

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

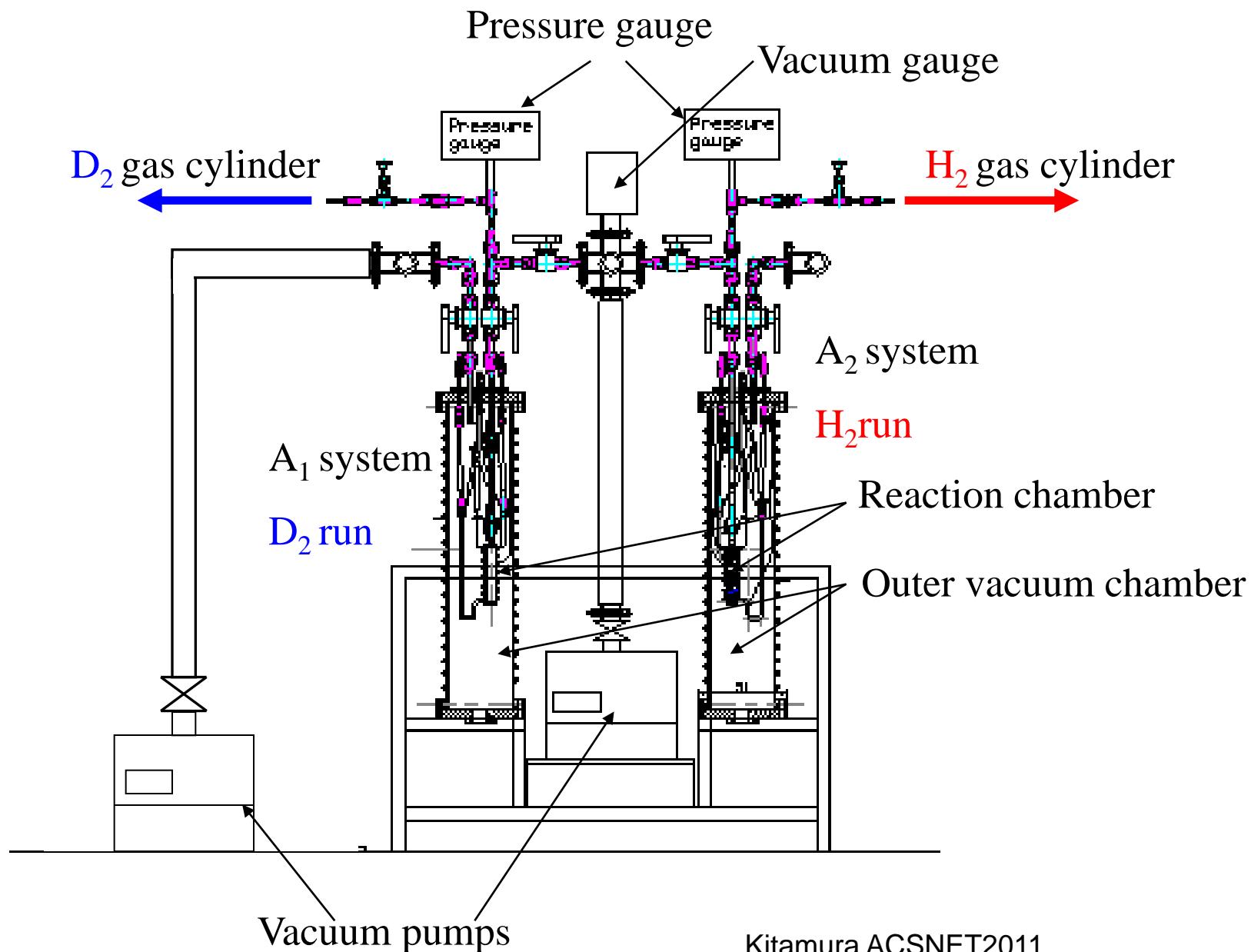
(Technova Inc)

