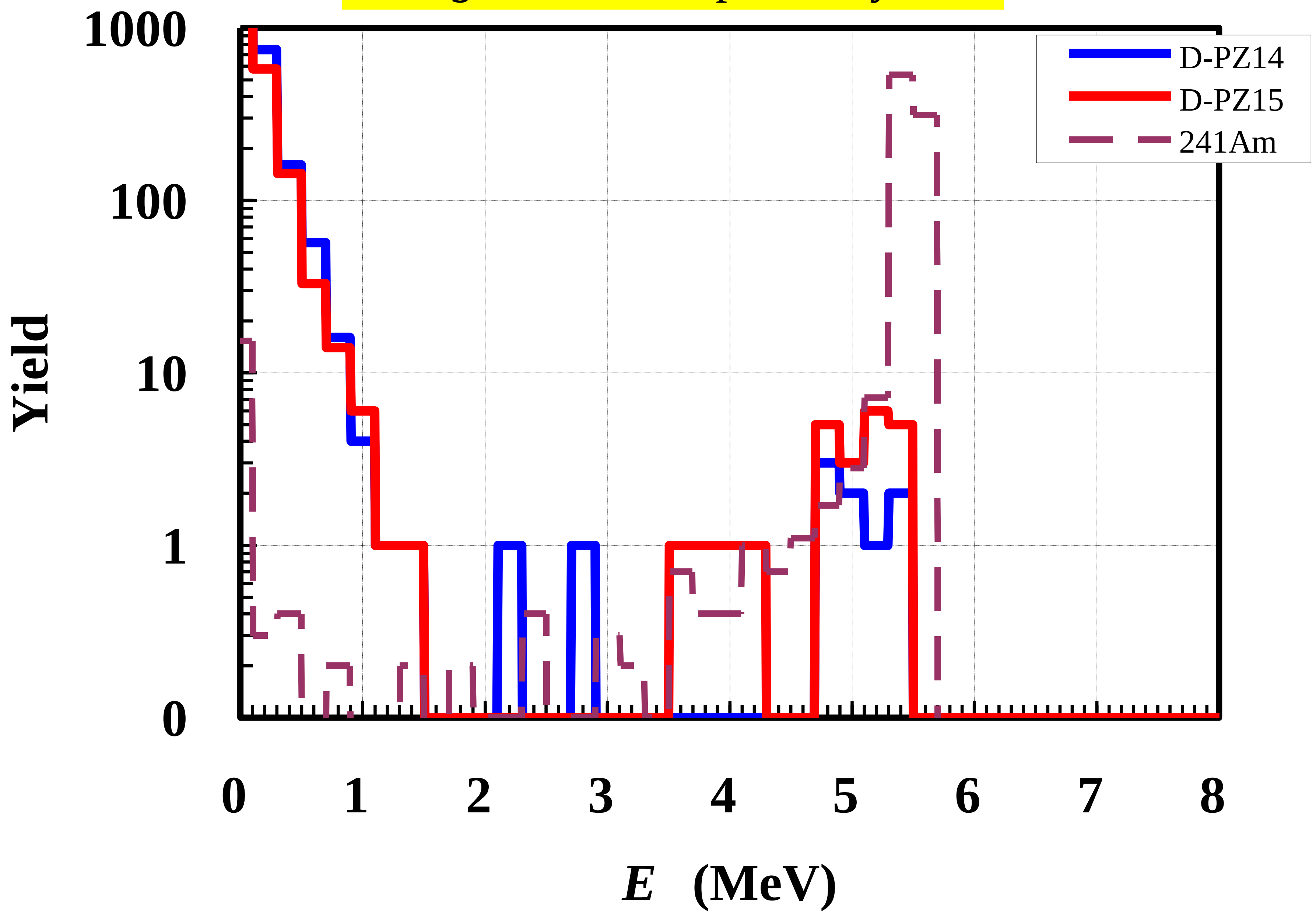
Charged Particle Spectra by SSBD (200 micron depletion layer) for D-PZ1#3B

