Hydrogen Isotope Gas Absorption/Adsorption Characteristics of Pd Nanopowders

A. Kitamura, Y. Miyoshi, H. Sakoh, A. Taniike
(Division of Marine Engineering,
Graduate School of Maritime Sciences, Kobe University)
A.Takahashi, R. Seto, and Y. Fujita
(Technova Inc)

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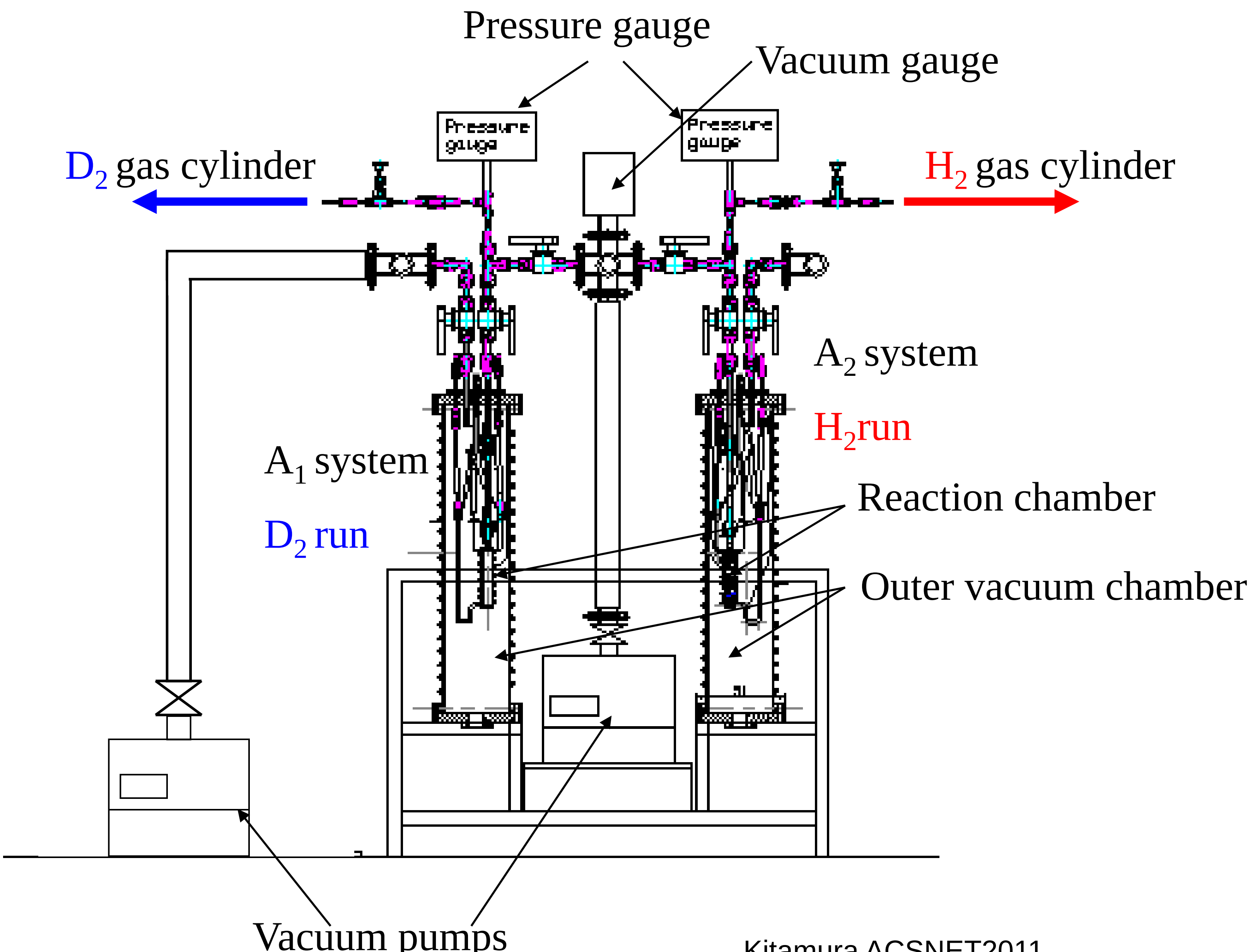
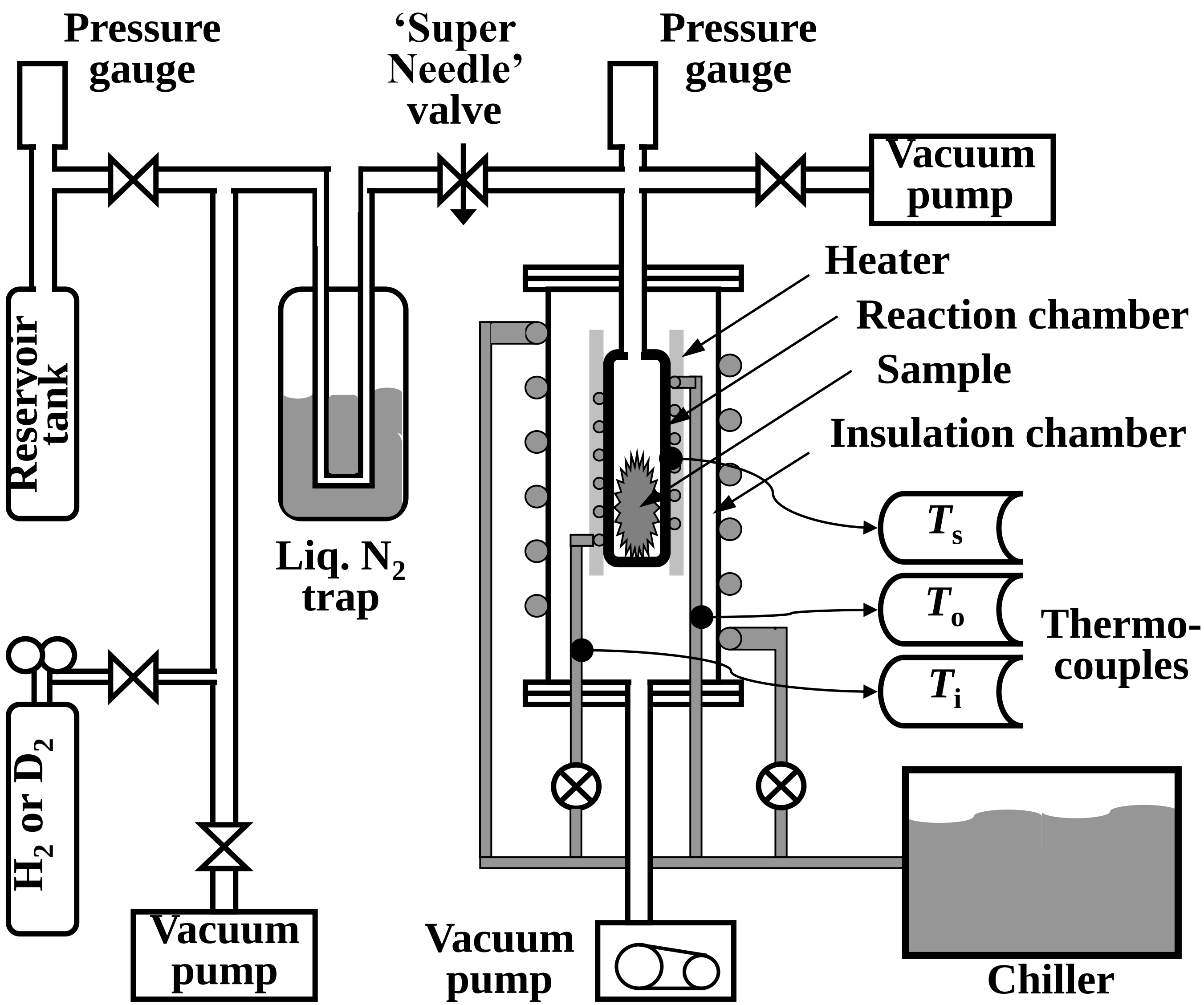
Outline

- Extensive measurements of heat release under hydrogen isotope absorption/adsorption of 7 kinds (PP, PB, PZ, NZ, PNZ-I,PNZ-II, PNZ2B) of Pd nano-powders in a twin gas charging system have been made by Kobe group in 2010-2011.
- Anomalies in heat and D(H)-absorption observed by Pd (and Pd-Ni) nano-powders dispersed into/onto ZrO_2 support are briefly overviewed.
- **Heat and absorption data for larger Pure Pd powder and Pd-Black are shown in concentration in the present report.**

A1･A2 twin system for simultaneous D2/H2 absorption experiments.



Schematic of one of the twin absorption system.

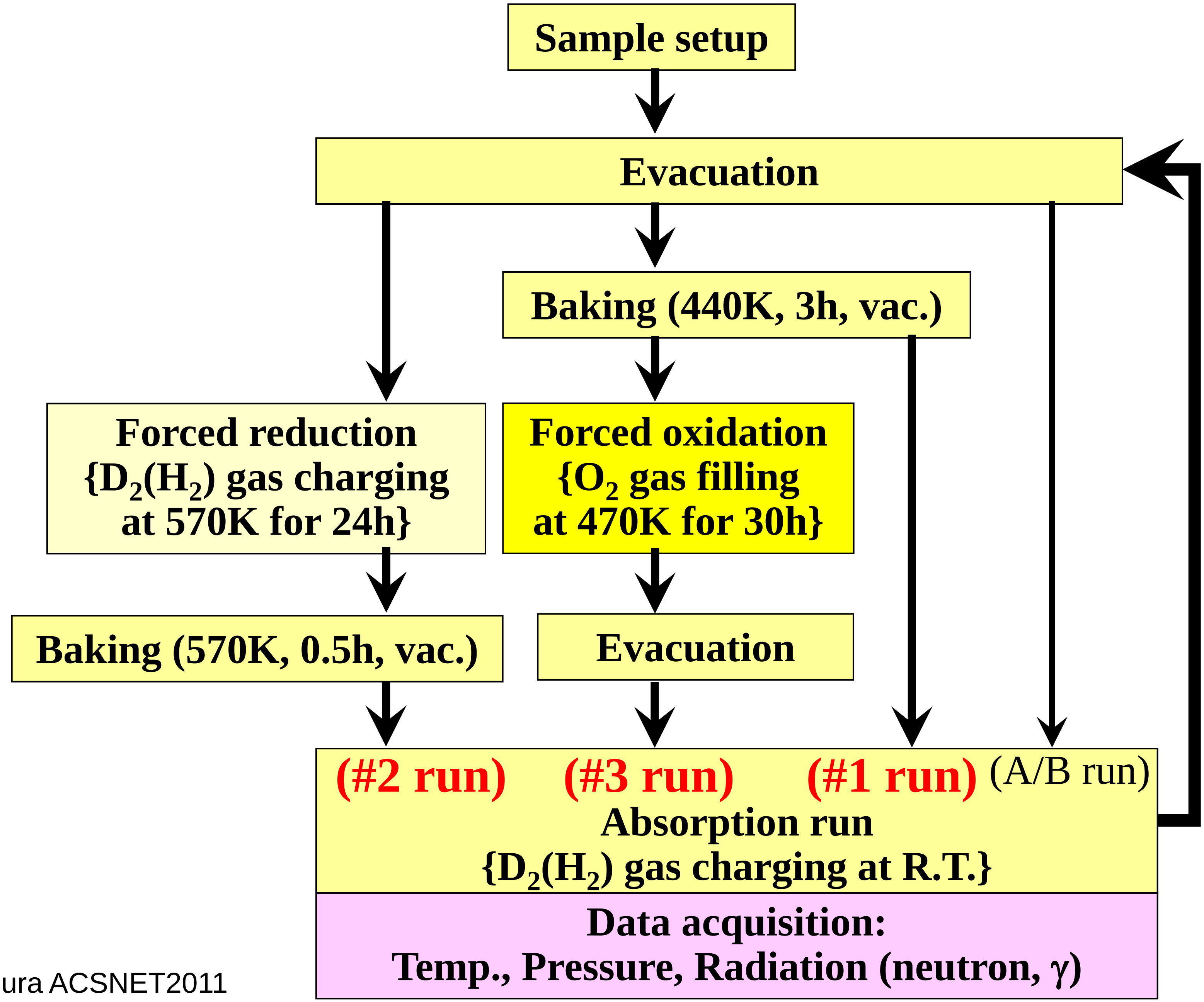


Samples tested: 7 kinds

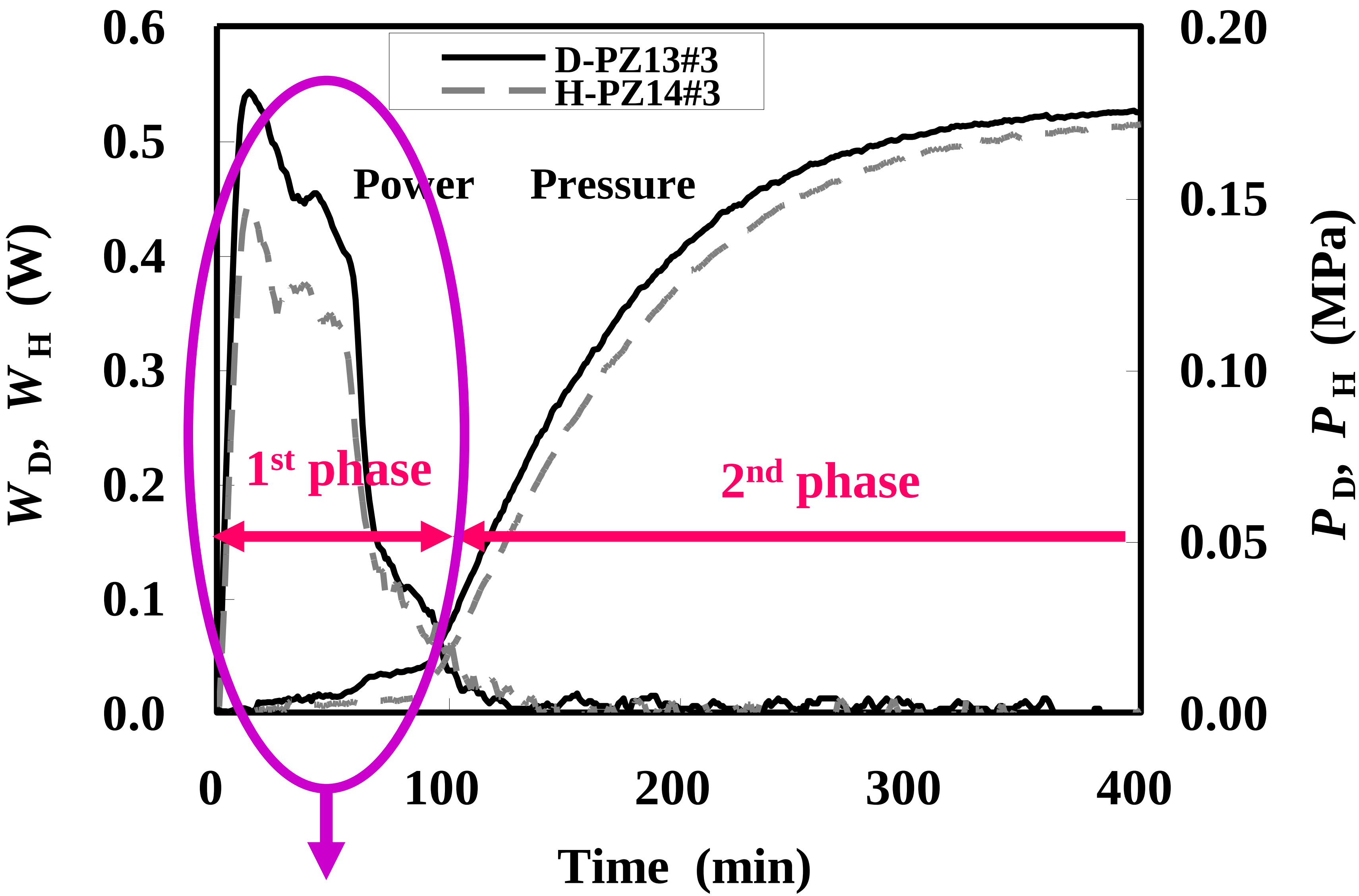
	Pd	Ni	Zr	O	Supplier	Remarks
100nmf -Pd **PP**	99.5%, 100nmf	---	---	---	Nilaco Corp.	[1],[2], **this report**
Pd-black **PB**	99.9%, 300mesh	---	---	---	Nilaco Corp.	[1],[2], **this report**
mixed oxide **PZ**	0.312	---	0.688	(1.69)	Santoku Corp.	[1],[2],[3], ICCF16, ACS2011
mixed oxide **NZ**	---	0.467	0.533	(1.53)	Santoku Corp.	[2]
mixed oxide **PNZ**	0.080	0.352	0.568	(1.57)	Santoku Corp.	[2]
mixed oxide **PNZII**	0.023	0.891	0.292	(1.50)	Santoku Corp.	
mixed oxide **PNZ2B**	0.04	0.29	0.67	(1.67)	Dr. B. Ahern	ICCF16, ACS2011

[1] Phys. Lett. A, 373 (2009) 3109-3112.
[2] ***Low Eergy Nuclear Reactions***, (AIP Conf. Proc. 1273, ed. Jan Marwan, 2010) to be changed to JCMNS4, 2011.
[3] ***LENR Source Book 3***, (ed. Jan Marwan, ACS) to be published.