To be presented at ACS-NET 2011, Anaheim

Outline

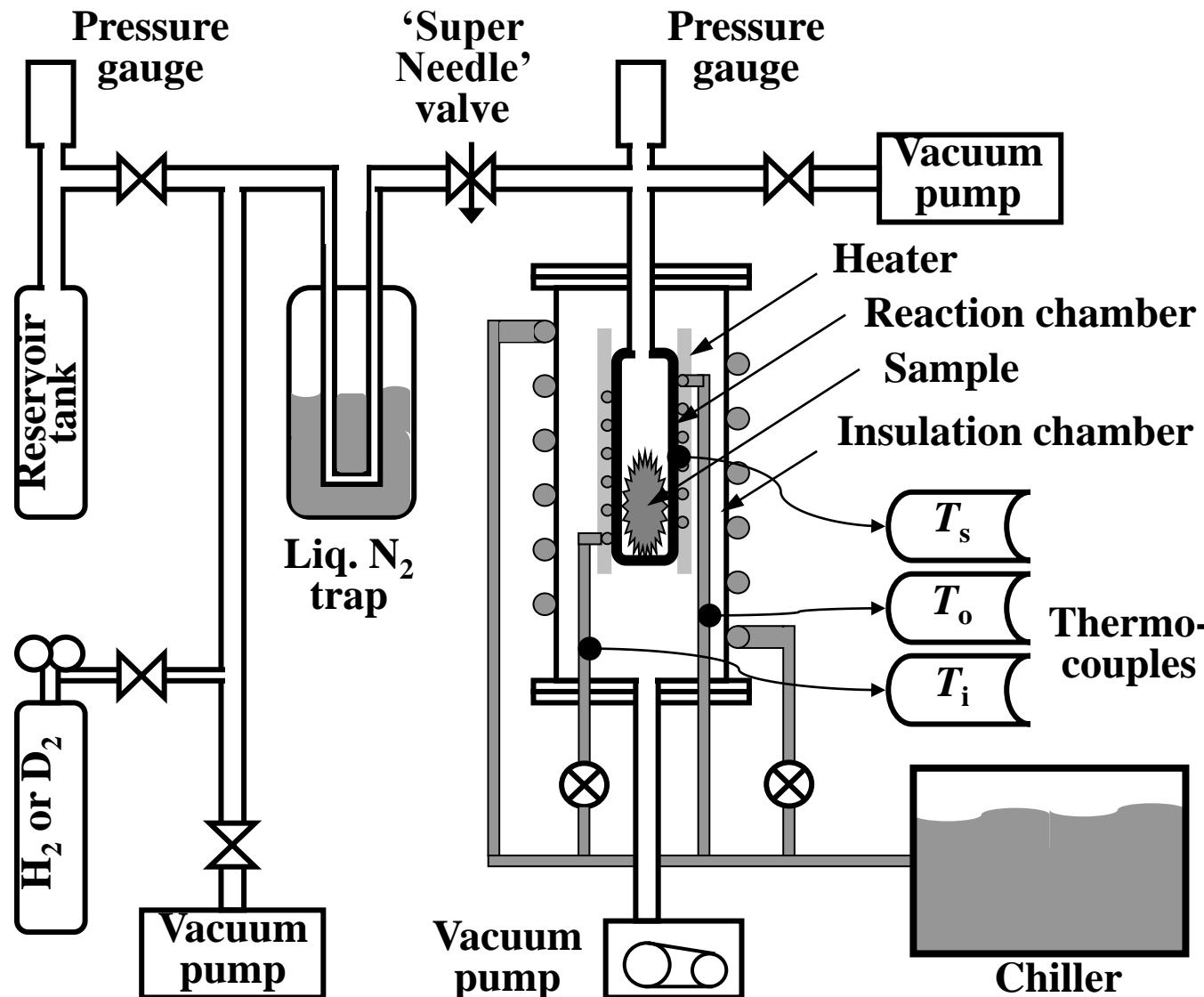
- Extensive measurements of heat release under hydrogen isotope absorption/adsorption of 7 kinds (PP, PB, PZ, NZ, PNZ-I, PNZ-II, PNZ2B) of Pd nano-powders in a twin gas charging system have been made by Kobe group in 2010-2011.
- Anomalies in heat and D(H)-absorption observed by Pd (and Pd-Ni) nano-powders dispersed into/onto ZrO₂ 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.3



Schematic of one of the twin absorption system.