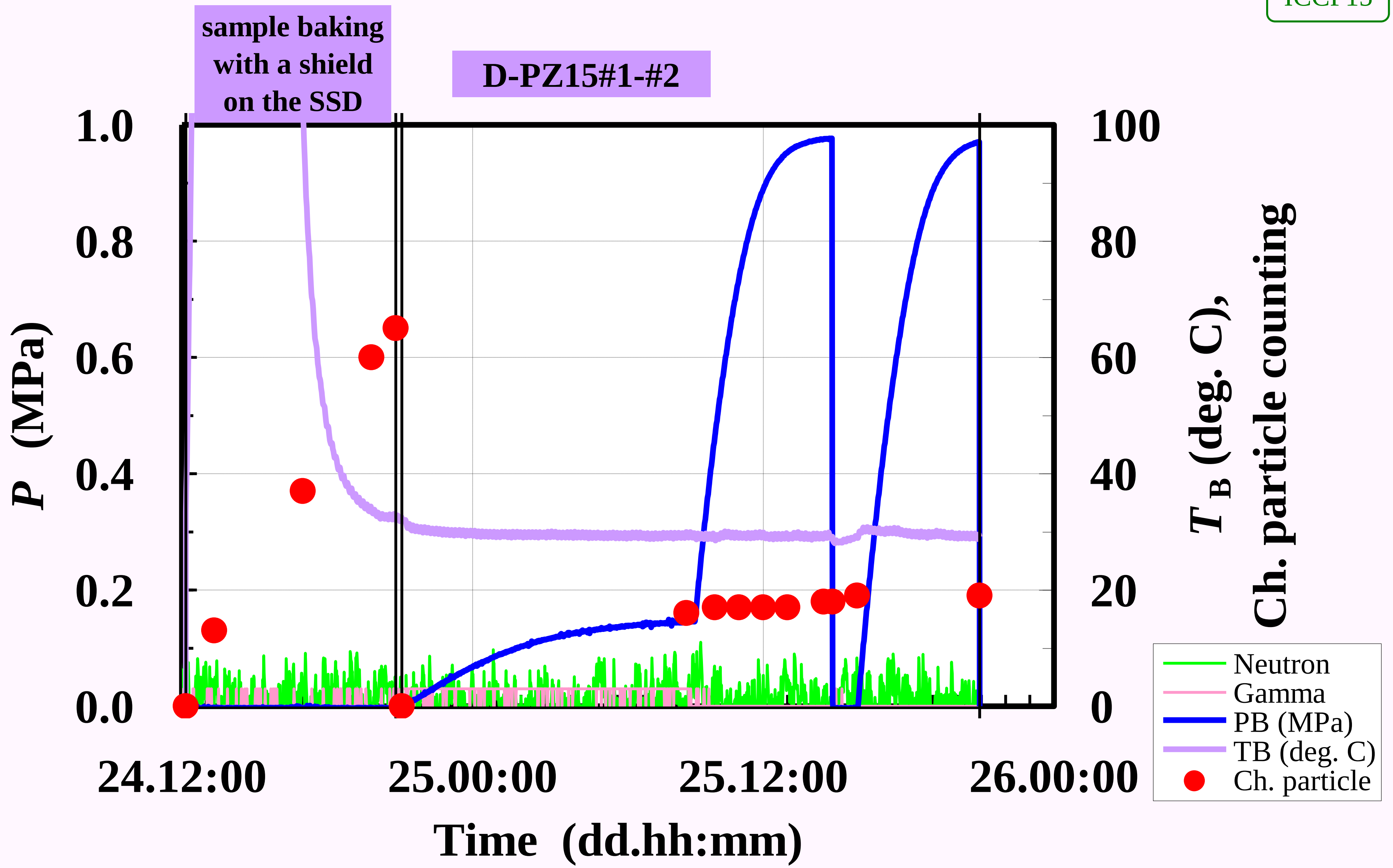



Charged Particle Spectra by SSD
D-PZ14#1B
D-PZ15#1B
1000
100
10
1
0
Yield
0
1
2
3
4
5
6
7
8
E (MeV)

Charged Particle Spectra by SSD

ICCF15




sample baking
with a shield
on the SSD
D-PZ15#1-#2
1.0
0.8
0.6
0.4
0.2
0.0
P (MPa)
100
80
60
40
20
0
T B (deg. C),
Ch. particle counting
24.12:00
25.00:00
25.12:00
26.00:00
Time (dd.hh:mm)
Neutron
Gamma
PB (MPa)
TB (deg. C)
Ch. particle