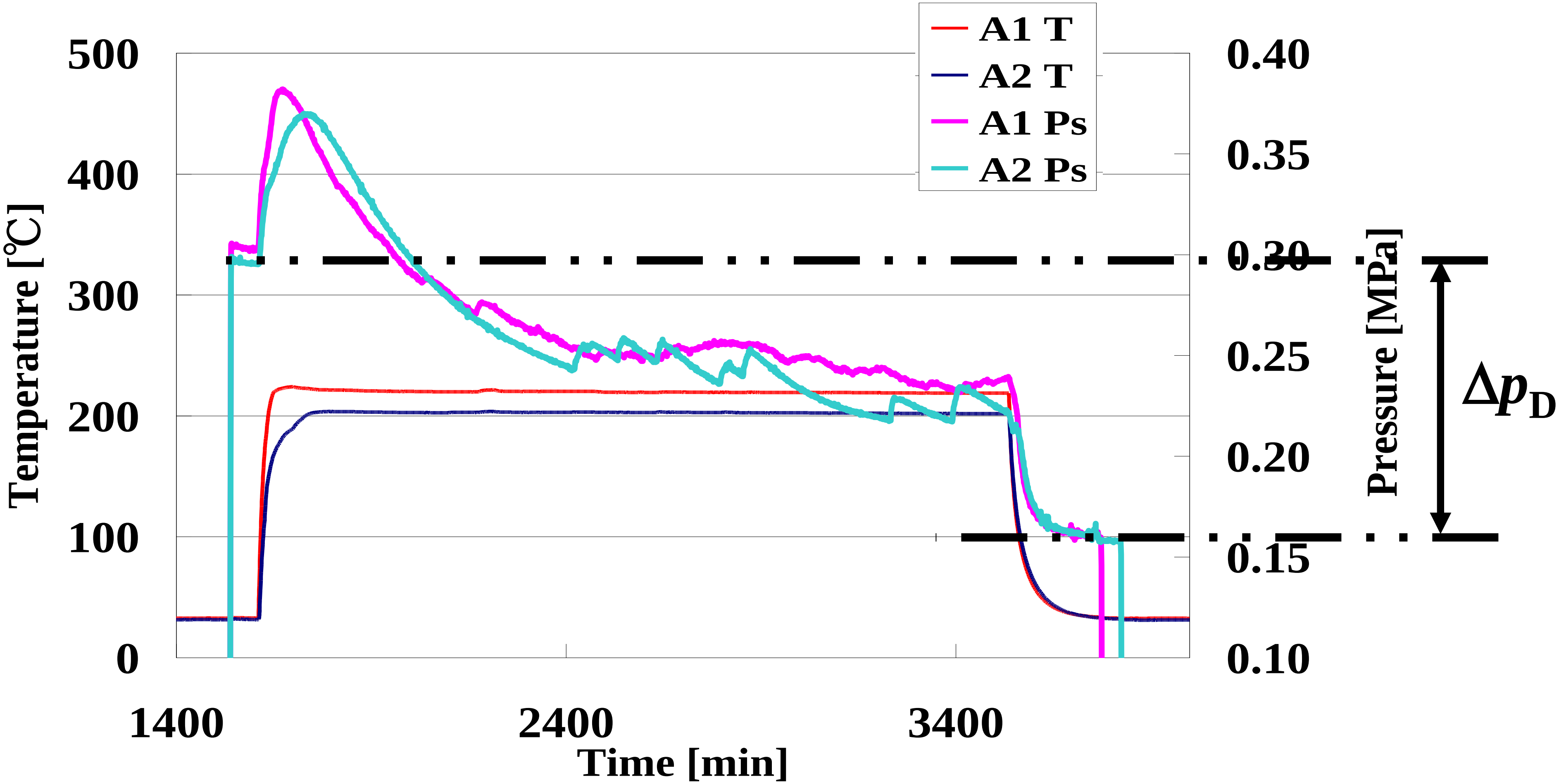
Experimental procedure



Heat Evolution appeared in Two Phases: for PZ Samples



Integration gives the 1st phase specific output energy E_1.



by introducing O_2 gas at a pressure of 0.2 MPa and a temperature of 470 K for 30 hours. The pressure difference Δp_D is used to calculate the degree of oxidization, x for $Pd+(x/2)\cdot O_2 \rightarrow PdO_x$

PZ11-14 sample (Pd:31.2% Zr:68.8%)

PZ11,12#3run

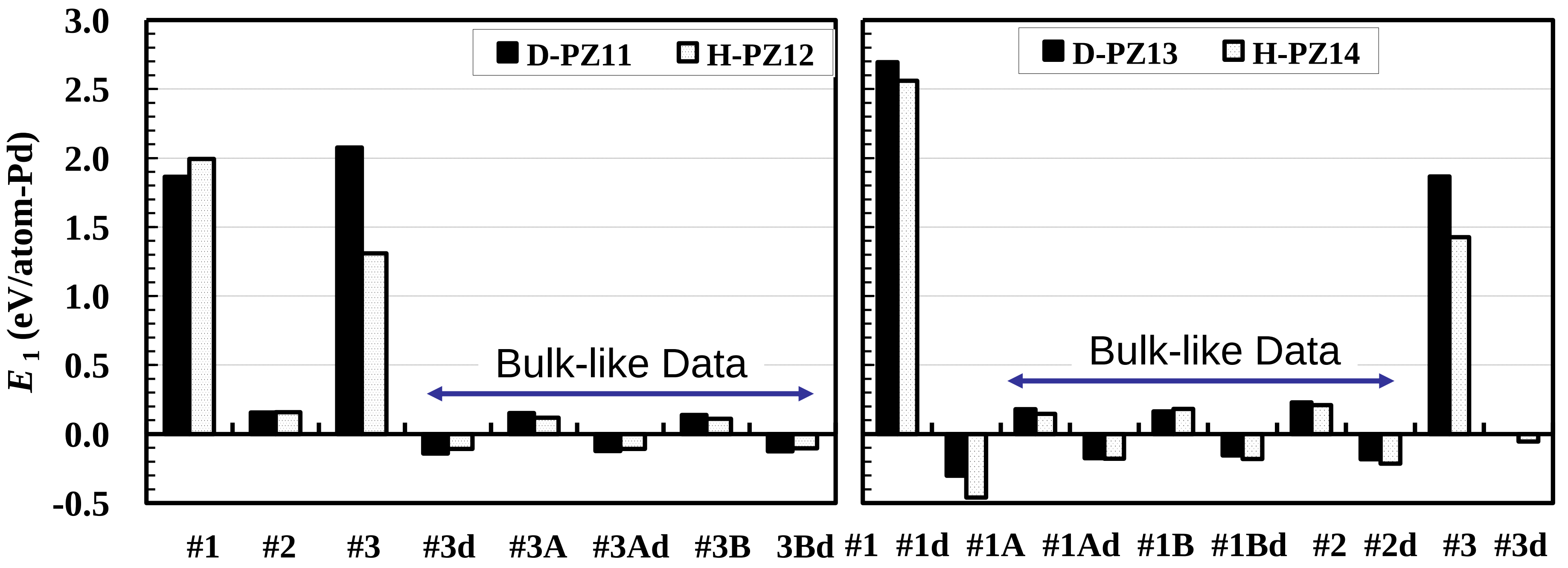
PdO/Pd(D2) : 0.086

PdO/Pd(H2) : 0.054

PZ13,14#3run

PdO/Pd(D2) : 0.073

PdO/Pd(H2) : 0.061



Comparison of the 1st-phase specific output energy E_1 for the runs D(H)-PZ11(12)#1 through D(H)-PZ13(14)#3Bd

PZ11-14 sample (Pd:31.2% Zr:68.8%)

PZ11,12#3run

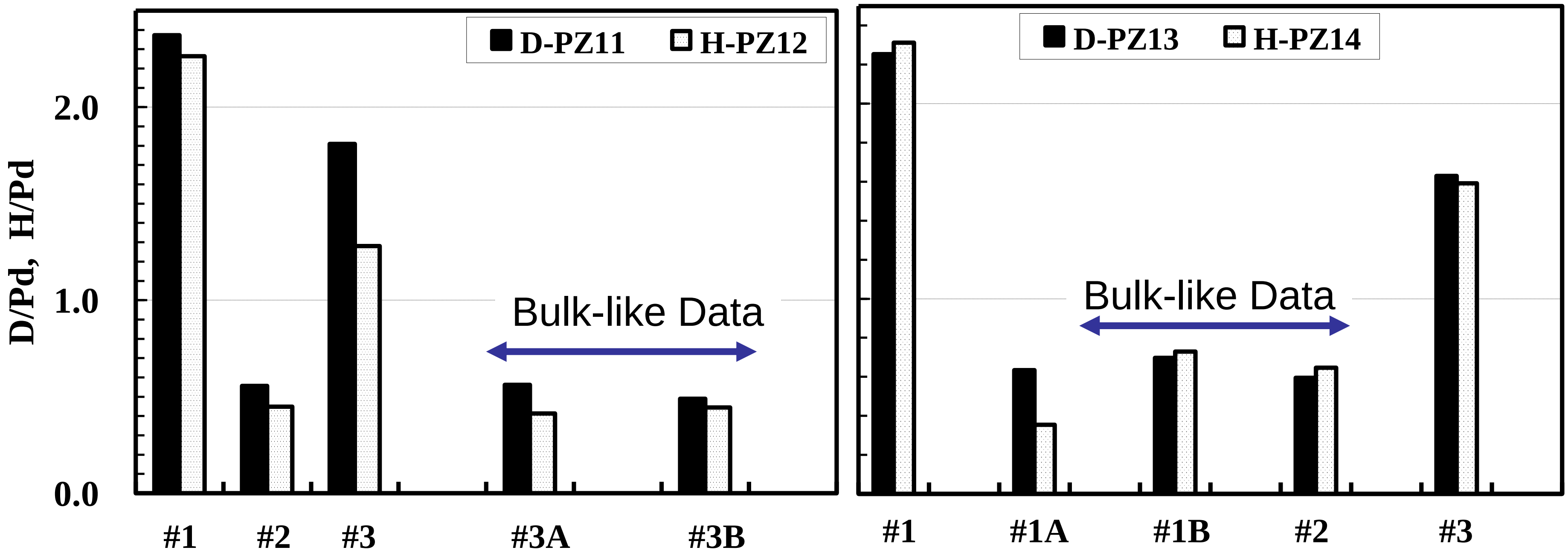
PdO/Pd(D2) : 0.086

PdO/Pd(H2) : 0.054

PZ13,14#3run

PdO/Pd(D2) : 0.073

PdO/Pd(H2) : 0.061



Comparison of the loading ratio D(H)/Pd for the runs D(H)-PZ11(12)#1 through D(H)-PZ13(14)#3Bd

PZ11-14 sample (Pd:31.2% Zr:68.8%)

PZ11,12#3run

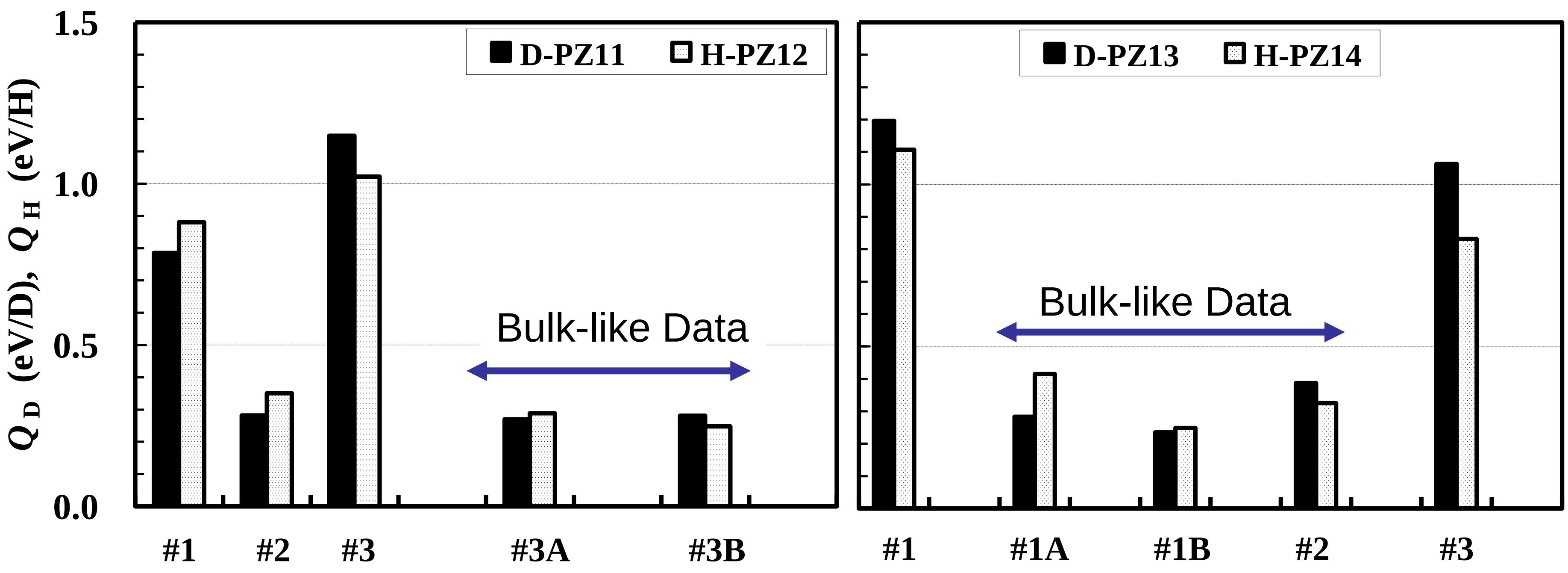
PdO/Pd(D2) : 0.086

PdO/Pd(H2) : 0.054

PZ13,14#3run

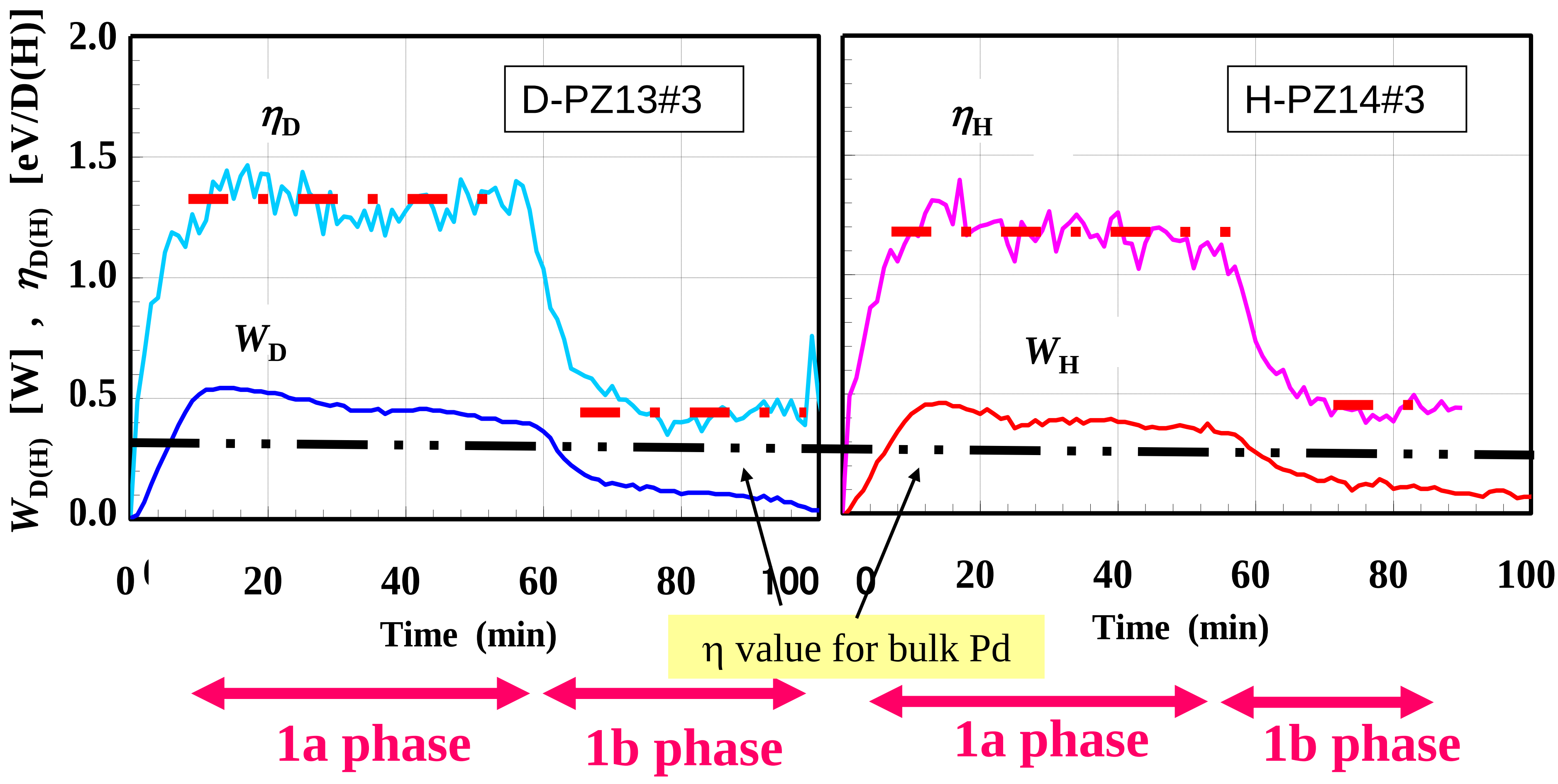
PdO/Pd(D2) : 0.073

PdO/Pd(H2) : 0.061



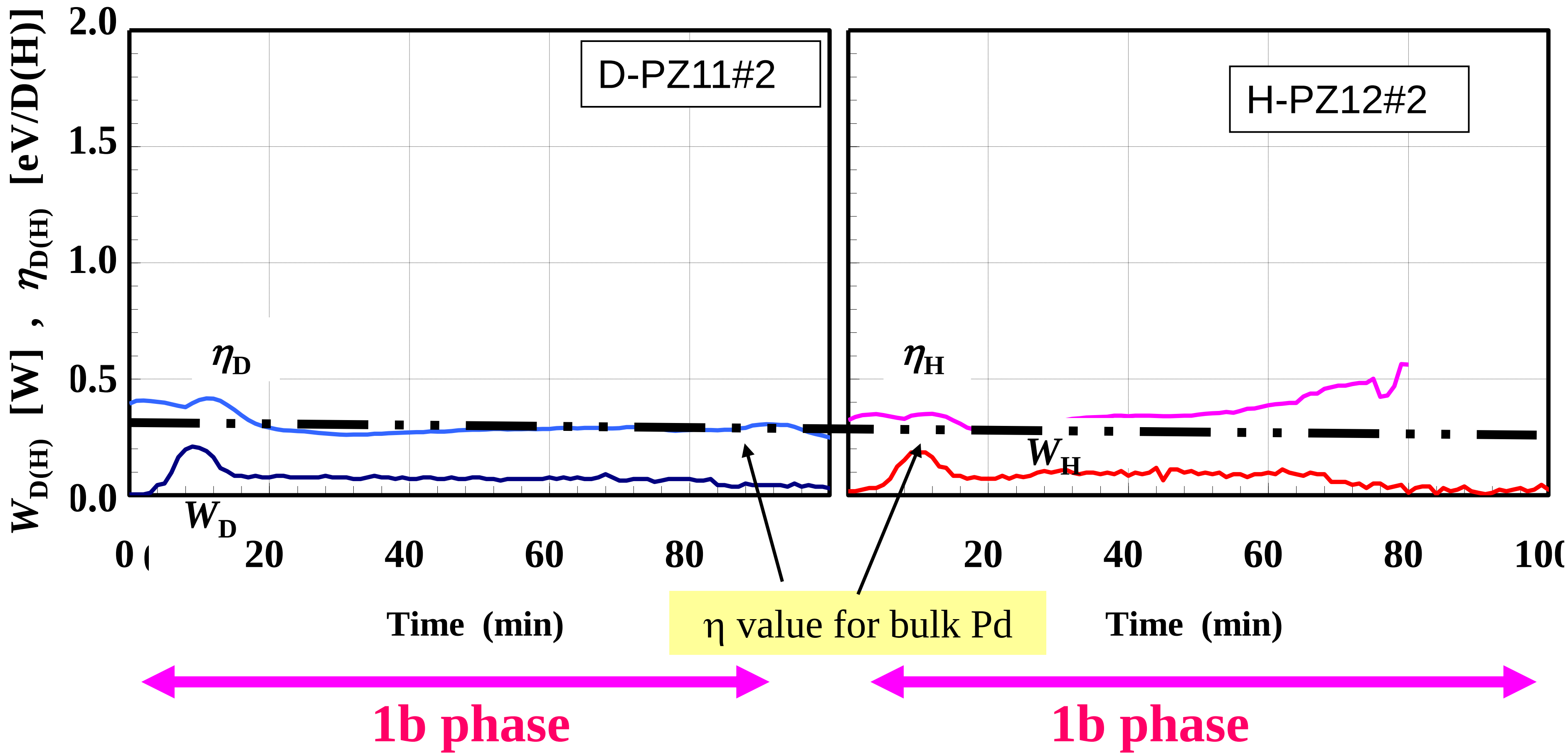
Comparison of the hydridation energy $Q_{D(H)}$ for the runs D(H)-PZ11(12)#1 through D(H)-PZ13(14)#3Bd