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Samples tested: 7 kinds

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	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

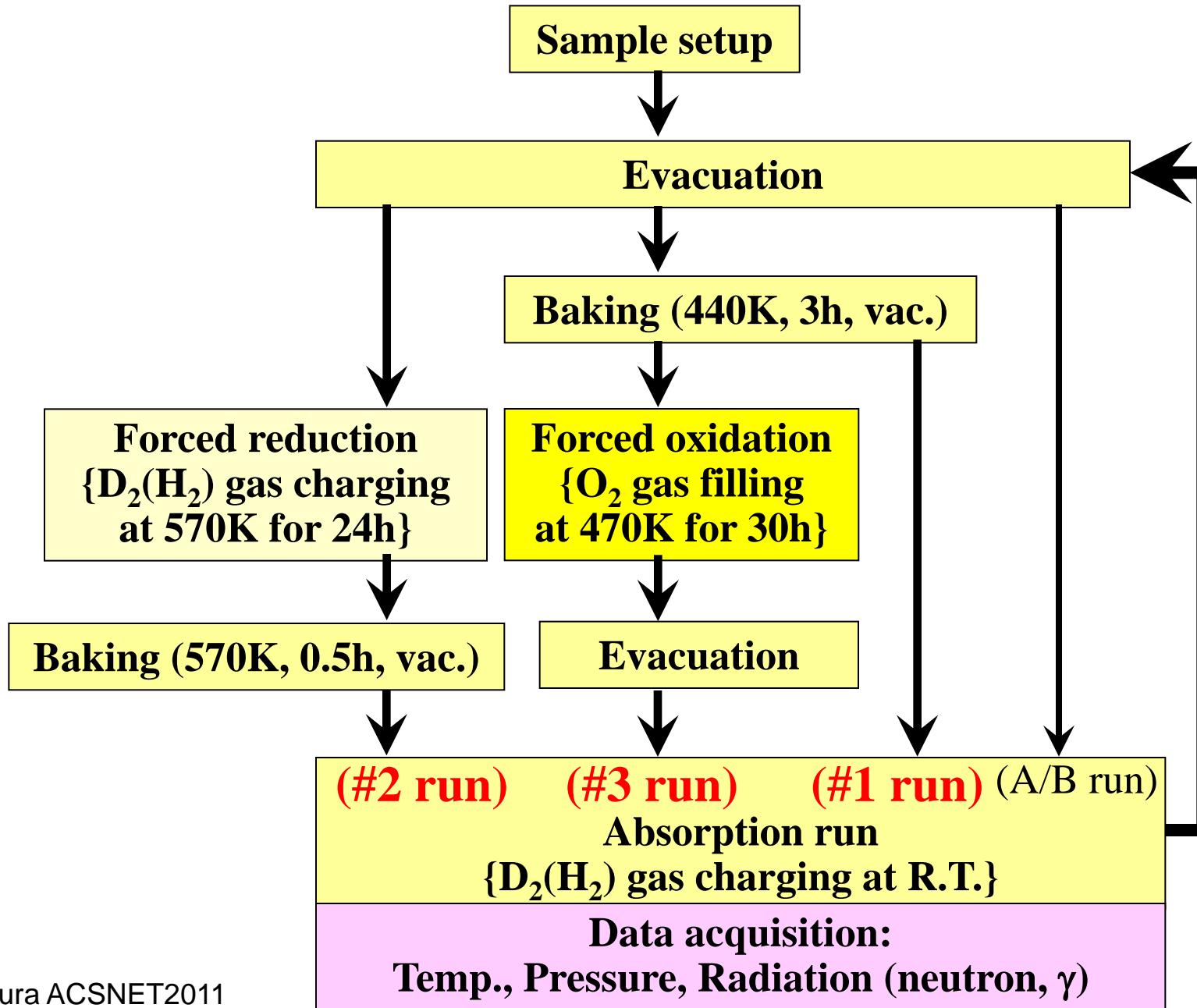
[1] Phys. Lett. A, 373 (2009) 3109-3112.

[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.