Dynamic D(H)-Sorption Energy observed for PZ Samples:
Larger for D-sorption in the Ia Phases



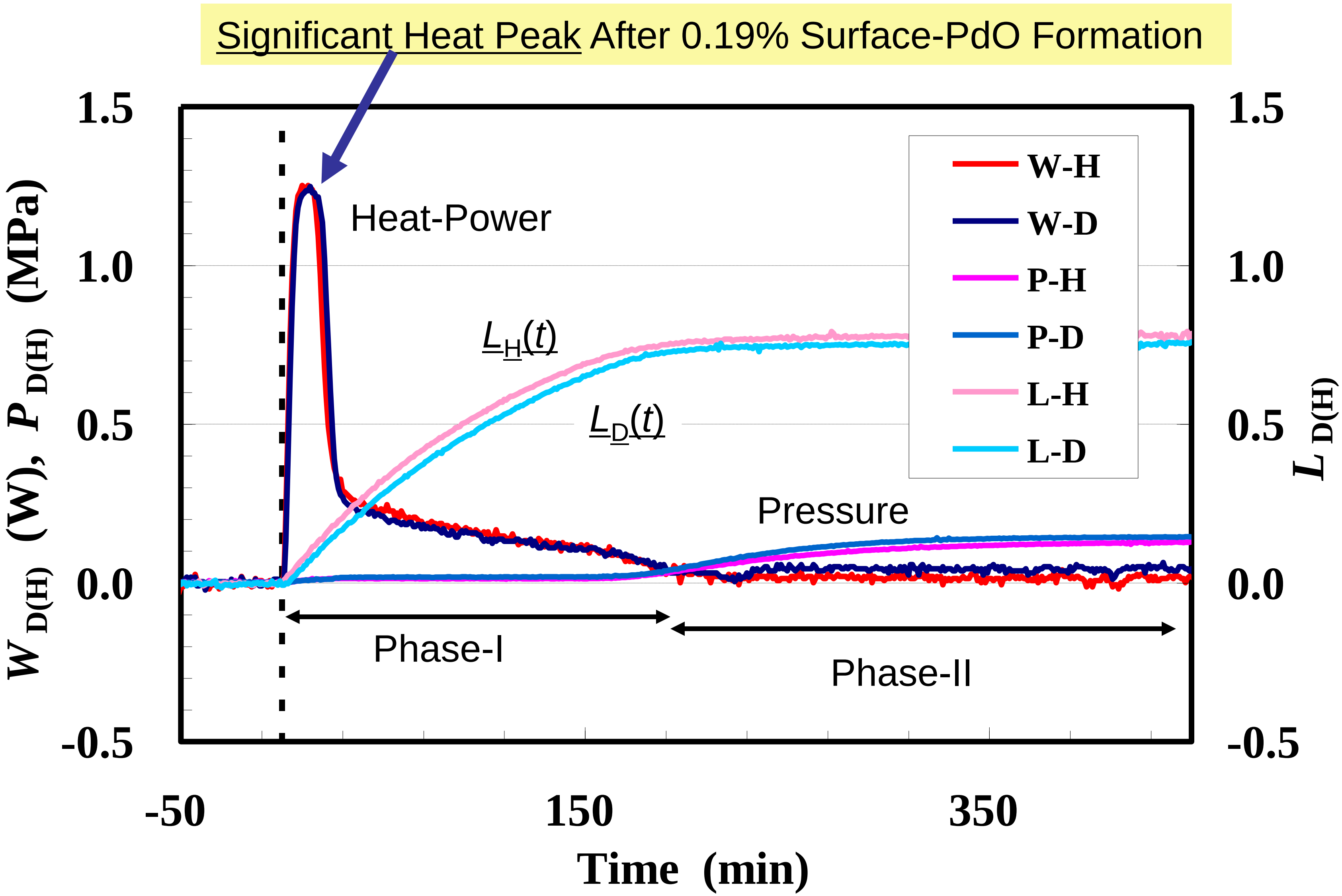
Typical variation of the specific sorption energy, η_D (η_H), compared with that of the power, W_D (W_H), in the #3 run for the PZ13(14) sample.

#2 Run (After O-Reduction) for PZ Samples showed bulk-like data.

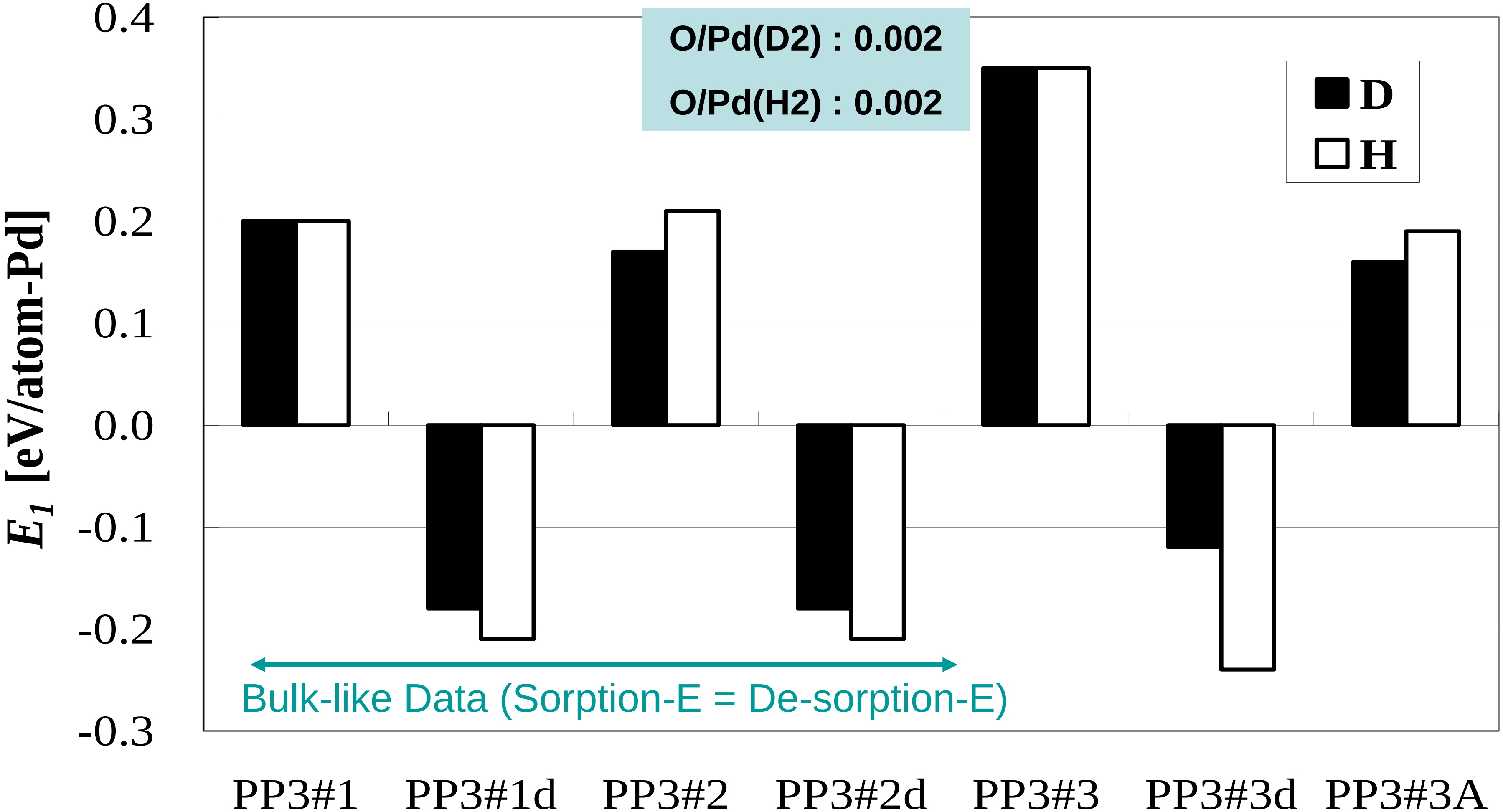


Typical variation of the specific sorption energy, η_D (η_H), compared with the power, W_D (W_H), in the #2 run for the PZ11(12) sample.

Large Powder of Pure Pd :PP3,4#3 100-nmϕ Pd

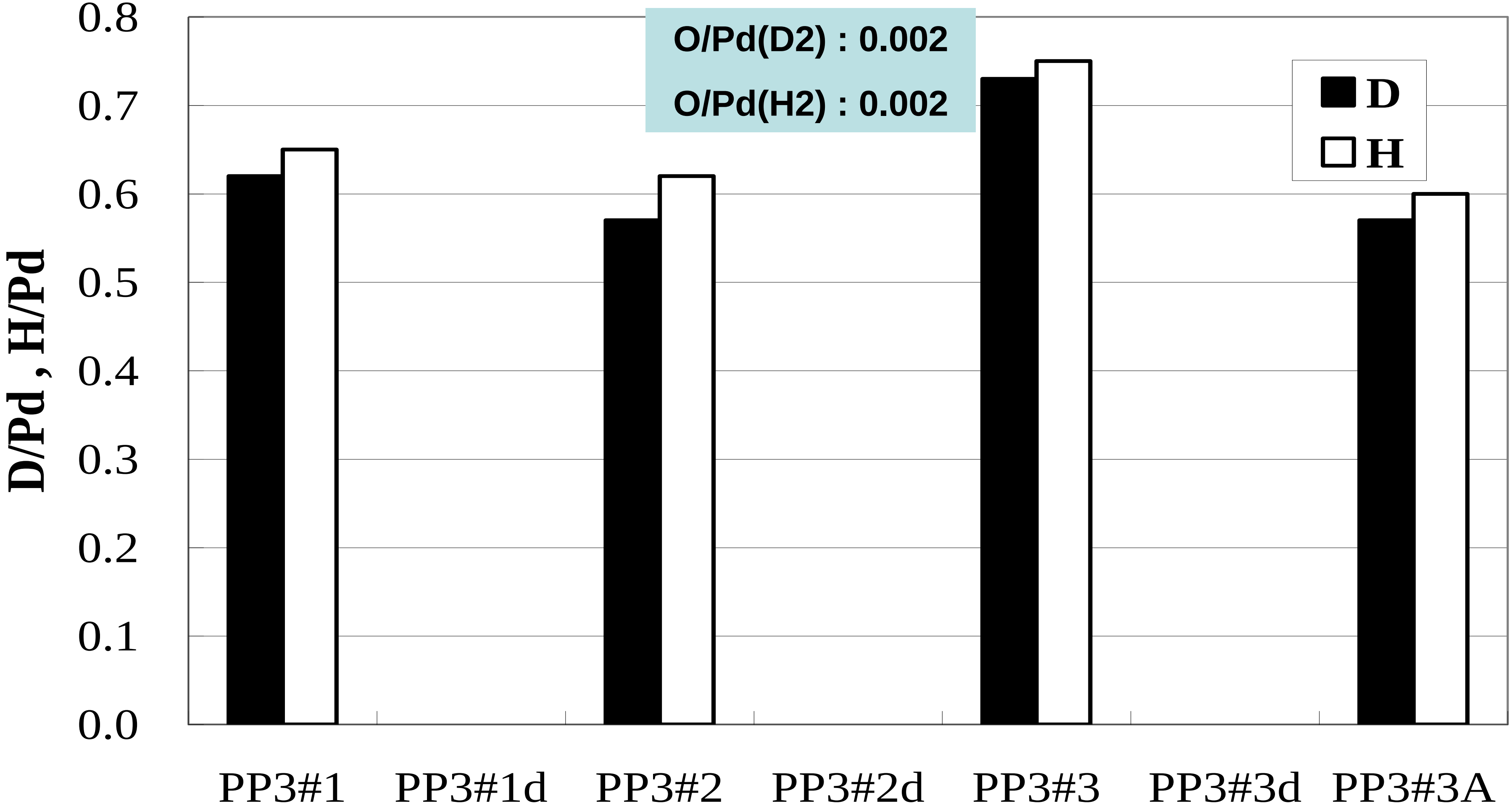


PP3,4 sample (100-nmϕ Pd)
; Show the similar (but smaller) effect of oxidization



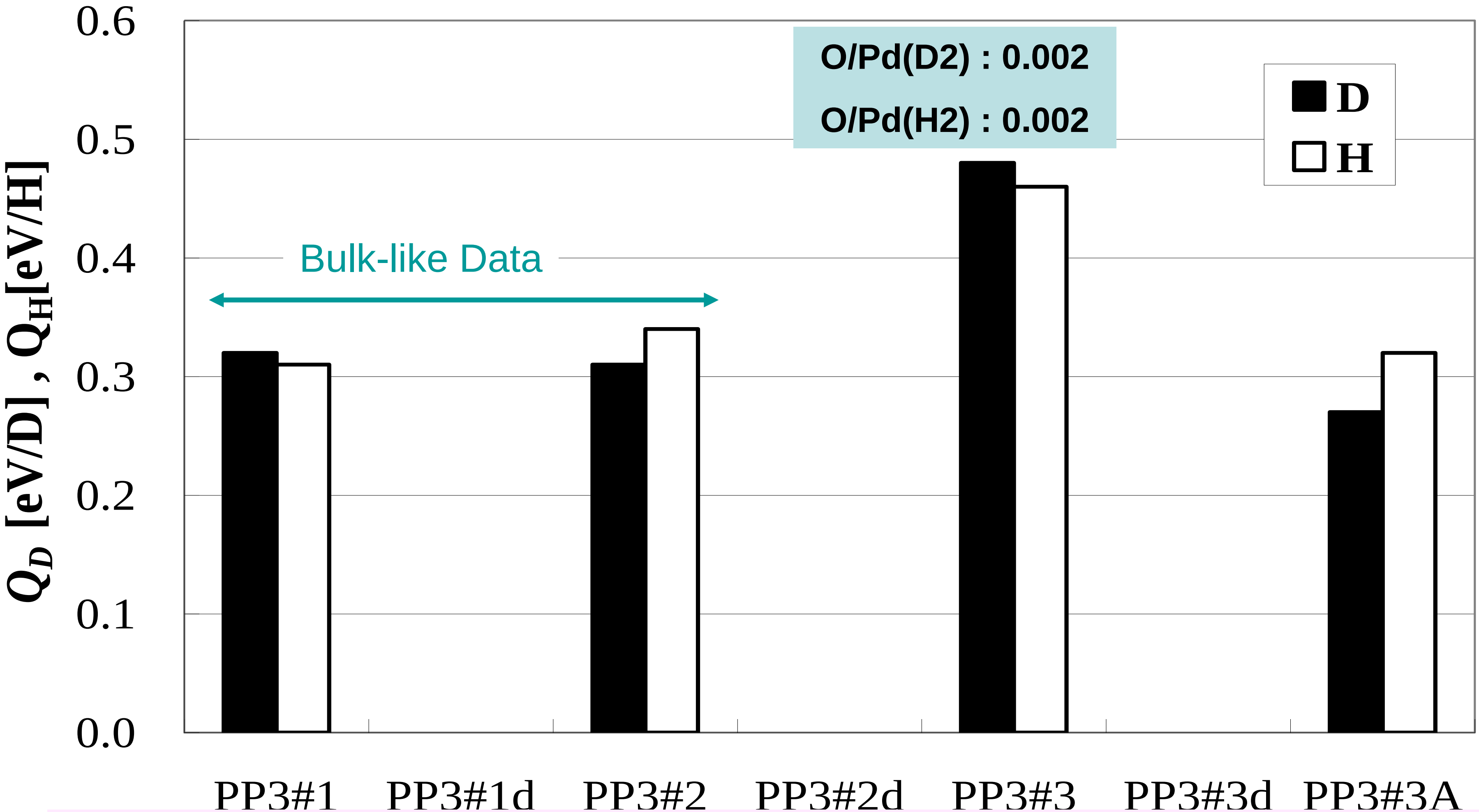
Comparison of the 1st-phase specific output energy E_1 for the runs D(H)-PP3(4)#1 through D(H)-PZ3(4)#3A

PP3,4 sample (100-nmϕ Pd)
; Show the similar (but smaller) effect of oxidization



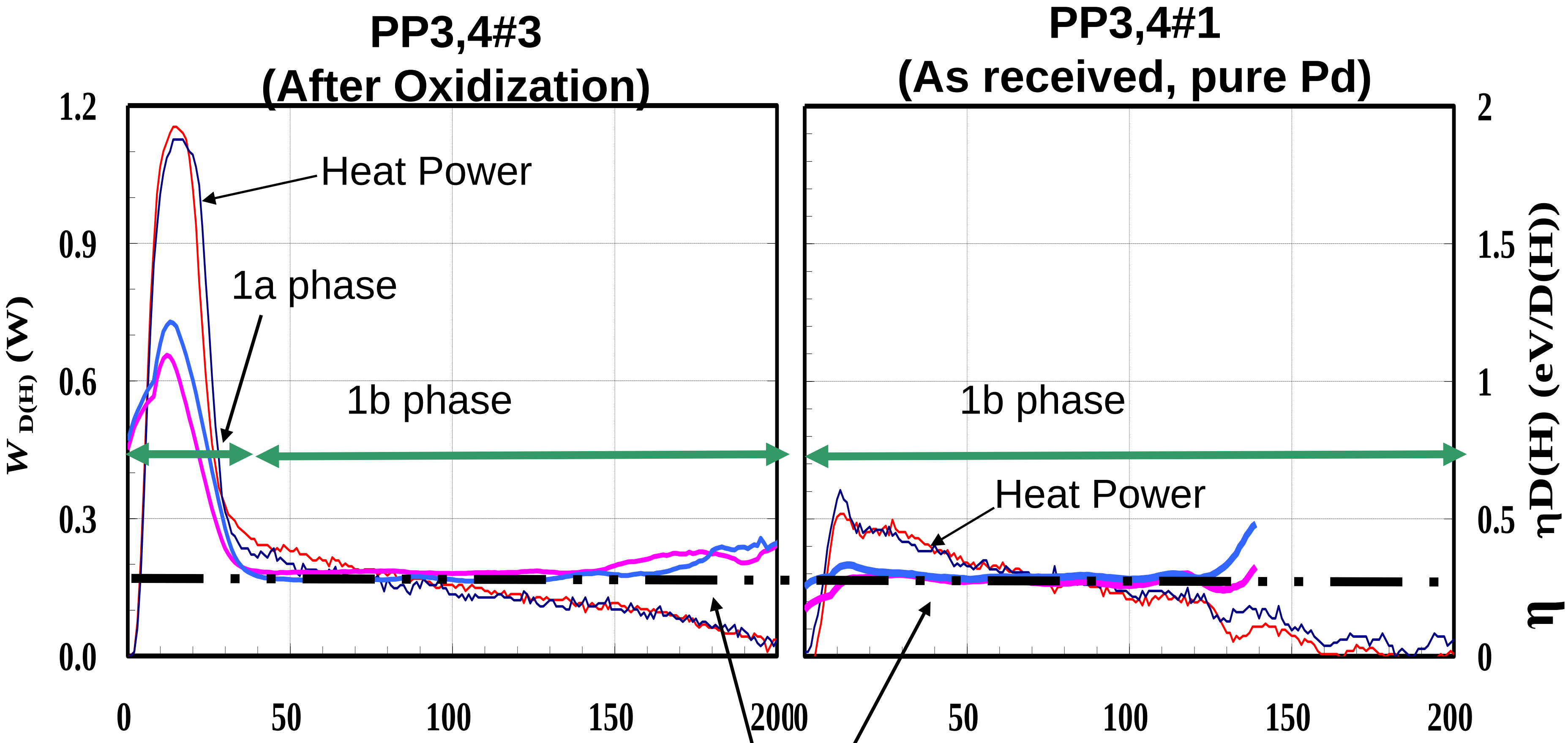
Comparison of the loading ratio D(H)/Pd for the runs D(H)-PP3(4)#1 through D(H)-PZ3(4)#3A

PP3,4 sample (100-nmϕ Pd)
; Show the similar (but smaller) effect of oxidization



Comparison of the hydridation energy QD(H) for the runs D(H)-PP3(4)#1 through D(H)-PZ3(4)#3A

PP3,4 #1(right) and #3(left) (100-nmϕ Pd): Effect of slight PdO layer is great (Ia) cf. bulky (Ib).