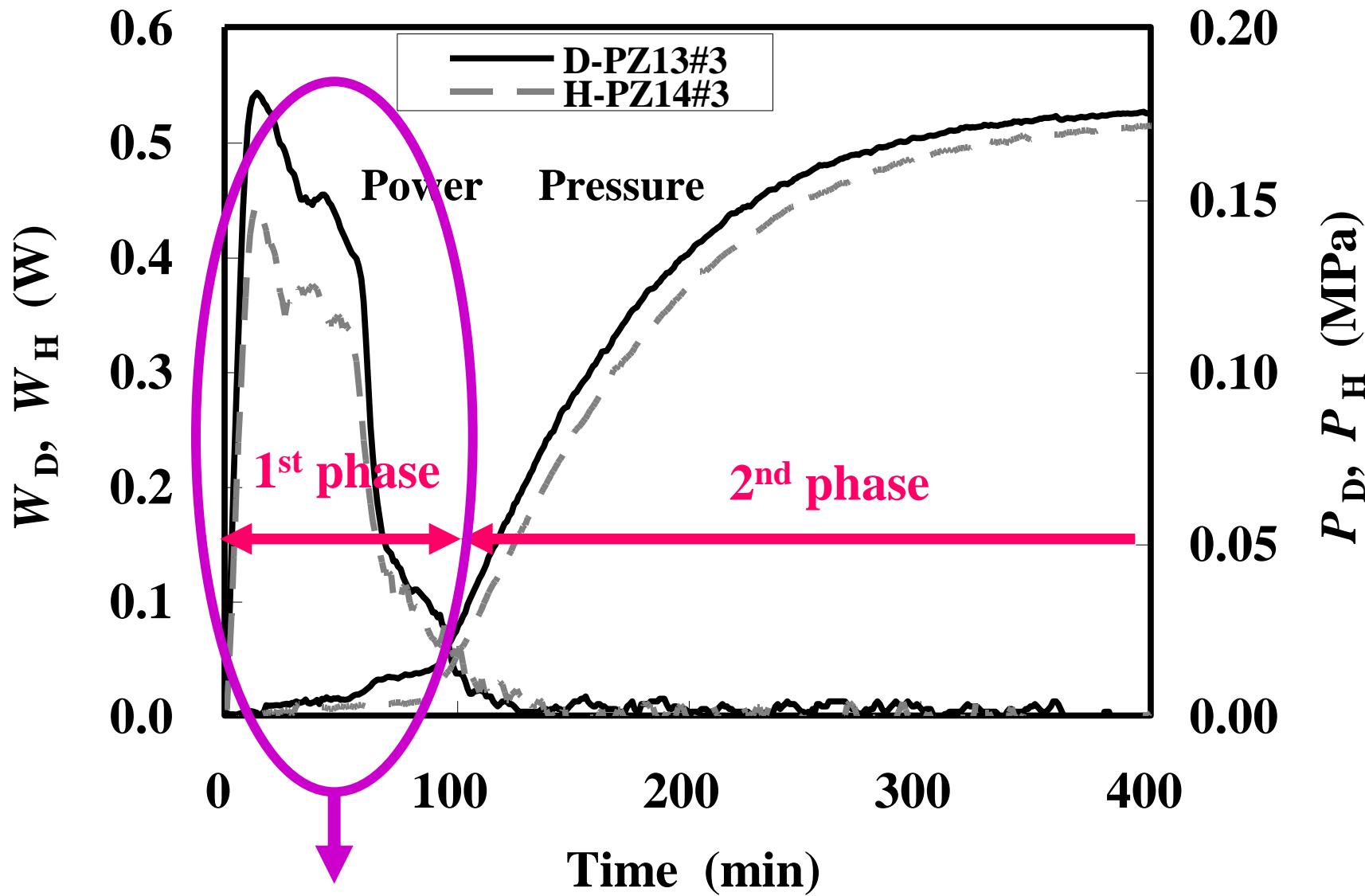
Experimental procedure

6



Heat Evolution appeared in Two Phases: for PZ Samples

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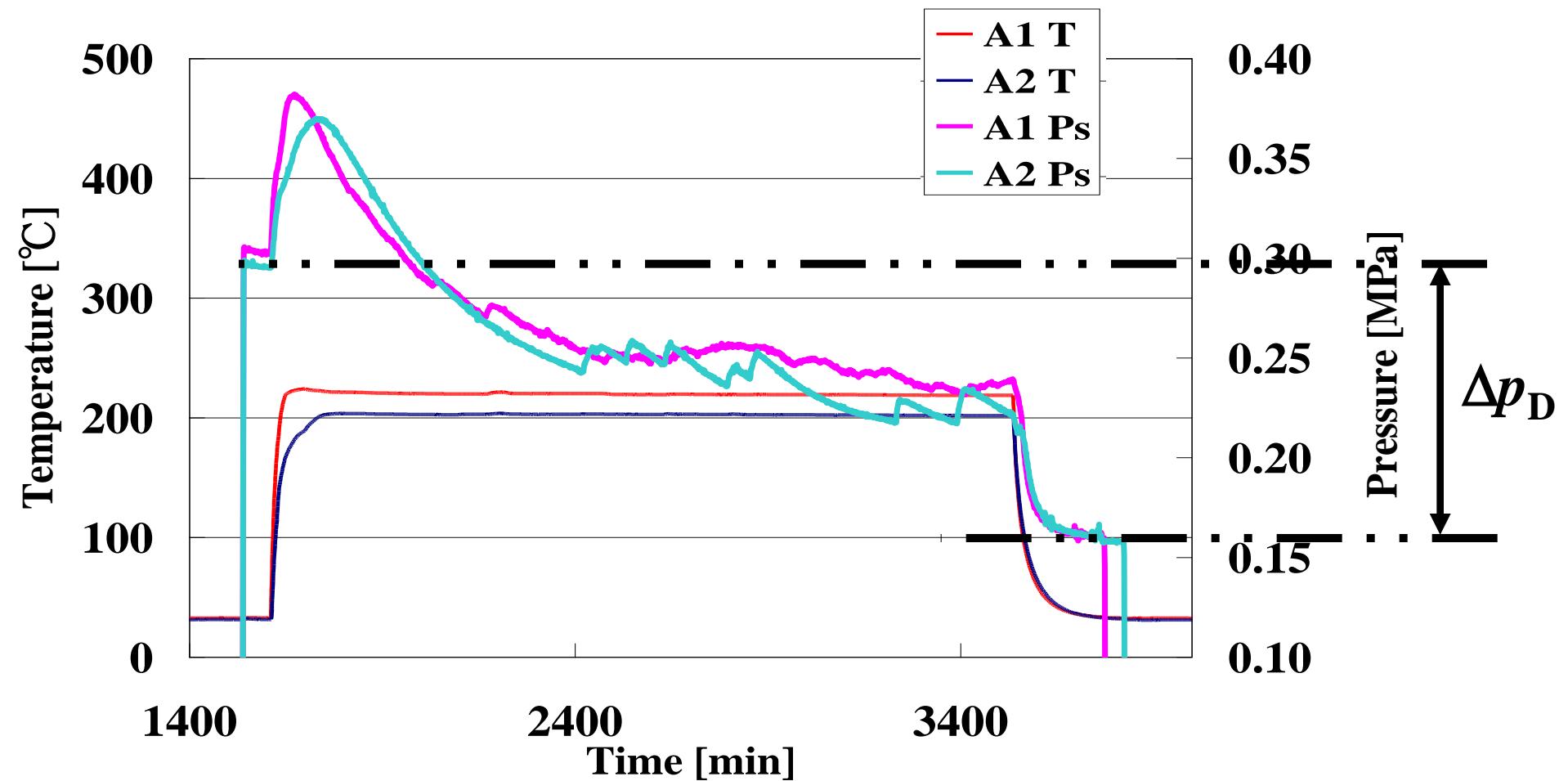


Integration gives the 1st phase specific output energy E_1 .