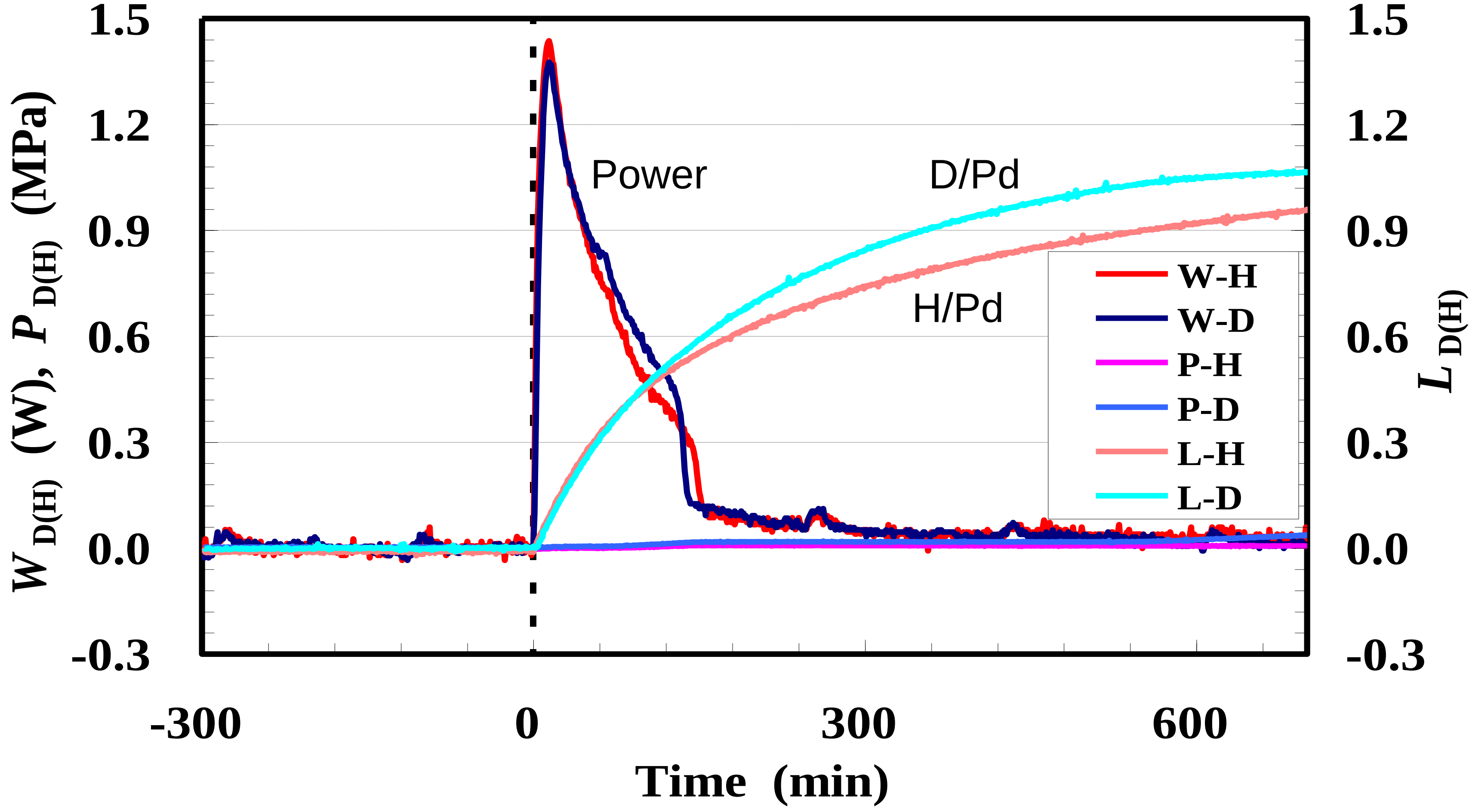
O/Pd(D2) : 0.002

O/Pd(H2) : 0.002

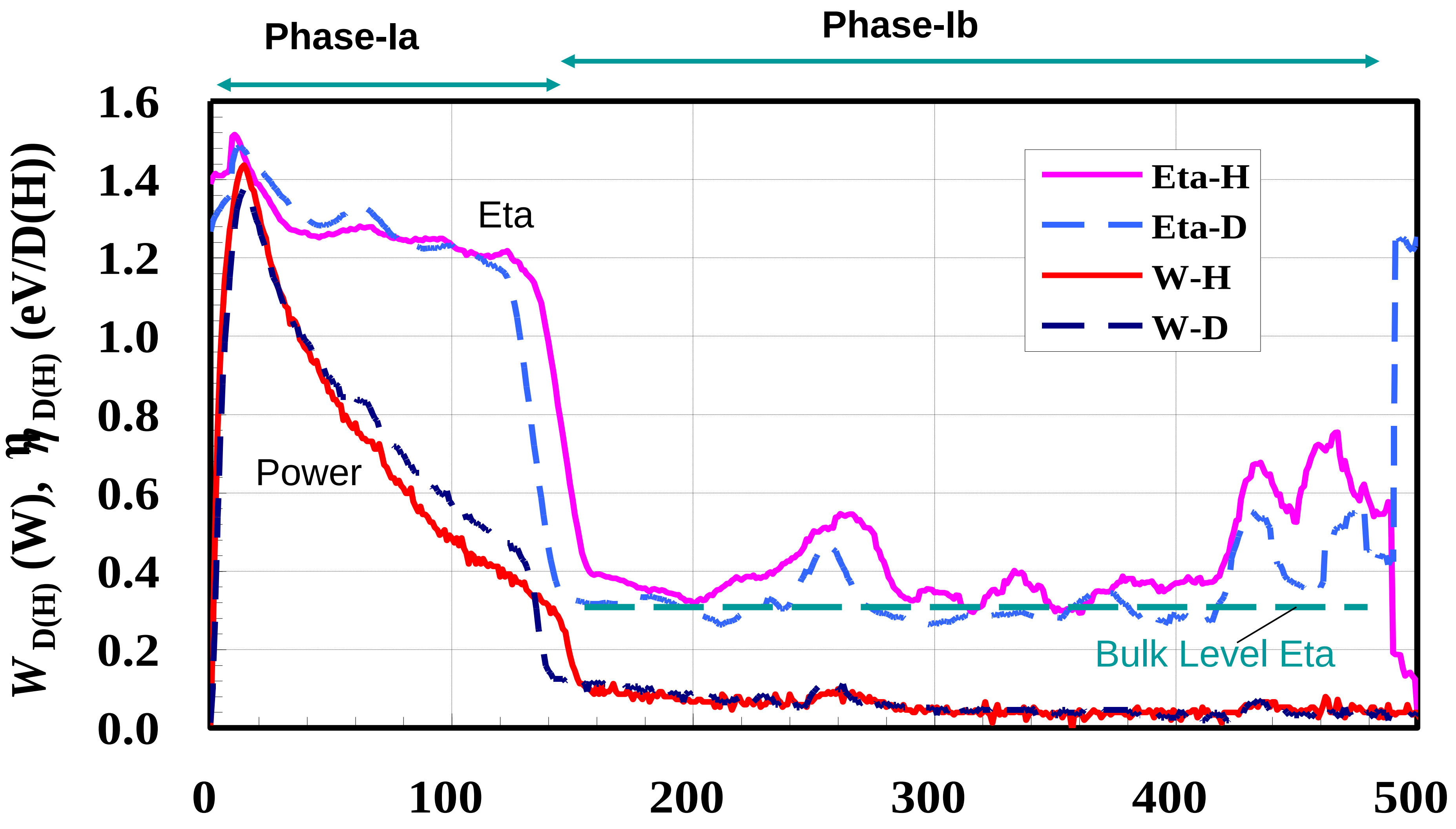
η value for bulk Pd (ca. 0.3 eV)

Palladium Black Samples

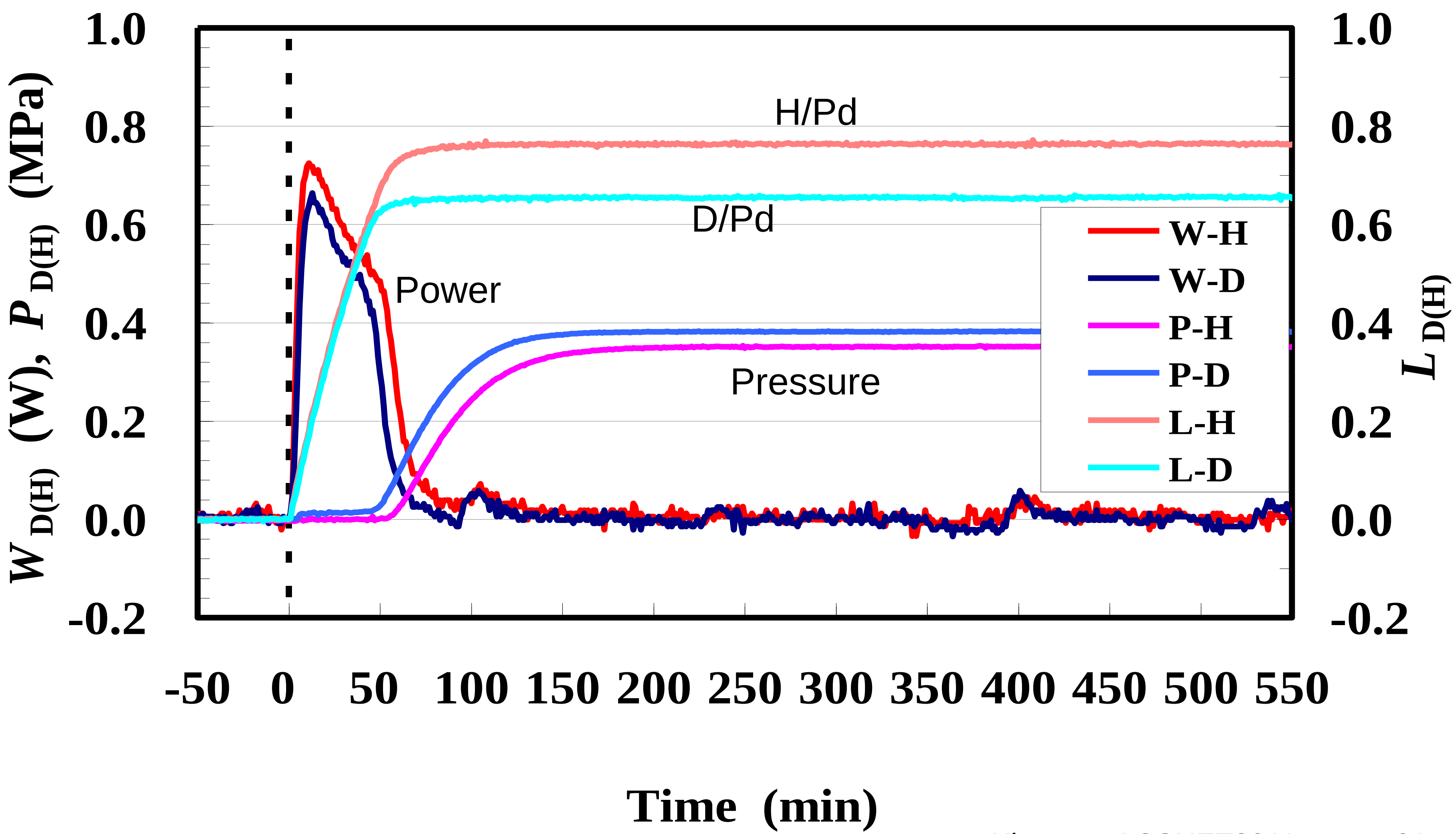
PB5,6#1: Virgin Runs (10g each)