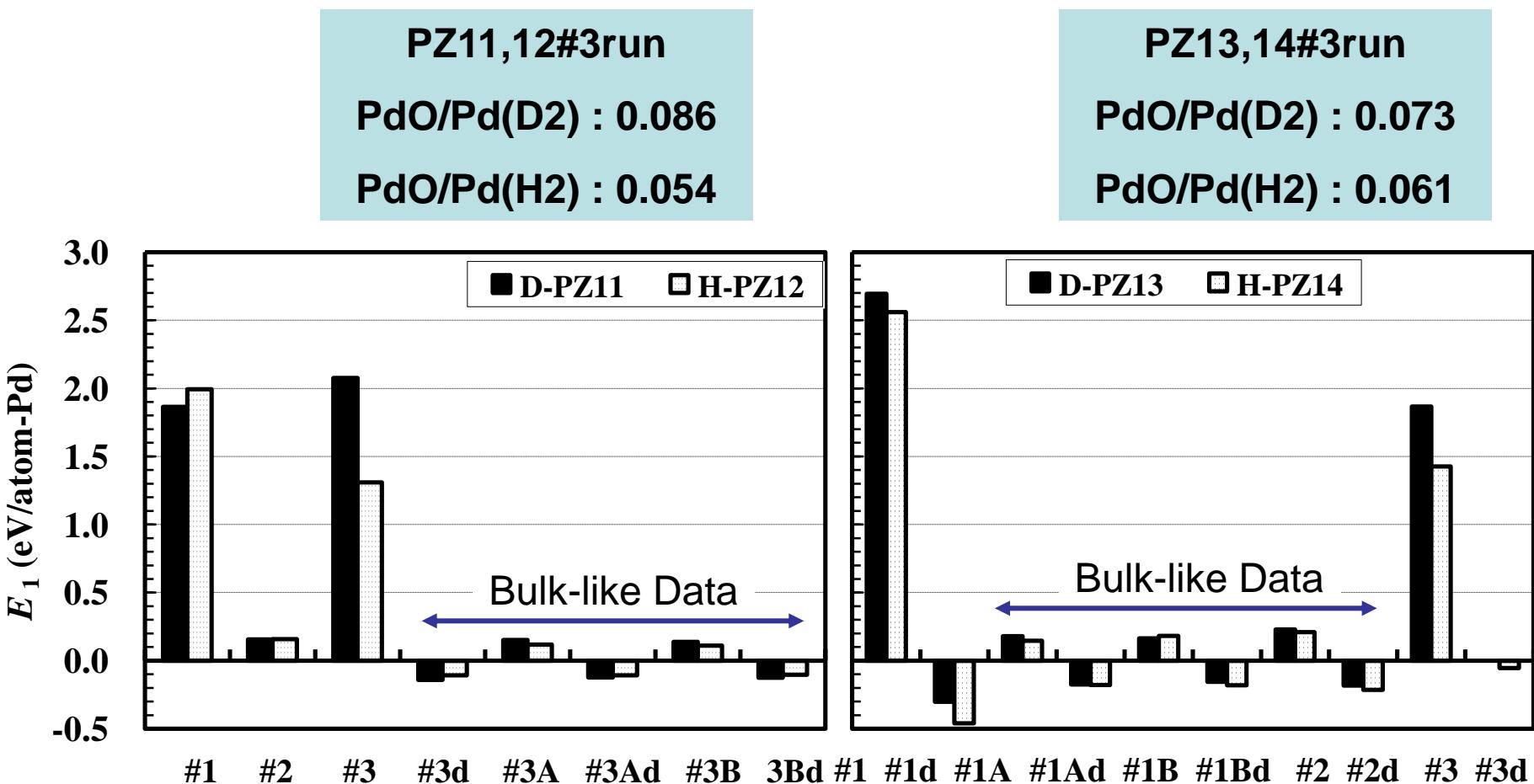
Forced oxidation

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by introducing O₂ 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 oxidation, x for Pd+($x/2$)·O₂→PdO_x