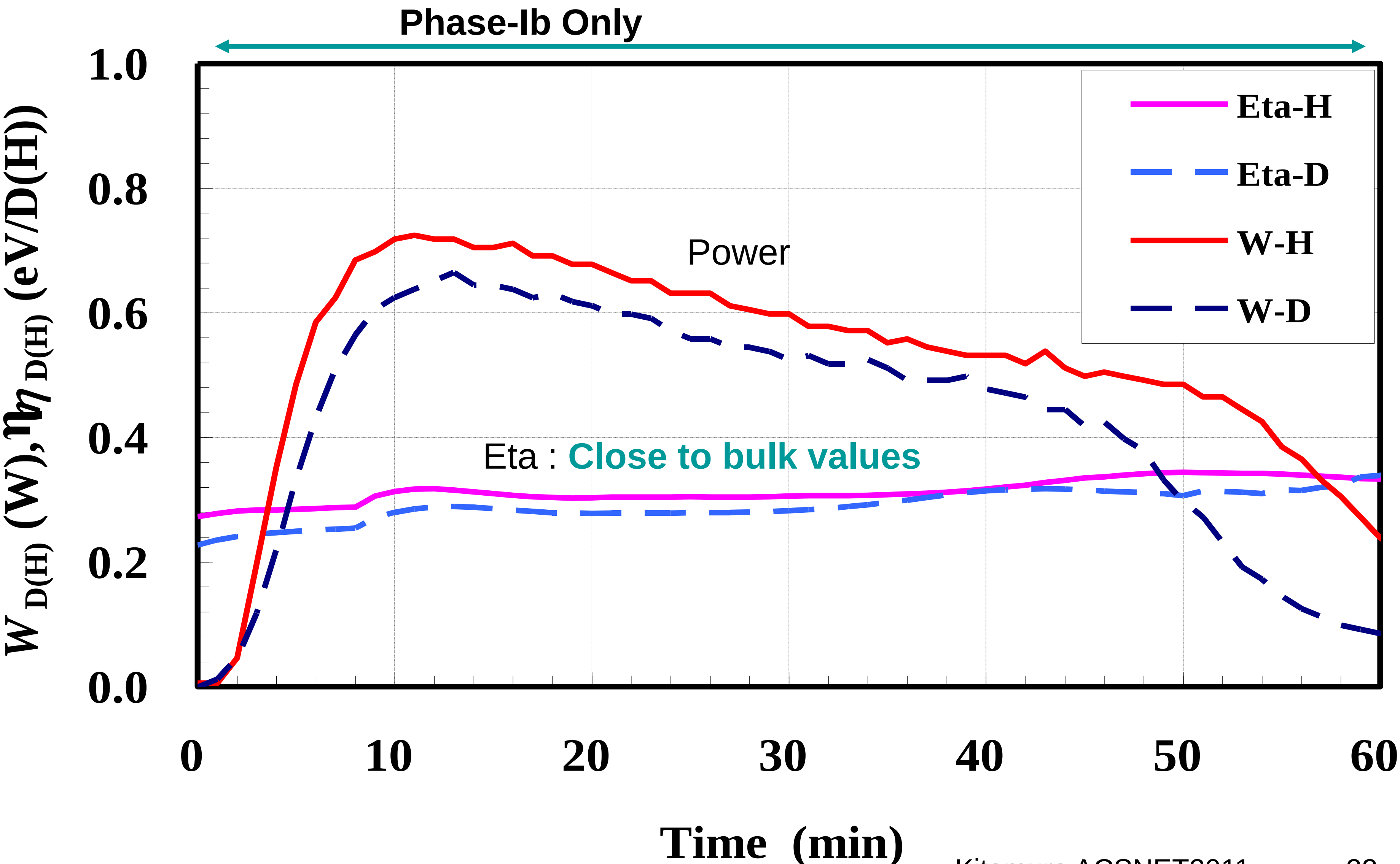
PB5,6#1; η-values vs. power



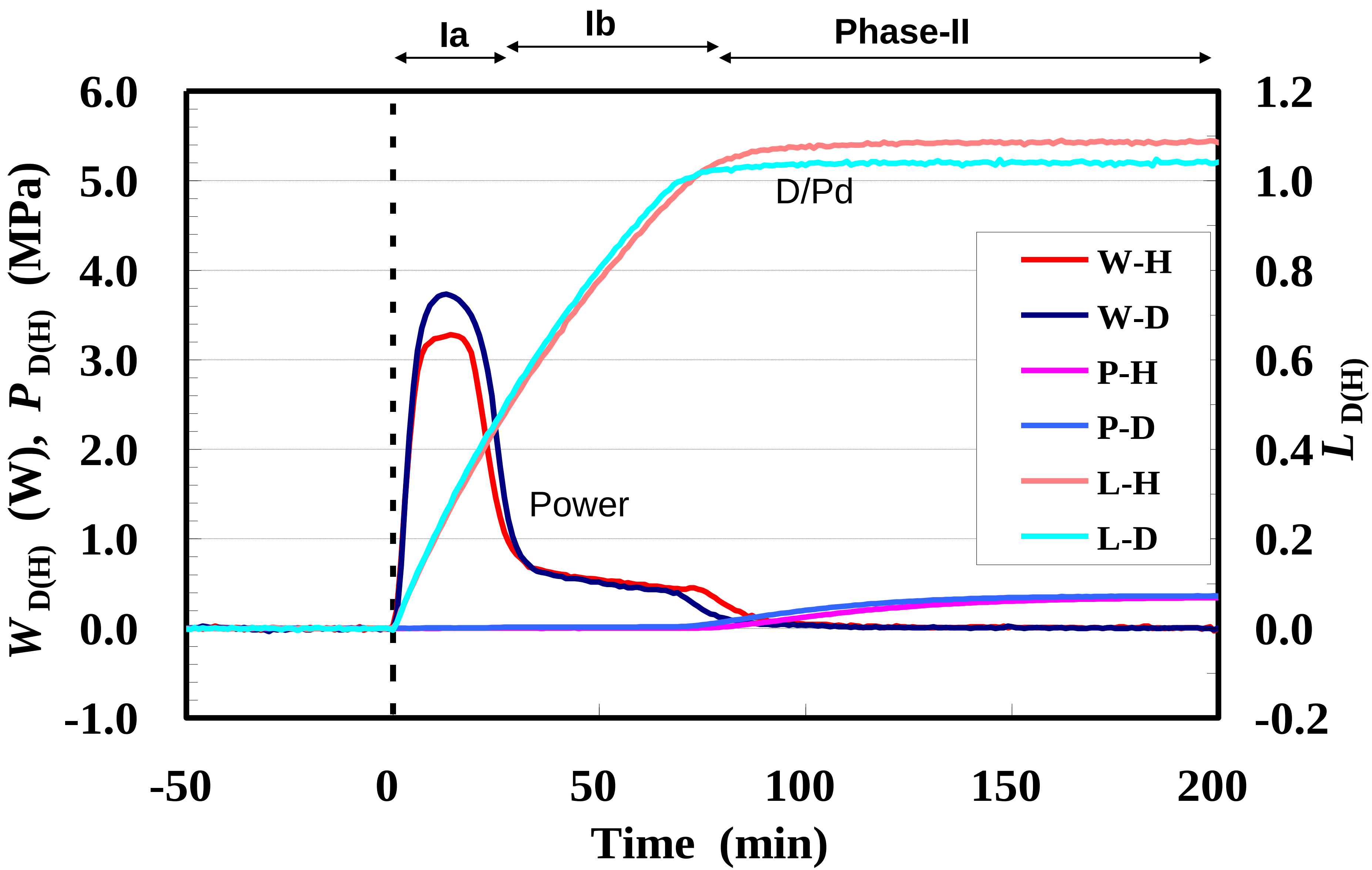
PB5,6#2; After Forced De-Oxidization



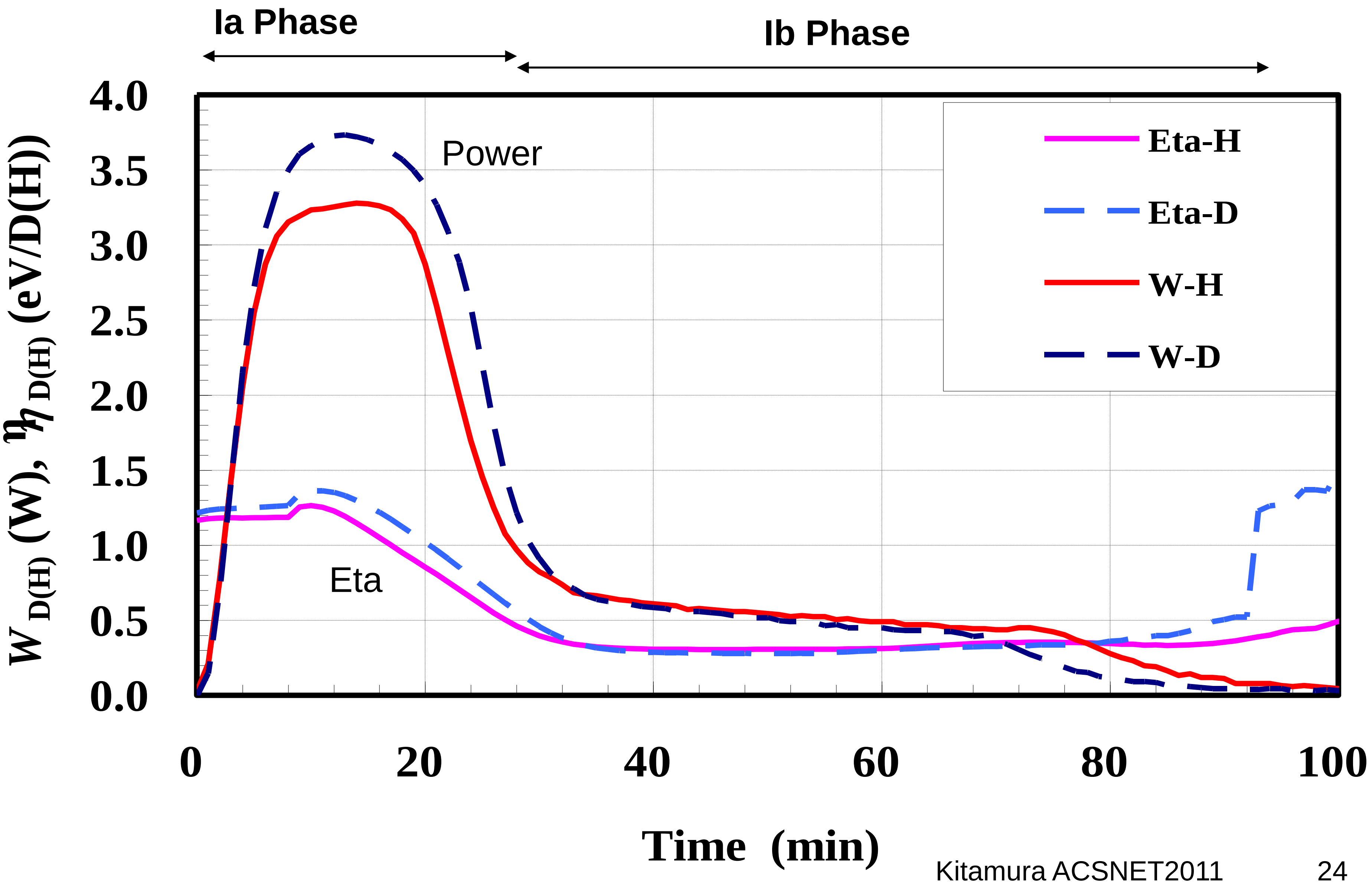
PB5,6#2 η-values vs. powers after De-oxidization



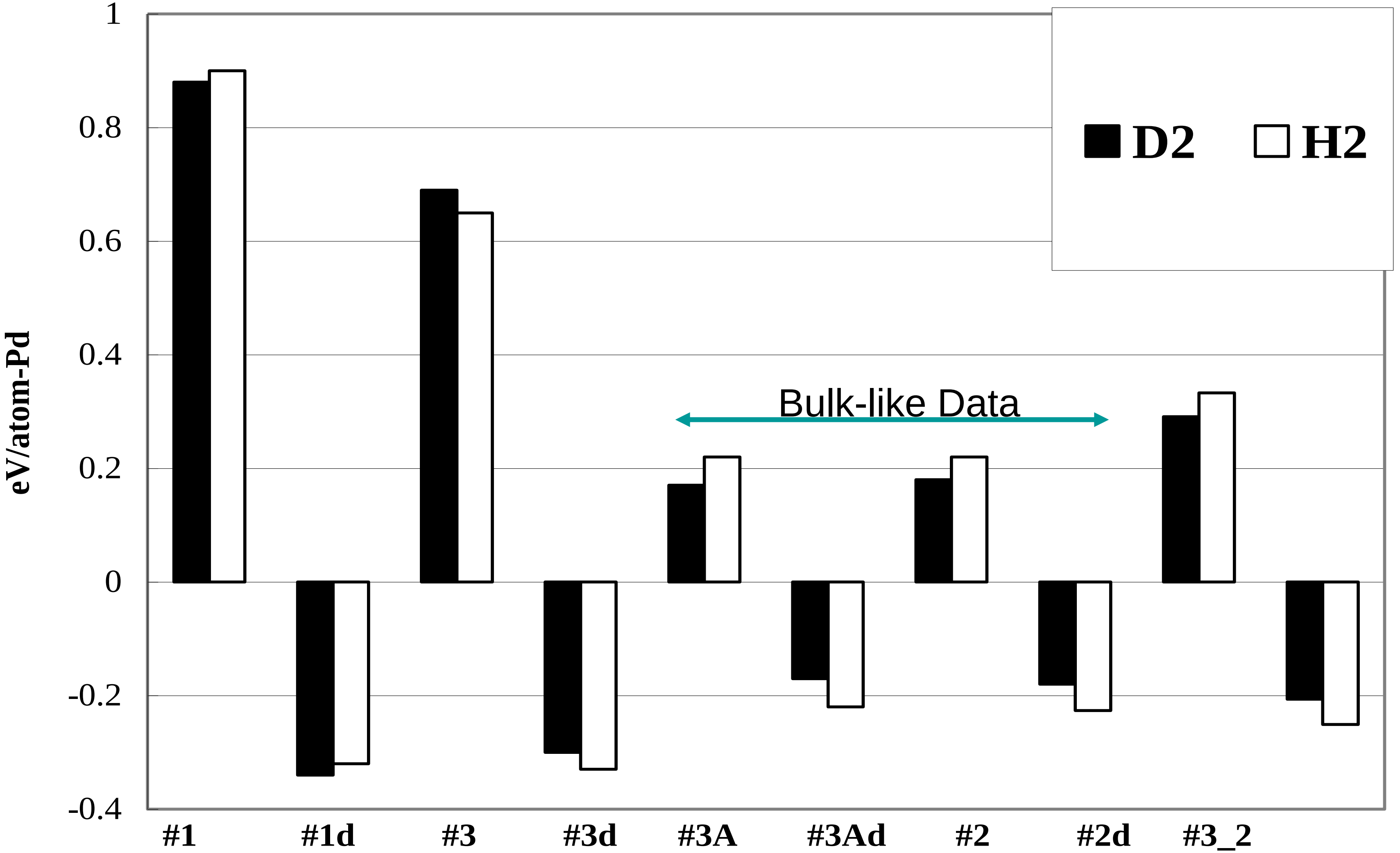
PB5,6#3: **2(D)-1.7(H)%PdO/Pd, After Oxidization**



PB5,6#3 η vs. Power: After Forced Oxidization (2-1.7%)

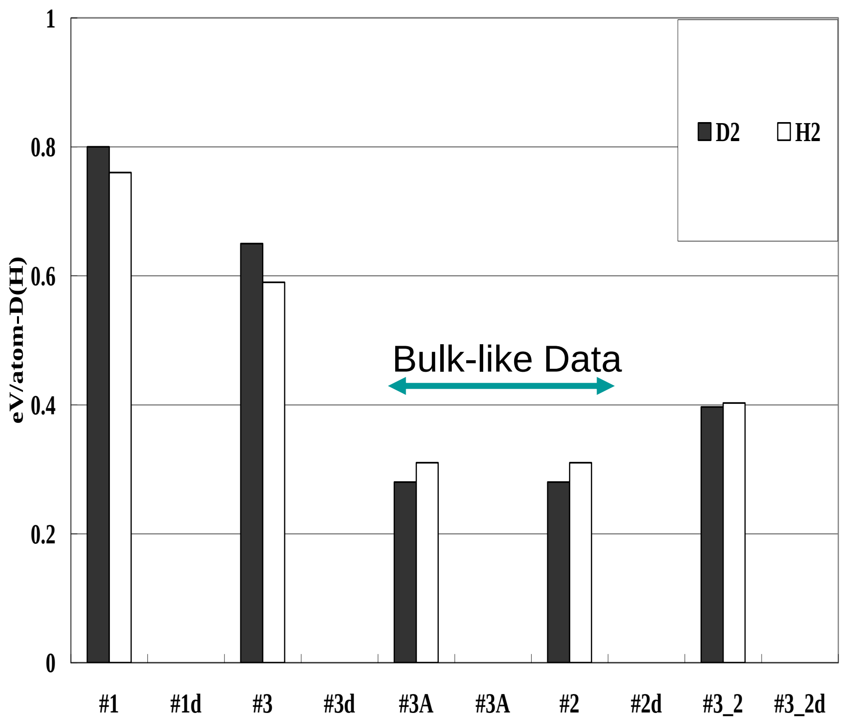


Integrated Heat Data for PB5,6 E_1

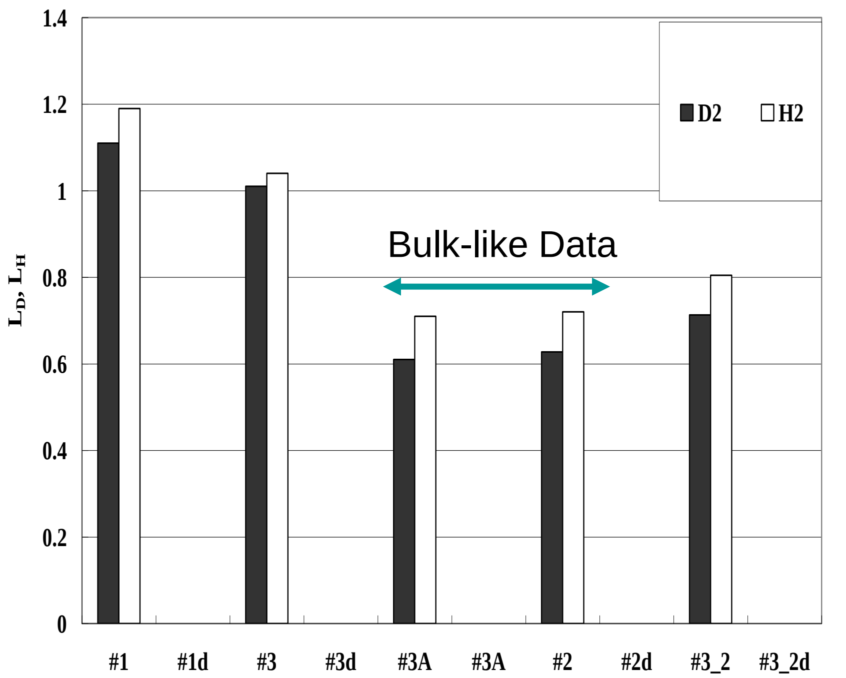


Integrated Data for PB

Absorption Energy per D(H)



Saturated Loading Ratios



Summary-1

PZ: 8-nmϕ Pd(31.2%)·Zr(68.8%)

(1)The 1st phase is found to be divided into **sub-phases Ia and Ib**;

- **1a phase**; with rapid absorption/adsorption and high heat output.
  - Probably occurring in the near-surface region
  - Oxygen incorporation is necessary for this phase to appear.
  - η_D value is larger than η_H., several times in some cases.
- **1b phase**; with a lower heat output nearly equal to the bulk value.

(2) The 1a phase is observed only in #1 and #3 runs.

(3)The **as-received** sample has very large 1st-phase parameters;
(specific output energy $E_{1D(H)}$, the loading ratio **D(H)/Pd~2.0**,
the hydridation energy $Q_{D(H)}$: **1.5(1.3) eV or more for D(H).)**
Forced **reduction** sample has given the significantly smaller
1st-phase parameters (close to those for bulk Pd sample).
Forced **oxidization** sample has **substantially recovered**
the large values of the 1st-phase parameters.

Summary-2

PP: 100-nmϕ Pd 99.5%

(1) The similar effects are observed less prominently;

- the existence of the 1a and 1b phases, and
- increased absorption parameters by oxygen incorporation.
- general trend is similar to the following PB behavior.

PB: palladium black

(1) Virgin (as received) samples gave high D(H)/Pd values (ca. 1.0) and higher heat release than PP.

(2) Slight PdO formation made more enhanced effect of initial large heat peak ($Q_{D(H)}$: **1.2(1.1) eV/D(H)-sorption**), Ia phase, and following Ib phase with bulky (ca. **0.3 eV/D(H)-sorption**) heat power.

(4) After the forced de-oxidization, heat levels and loading ratios gave bulk-like values (0.3 eV/D(H) and D(H)/Pd = ca. 0.6)

(5) The ratio of η_D/η_H is a little bit larger than 1.0 for Ia phases.

Summary-3:Tested Metal/Ceramics Powders and Results

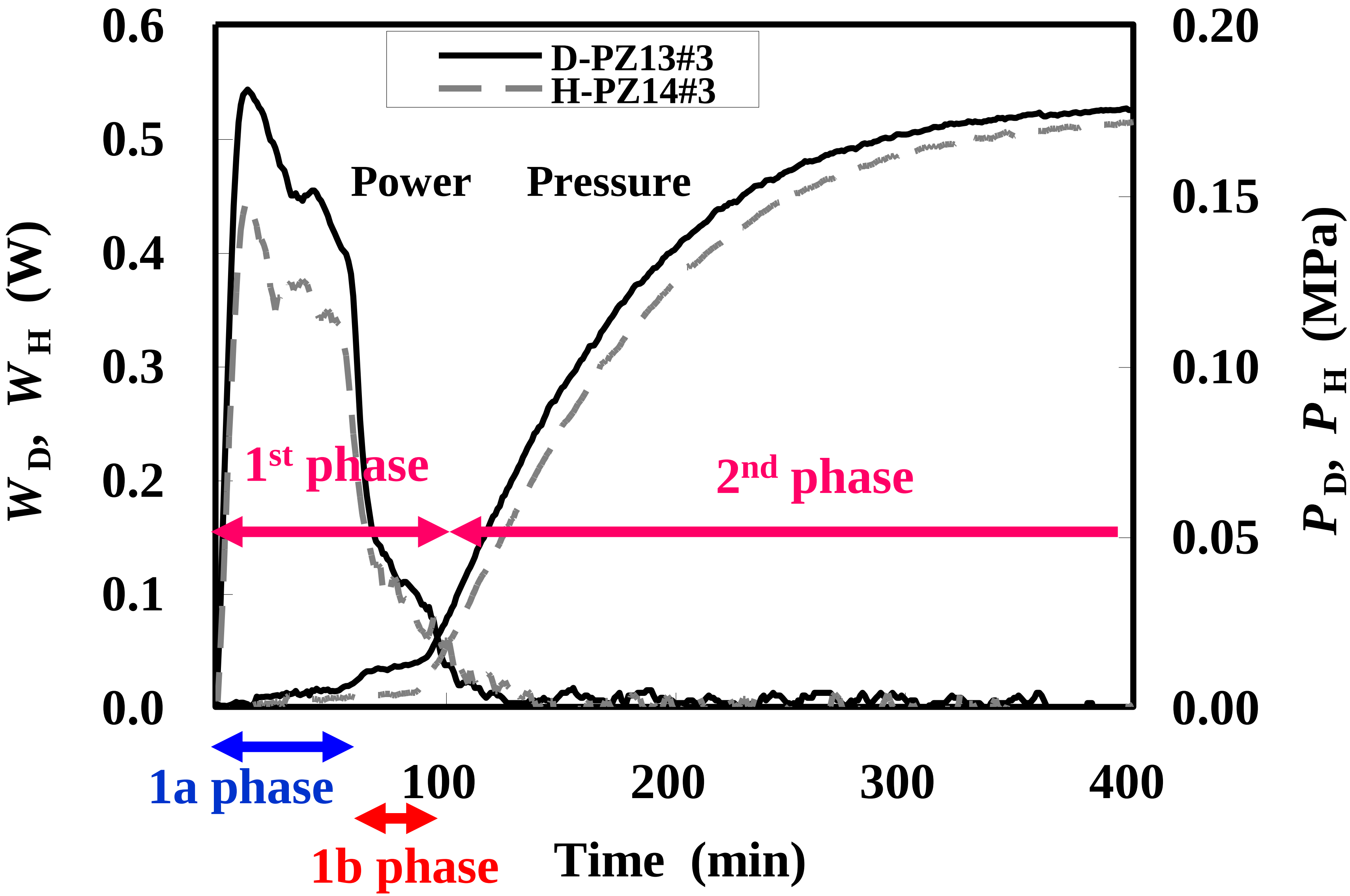
	Pd	Ni	Zr	O	Supplier	Anomalies observed?
100nmϕ-Pd **PP**	995%, 100nmϕ	---	---	---	Nilaco Corp.	[1],[2] No, bulk metal data, but PdO
Pd-black **PB**	99.9%, 300mesh	---	---	---	Nilaco Corp.	[1],[2] Yes, a little large heat & D/Pd
8-10nmϕ-*Pd* **PZ**	0.346	---	0.654	(1.64)	Santoku Corp.	[1],[2],[3], discussed **Yes**, Heat and D/Pd reproducible
mixed oxide **NZ**	---	0.358	0.642	(1.64)	Santoku Corp.	[2] No heat and loading
mixed oxide **PNZ**	0.105	0.253	0.642	(1.64)	Santoku Corp.	[2] Yes, but weak
2nmϕ-*PdNi* **PNZ2B**	0.04	0.29	0.67	(1.67)	Dr. B. Ahern	**Yes**, very large heat and D(H)/M, reproducible

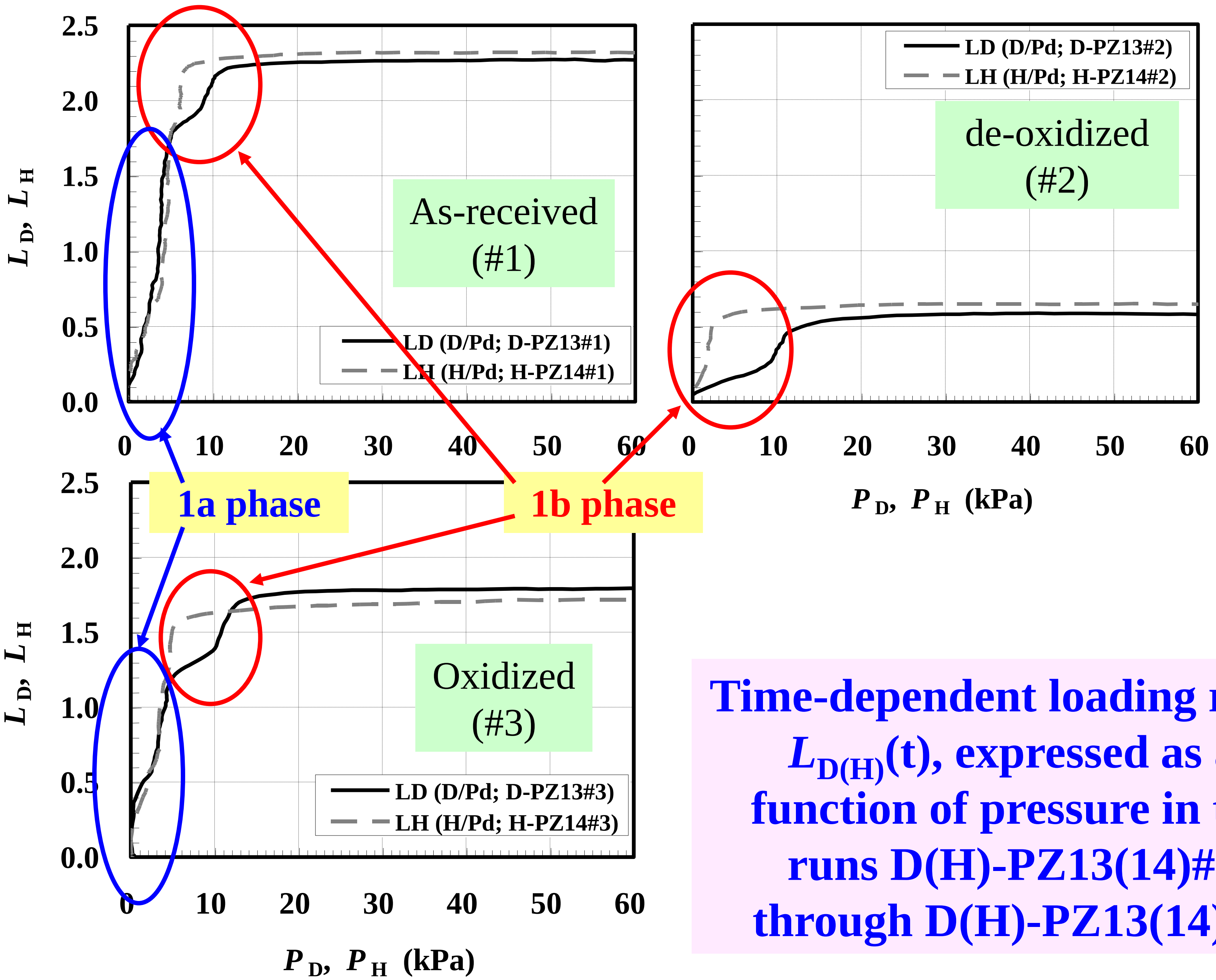
Drastic change happens by Meso-Catalyst! **Why?**

[1] Phys. Lett. A, 373 (2009) 3109-3
[2] ***Low Eergy Nuclear Reactions***, (AIP Conf. Proc. 1273, ed. Jan Marwan, 2010).
[3] ***LENR Source Book 3***, (ed. Jan Marwan, ACS) to be published.

Supplement Data below

The 1st phase is divided into the 1a-phase and the 1b-phase.





Time-dependent loading ratio, $L_{D(H)}$(t), expressed as a function of pressure in the runs D(H)-PZ13(14)#3 through D(H)-PZ13(14)#3

- **Time-resolved specific sorption energy,** **15**
  or differential heat of hydrogen uptake,
  defined as the output energy per one hydrogen isotope atom absorbed/adsorbed,

$$\eta(t) \equiv \frac{\int_t^{t+\Delta t} W_{\mathrm{true}}(t)\mathrm{d}t}{L(t+\Delta t)-L(t)}$$

$$\eta(t) \approx \frac{\int_t^{t+\Delta t} \overline{W(t,\tau)}\mathrm{d}t}{L(t+\Delta t)-L(t)}, \qquad \overline{W(t,\tau)} = \frac{\int_t^{t+\tau} W_{\mathrm{meas}}(t)\mathrm{d}t}{\tau}$$

- **The values of W_{true}(t) should be de-convoluted from the measured output power W_{meas}(t), which has an indicial delay with a time constant of τ, and is approximated here by *W(t,τ)* averaged over τ.**
- **The hydridation energy $Q_{D(H)}$ introduced earlier is equal to the integrated power over the 1st phase divided by D(H)/Pd at the end of the 1st phase in the absence of oxygen.**
- **The interval Δt is arbitrary, and chosen here to be 1 min.**

PNZ2B3,4#1

Pd	Ni	Zr	O	Supplier
0.04	0.29	0.67	(1.67)	Dr. B. Ahern

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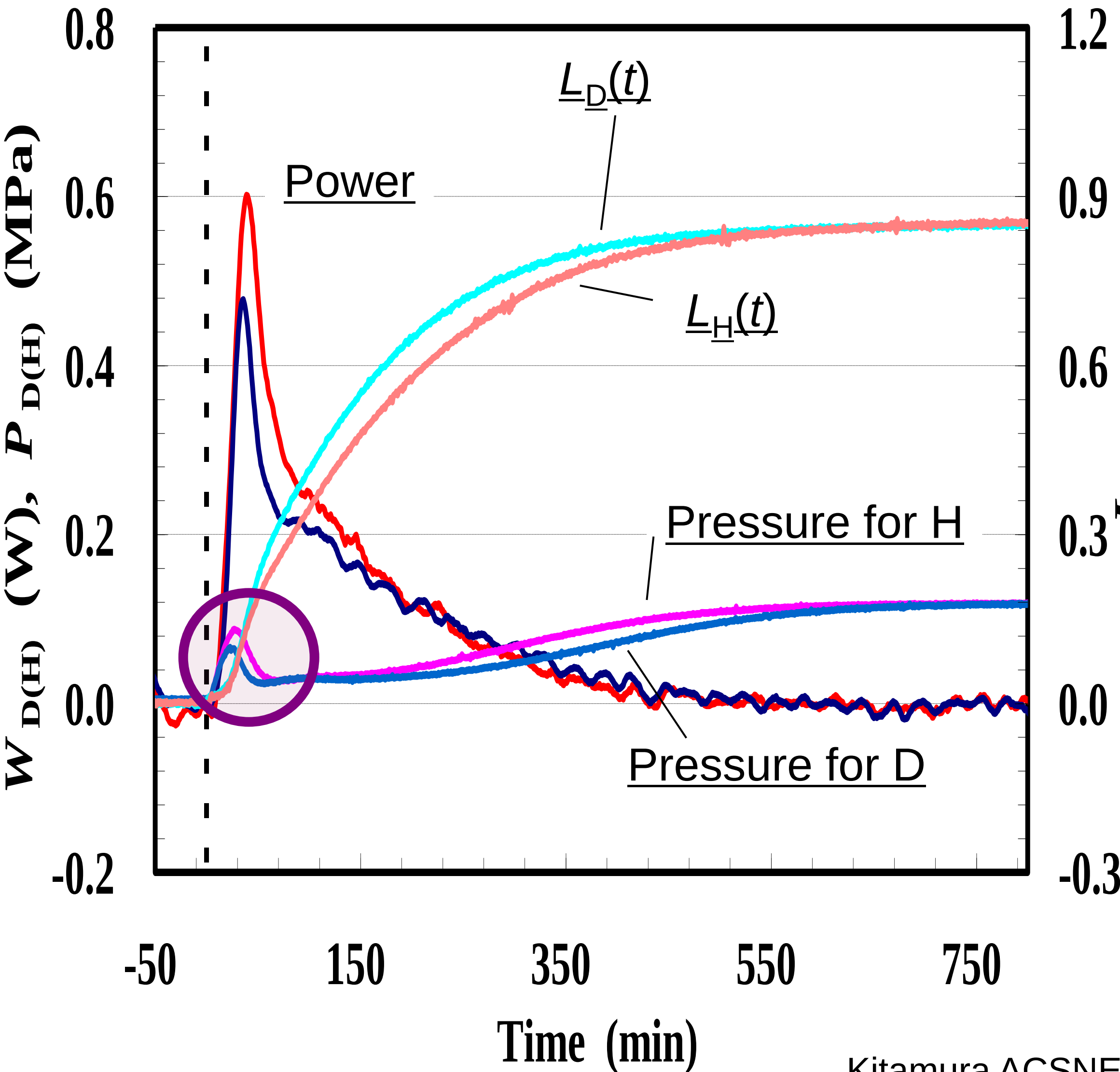
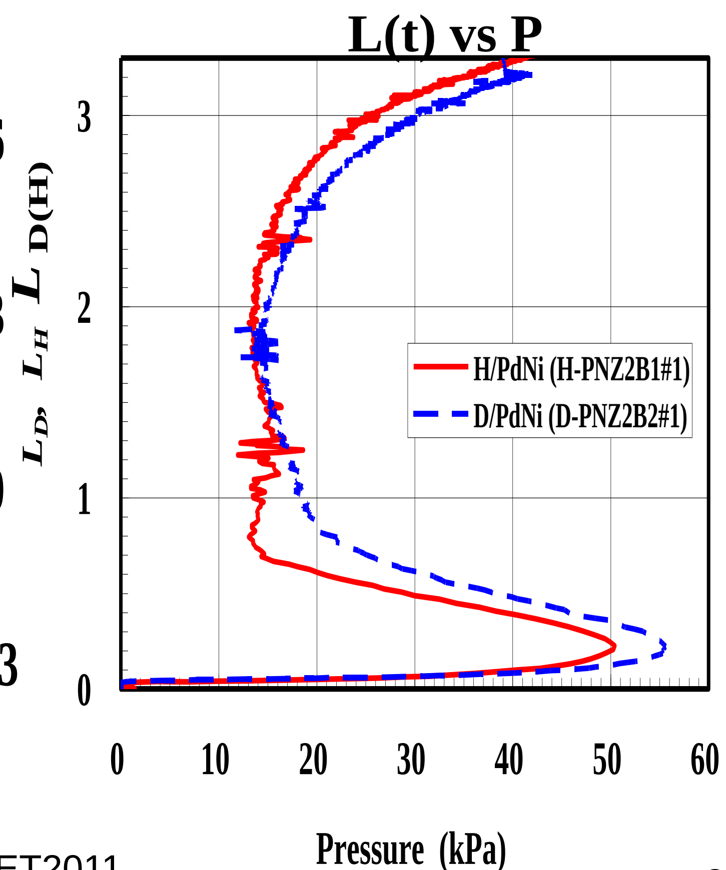
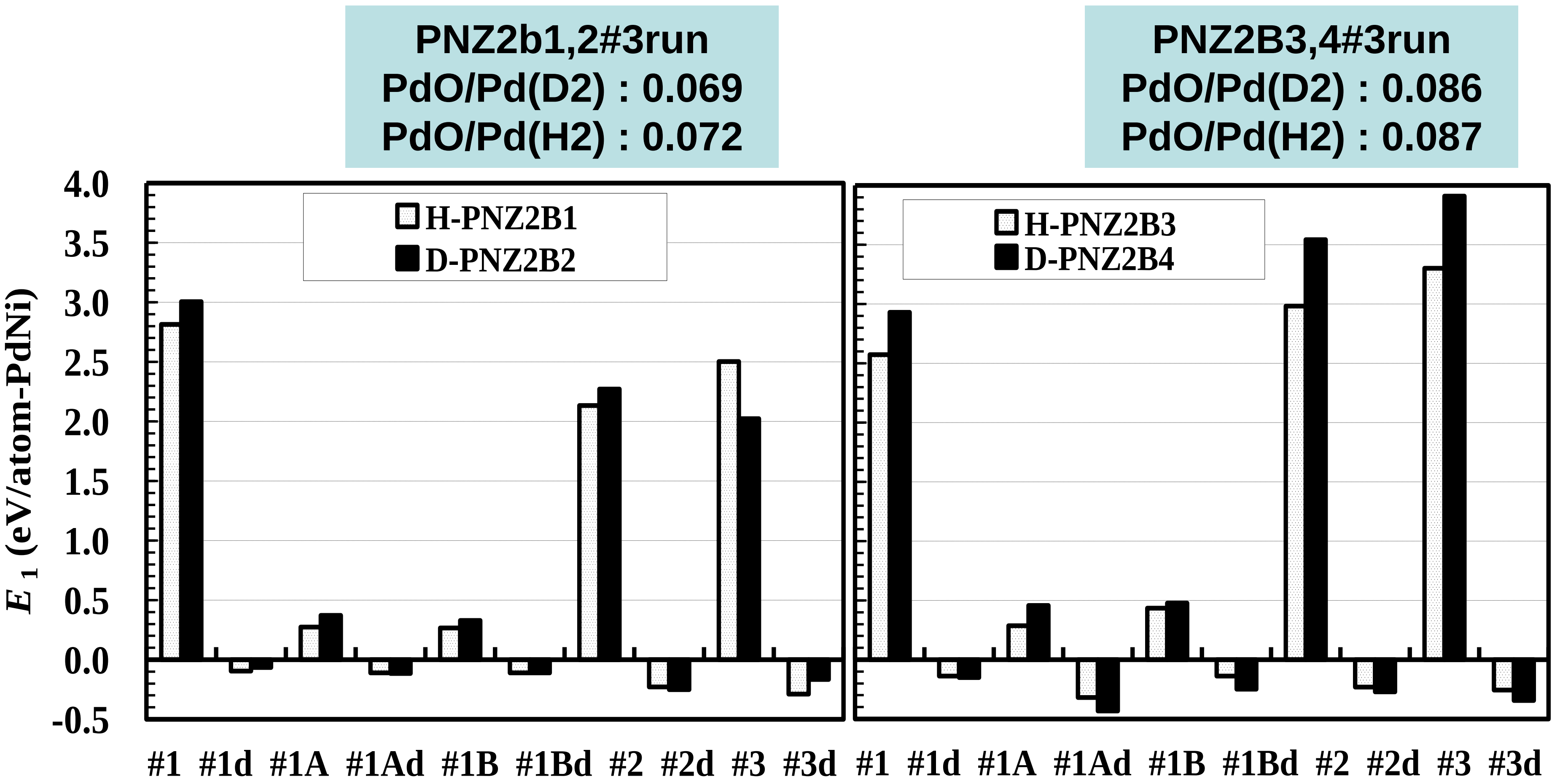




Kitamura ACSNET2011

PNZ2B1-4 sample (Pd : 4% Ni : 29% Zr : 67%) ; Deoxidization works as well as oxidization

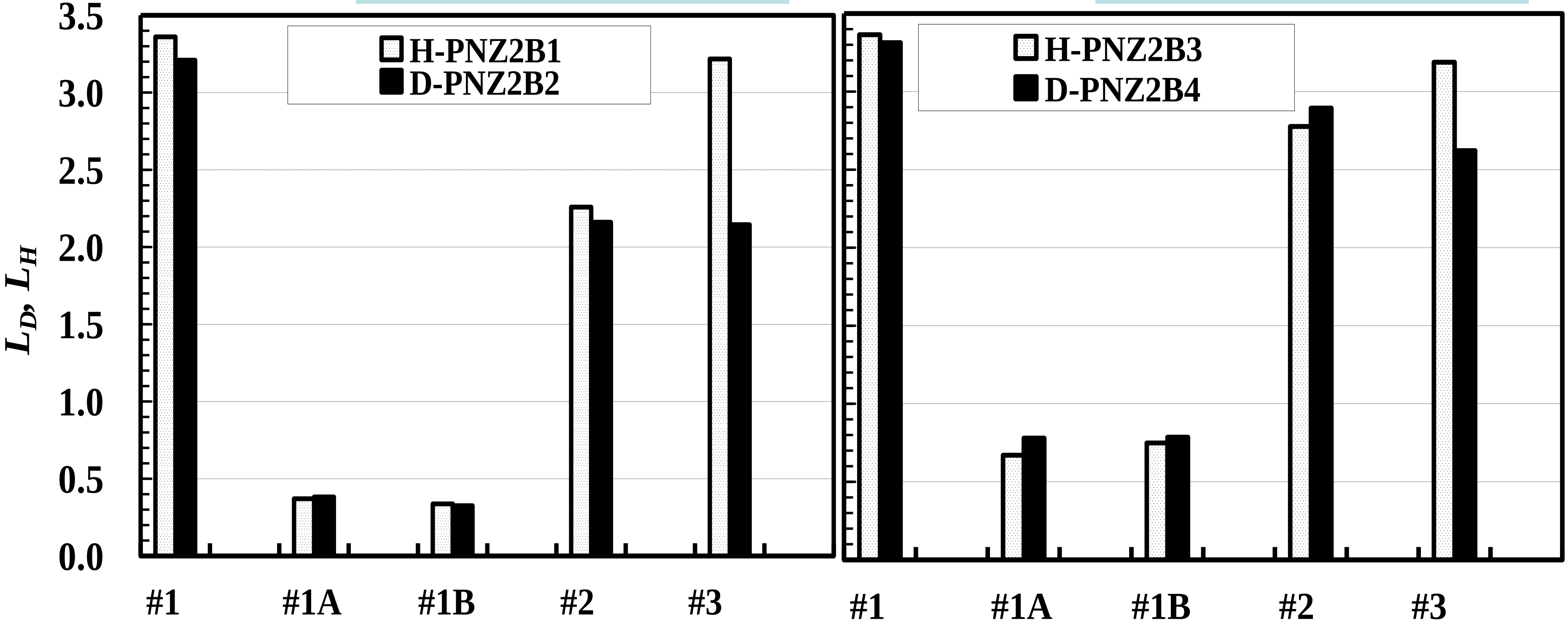


Comparison of the 1st-phase specific output energy E_1 for the runs D(H)-PNZ2B2(1)#1 through D(H)-PNZ2B4(3)#3d

PNZ2B1-4 sample (Pd : 4% Ni : 29% Zr : 67%) ; Deoxidization works as well as oxidization

PNZ2b1,2#3run
PdO/Pd(D2) : 0.069
PdO/Pd(H2) : 0.072

PNZ2B3,4#3run
PdO/Pd(D2) : 0.086
PdO/Pd(H2) : 0.087



Comparison of the loading ratio D(H)/[Pd･Ni] for the runs D(H)-PNZ2B2(1)#1 through D(H)-PZ4(3)#3

PNZ2B1-4 sample (Pd : 4% Ni : 29% Zr : 67%) ; Deoxidization works as well as oxidization

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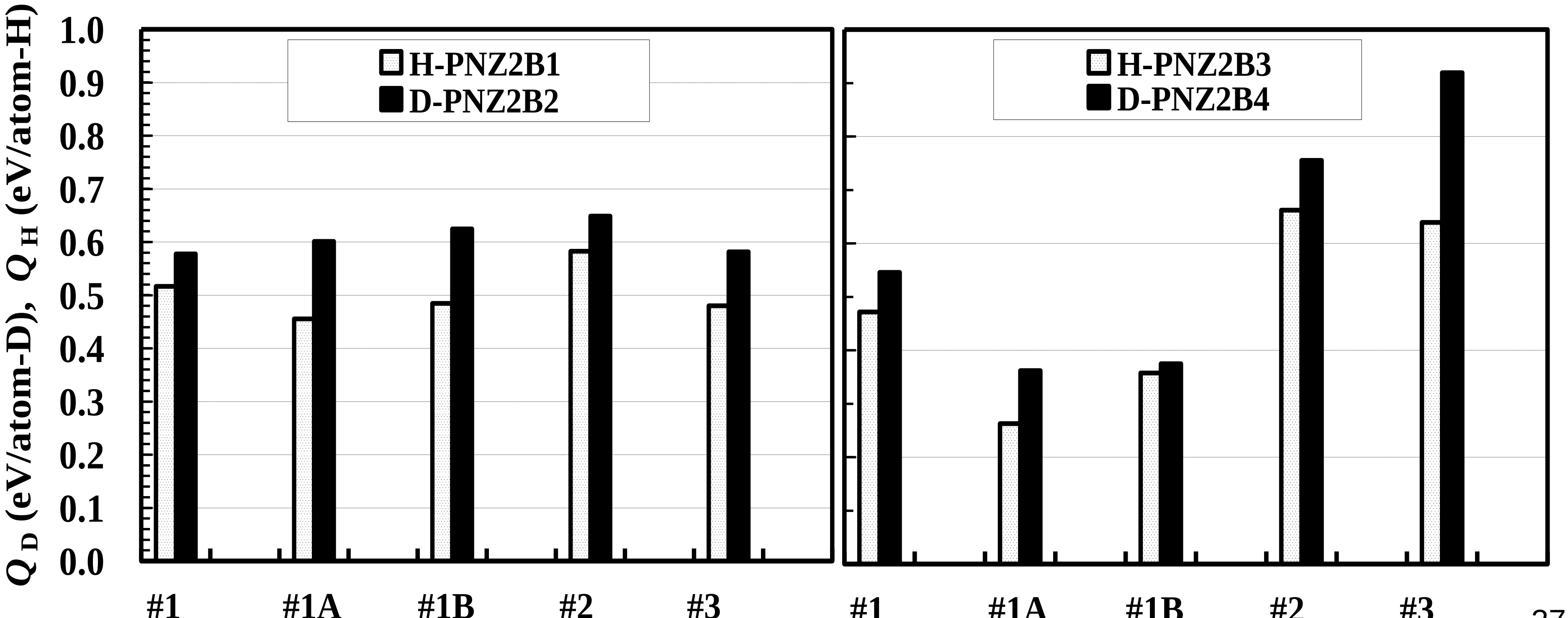
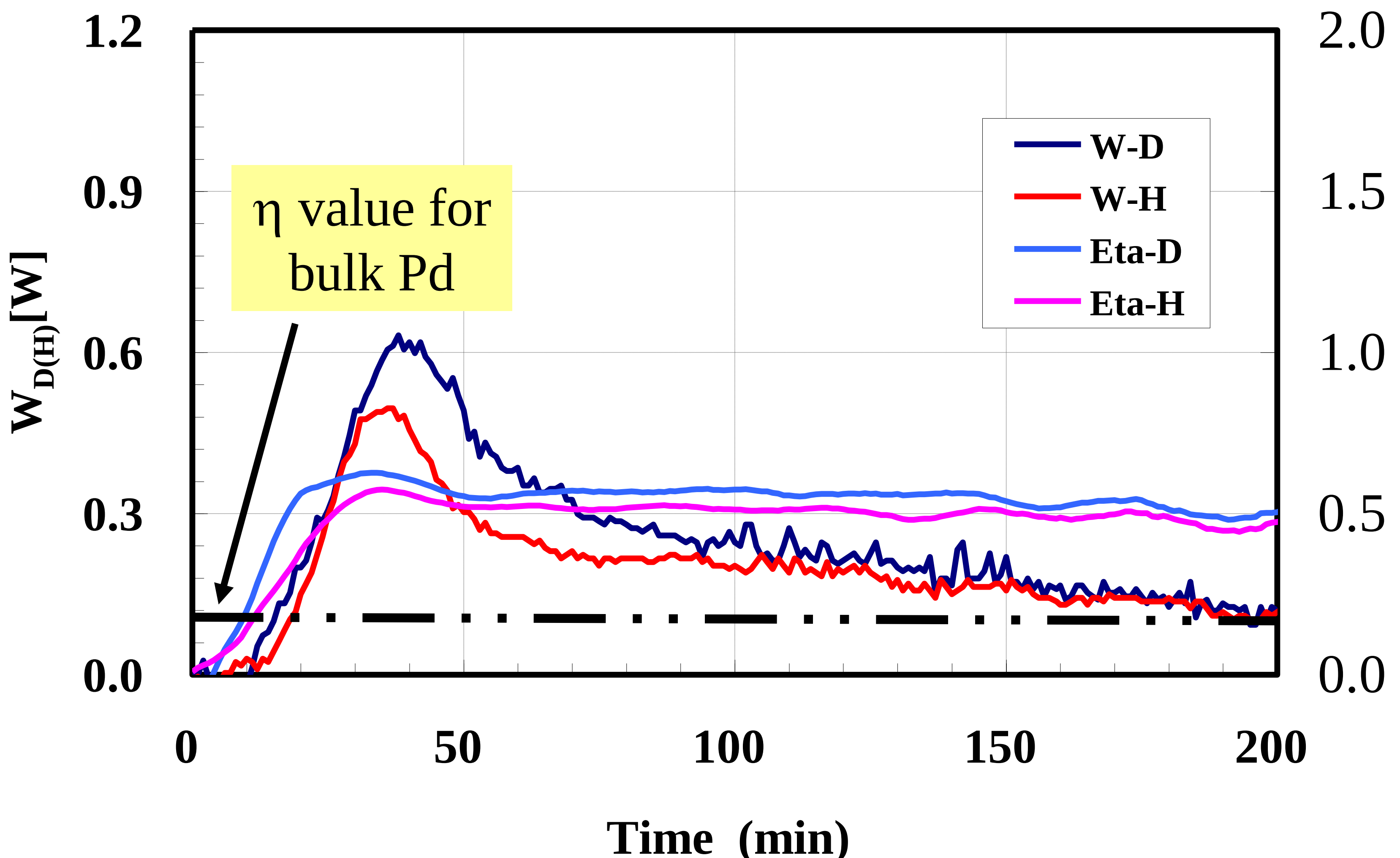
Larger energy $Q_{D(H)}$ for the D-runs
D(H)-PNZ2B2(1)#1 through D(H)-PNZ2B4(3)#3

PNZ2b1,2#3run	PNZ2B3,4#3run
PdO/Pd(D2) : 0.069	PdO/Pd(D2) : 0.086
PdO/Pd(H2) : 0.072	PdO/Pd(H2) : 0.087



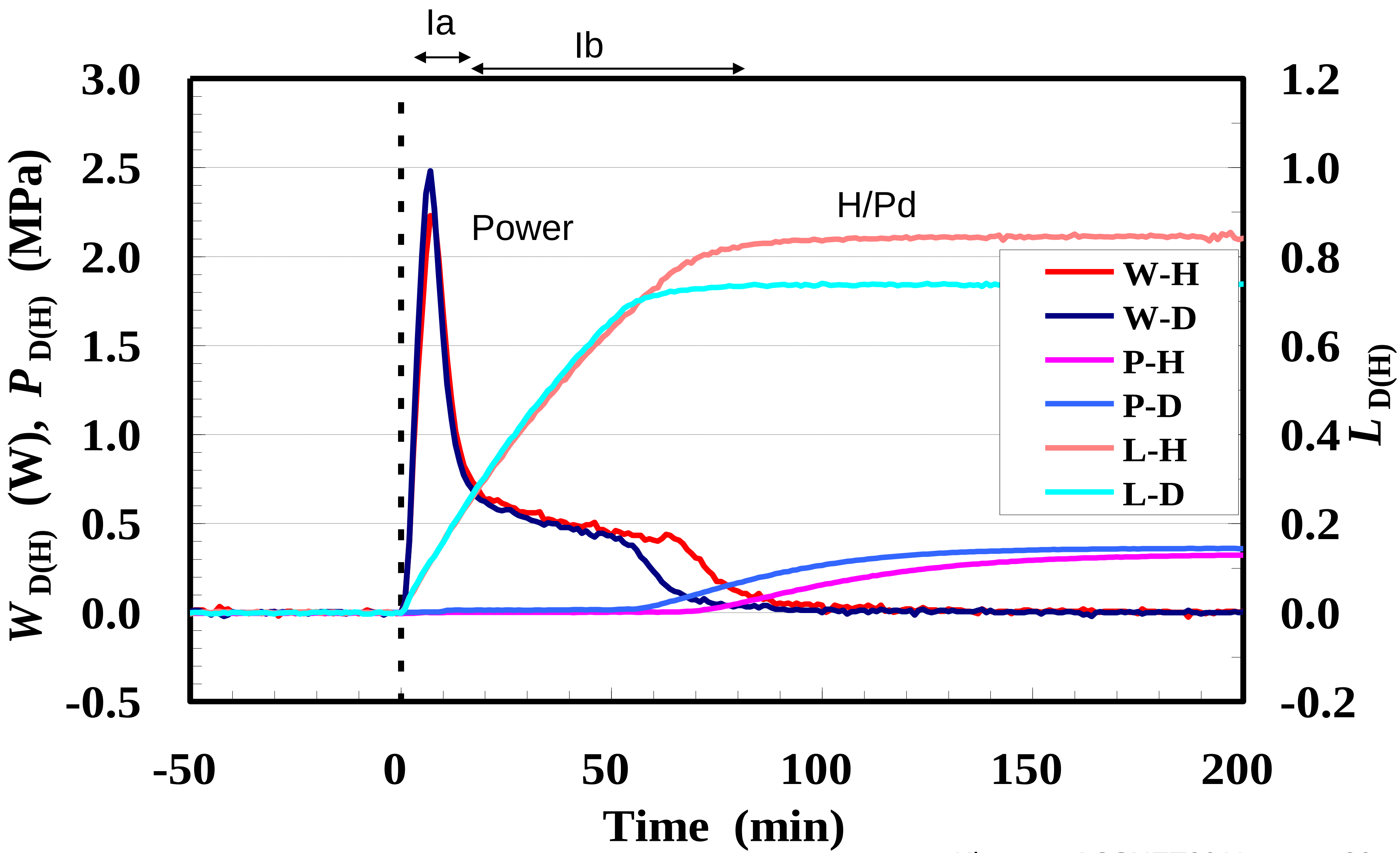
PNZ2B3,4#1

Absorption / desorption energies are constant and anomalously large, while Ni does not absorb D(H) at all at room temperature.

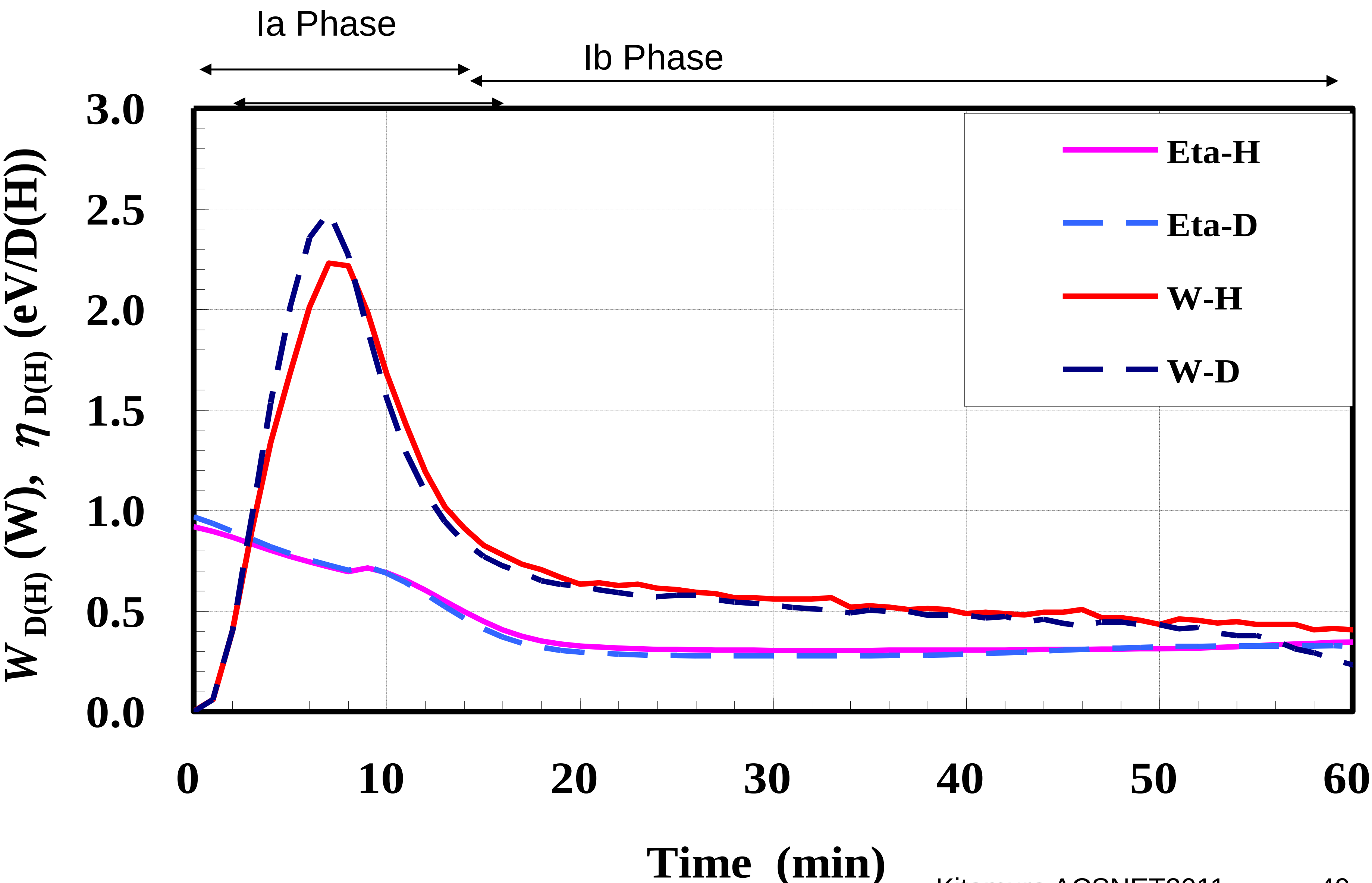


PB5,6#3_2: 0.47%PdO/Pd

The second forced-oxidization runs gave smaller Ia phase.

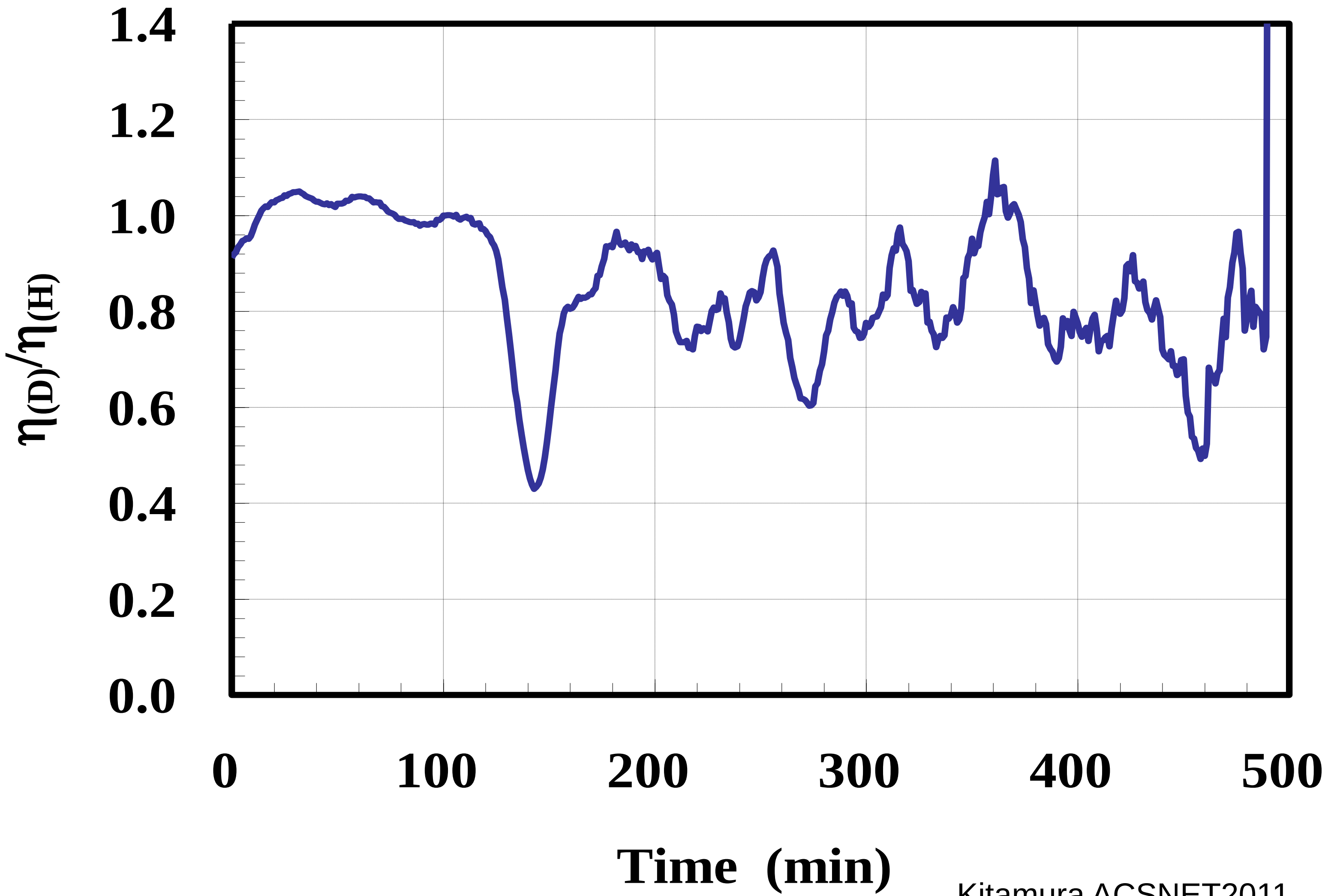


PB5,6#3_2 η

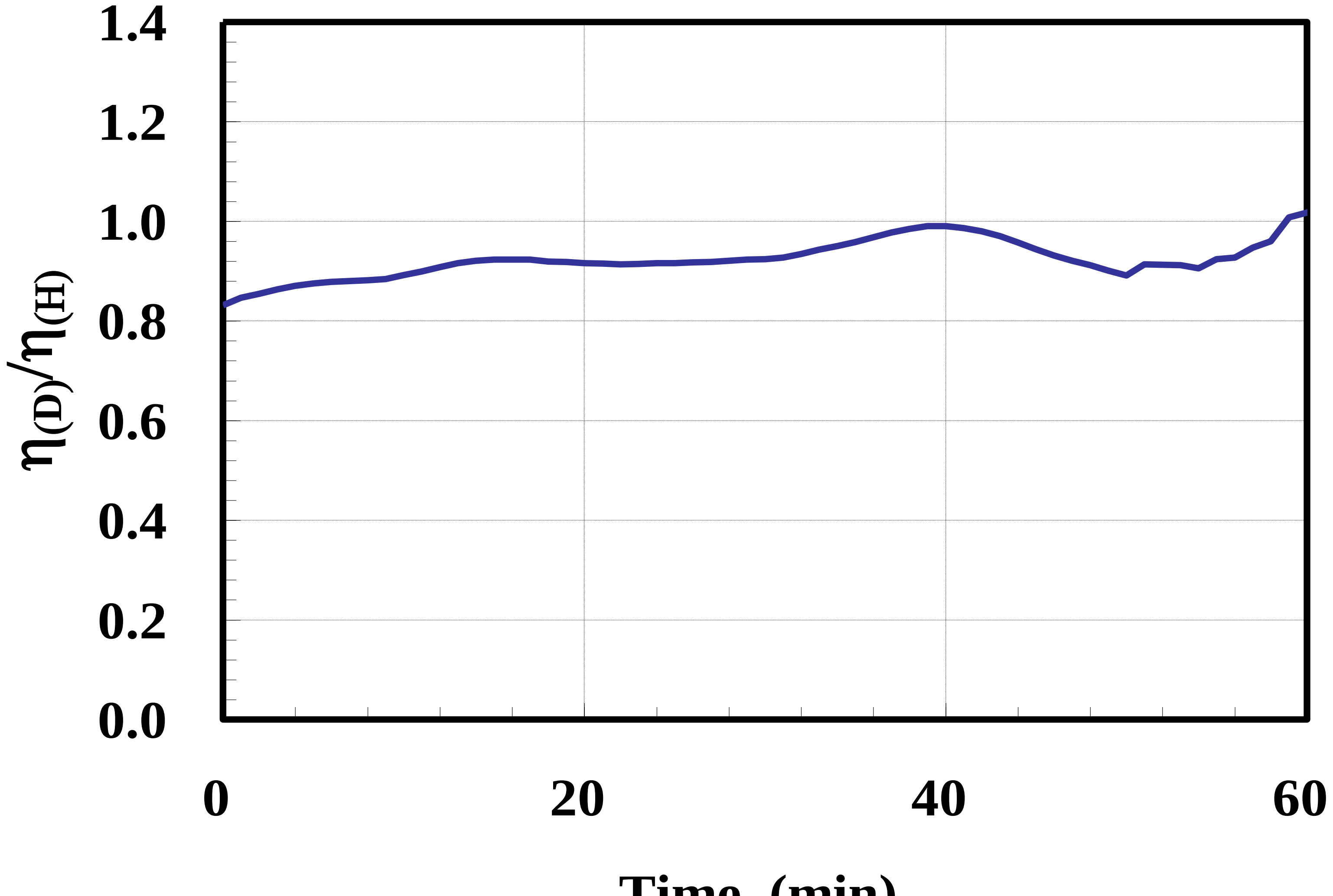


Ia Phase
Ib Phase
3.0
2.5
2.0
1.5
1.0
0.5
0.0
W D(H) (W), η D(H) (eV/D(H))
Eta-H
Eta-D
W-H
W-D
0
10
20
30
40
50
60
Time (min)

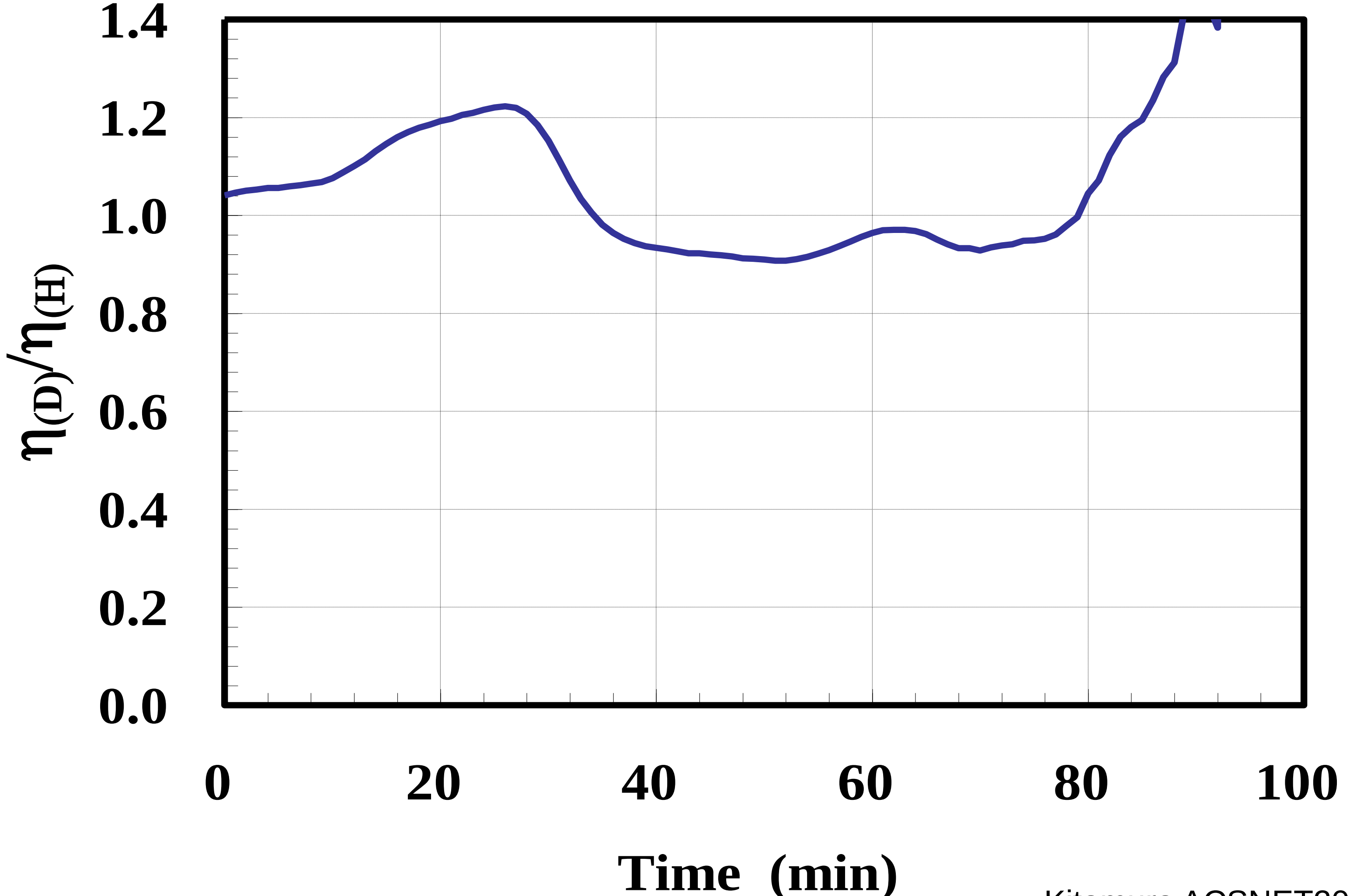
PB5,6#1 η_D/η_H



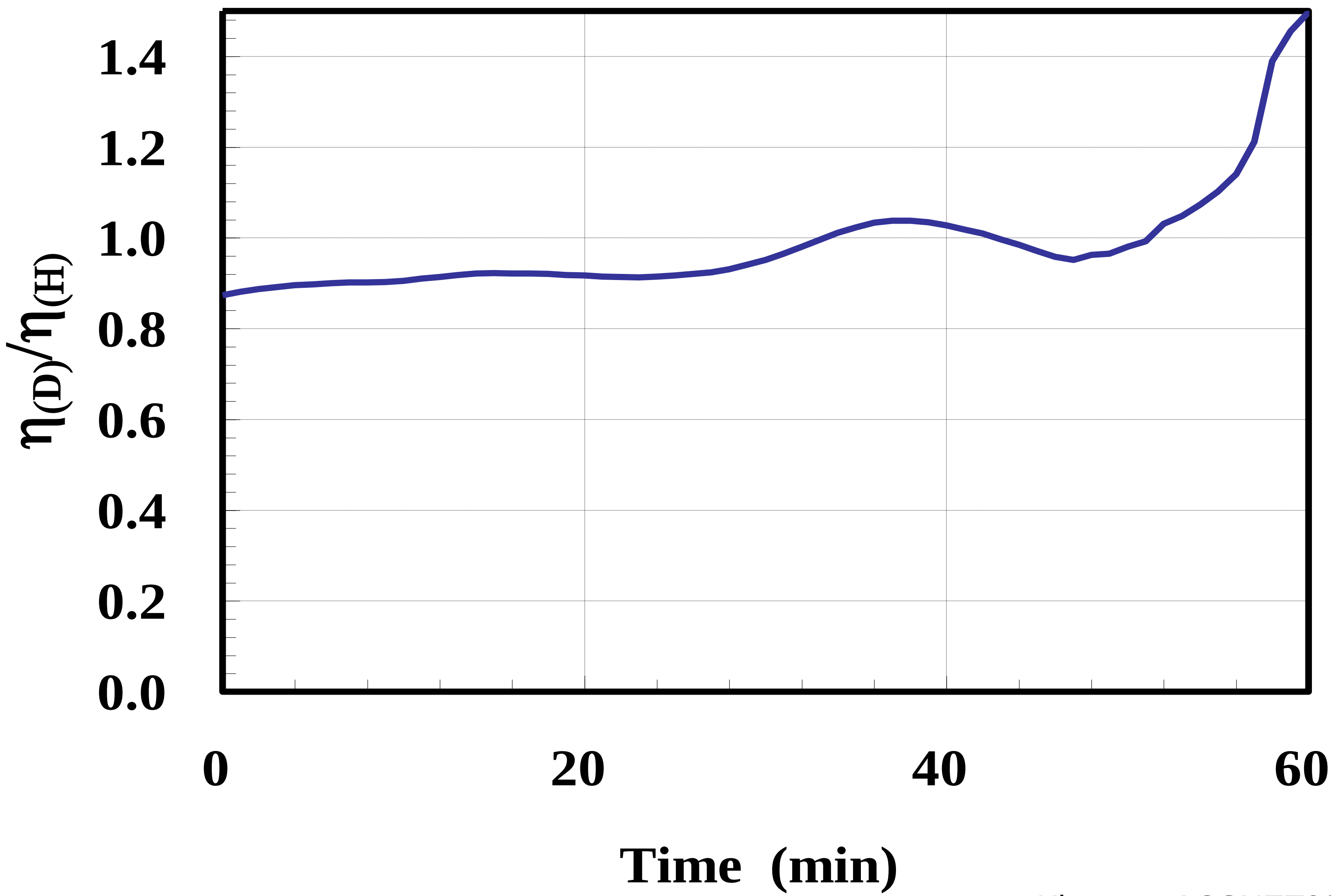
PB5,6#2 η_D/η_H



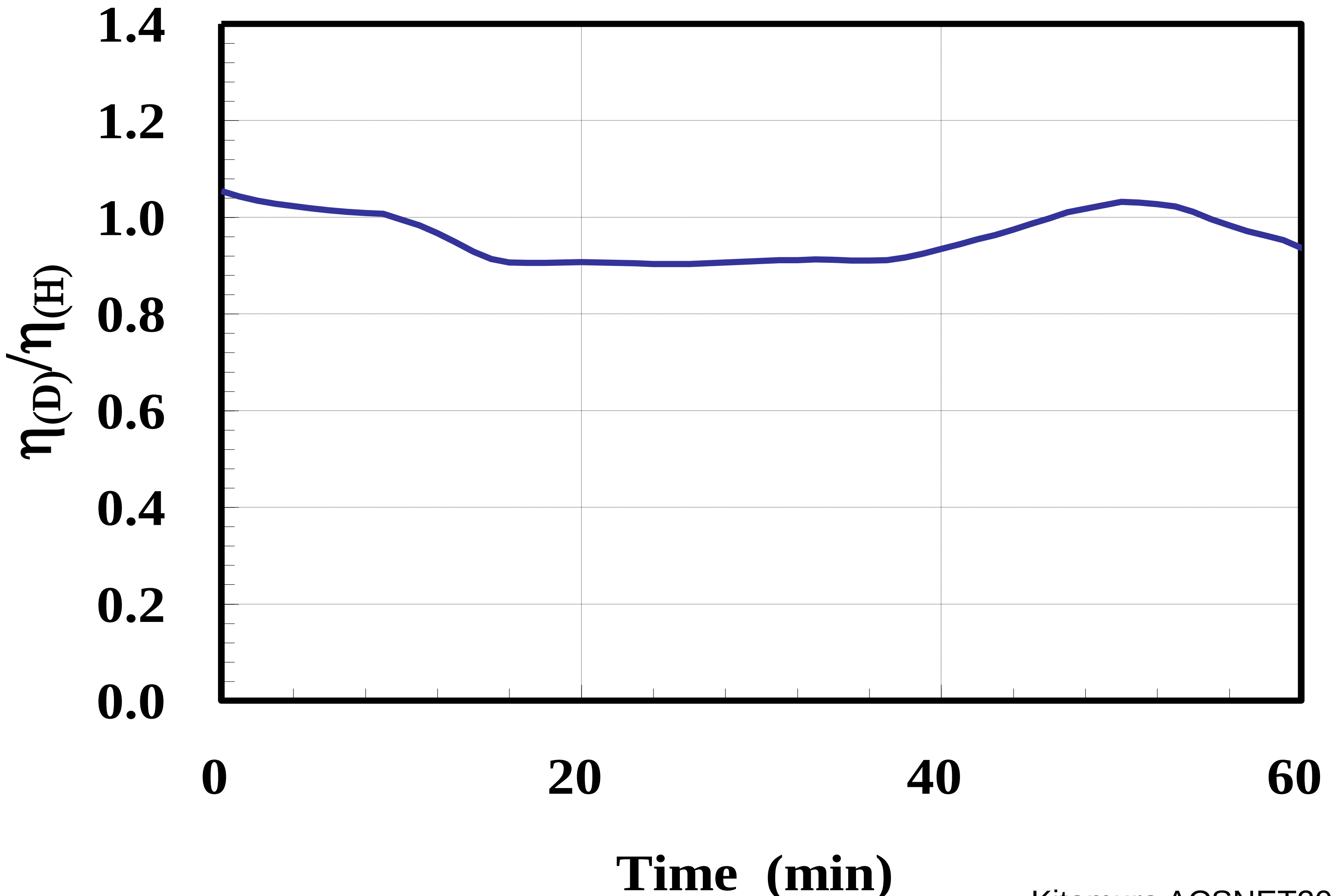
PB5,6#3 η_D/η_H



PB5,6#3A η_D/η_H



PB5,6#3_2 η_D/η_H



PB5,6 Integrated Data Table

		1st phase								desorption	
		PdO/Pd	E1			D(H)/Pd	QD	xQR		kJ	eV/atom-Pd
			kJ	kJ/g-Pd	eV/atom-Pd		eV/D(H)	eV/atom-Pd			
PB5,6#1	D2	unknown	8.00	0.80	0.88	1.11	0.80	0.00		-3.11	-0.34
	H2	unknown	8.16	0.82	0.90	1.19	0.76	0.00		-2.92	-0.32
PB5,6#3	D2	0.0203	5.97	0.60	0.69	1.01	0.65	0.03		-2.74	-0.30
	H2	0.0171	5.56	0.56	0.65	1.04	0.59	0.03		-2.98	-0.33
PB5,6#3A	D2	0.0000	1.57	0.16	0.17	0.61	0.28	0.00		-1.59	-0.17
	H2	0.0000	1.97	0.20	0.22	0.71	0.31	0.00		-2.01	-0.22
PB5,6#2	D2	0.0000	1.59	0.16	0.18	0.63	0.28	0.00		-1.63	-0.18
	H2	0.0000	2.02	0.20	0.22	0.72	0.31	0.00		-2.05	-0.23
PB5,6#3_2	D2	0.0047	2.56	0.26	0.29	0.71	0.40	0.01		-1.87	-0.21
	H2	0.0047	2.93	0.29	0.33	0.80	0.40	0.01		-2.27	-0.25

Summary of the results obtained so far

(1) PZ sample (Santoku; $Pd_{36}Zr_{64}$)
- very large specific energy of absorption/adsorption, $E_1 \sim 2$ eV/Pd,
- very large loading ratio, D(H)/Pd ~ 1.5 - 2.3,
- very large hydridation energy, $Q_{D(H)}$ ~1.0 eV/D(H),
- 1a-phase; near-surface phenomenon with η(1a) = 1.33(1.15) eV/D(H), while 1b-phase; bulk characteristics with η(1b) = 0.47(0.41) eV/D(H),
- deteriorates after an absorption run, and recovers after forced oxidization.

(2) PP sample (Nilaco; 0.1-μmϕ)
- $E_1 \sim 0.2$ eV/Pd, D(H)/Pd ~ 0.6, $Q_{D(H)} \sim 0.3$ eV/D(H),
- less prominent 1a-phase, and less effective enhancement by oxidization.

(3) PB sample (Nilaco; Pd-black)
- intermediate characteristic values.

(4) PNZ (Santoku; $Pd_{11}Ni_{25}Zr_{64}$, $Pd_2Ni_{44}Zr_{54}$) and NZ ($Ni_{36}Zr_{64}$)
- absorption in proportion to Pd content.

(5) PNZ2B (B.Ahern; $Pd_4Ni_{29}Zr_{67}$; melt spinning)
- absorption occurs at R.T. with $E_1 \sim 2.0$ (1.8) eV/atom-[Pd·Ni],
- D(H)/[Pd·Ni] ~ 3.3 (3.3),
- $Q_{D(H)}$ (and η) ~ 0.55 (0.50) eV/atom-D(H),
- 1a-phase / 1b-phase ; indistinguishable,
- modest deterioration after absorption runs.