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

PZ11,12#3run

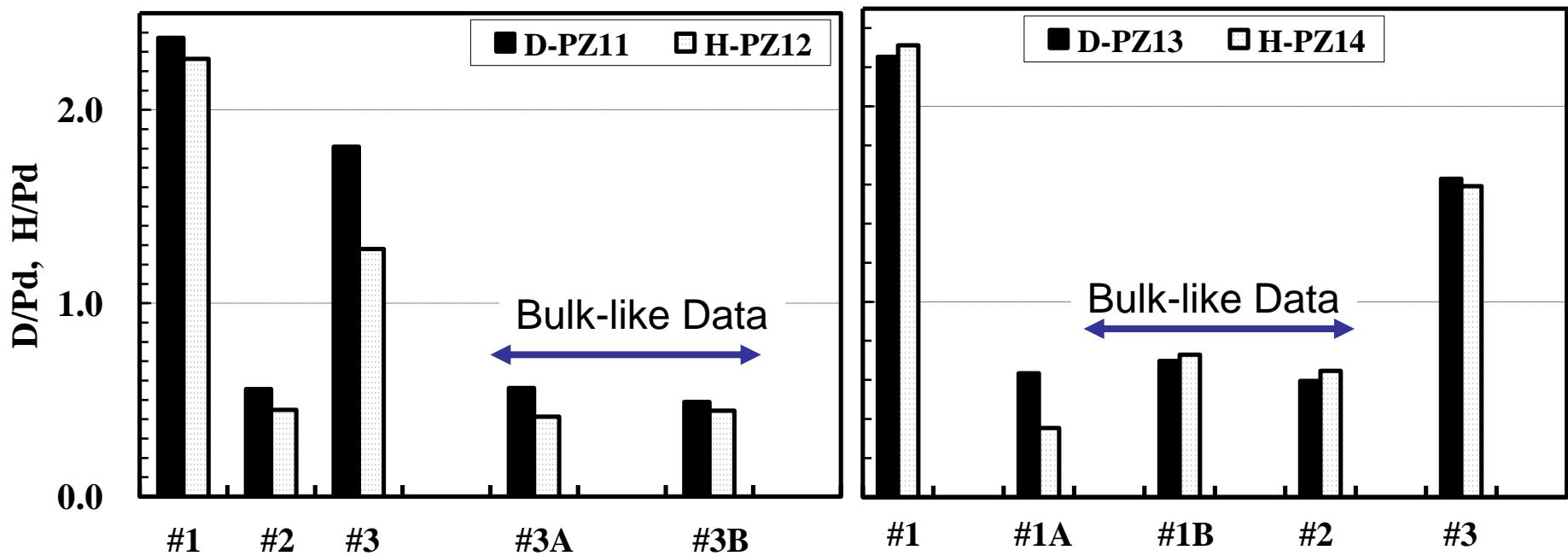
$\text{PdO/Pd(D}_2\text{)} : 0.086$

$\text{PdO/Pd(H}_2\text{)} : 0.054$

PZ13,14#3run

$\text{PdO/Pd(D}_2\text{)} : 0.073$

$\text{PdO/Pd(H}_2\text{)} : 0.061$



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

PZ11,12#3run

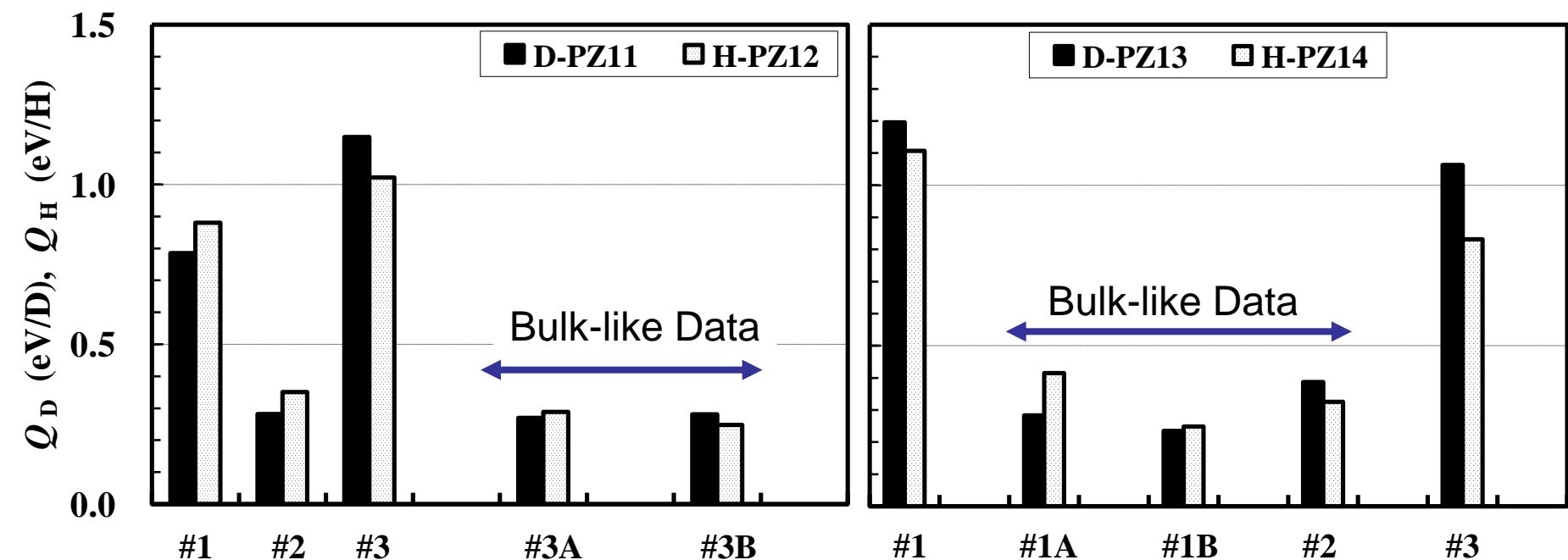
PdO/Pd(D₂) : 0.086

PdO/Pd(H₂) : 0.054

PZ13,14#3run

PdO/Pd(D₂) : 0.073

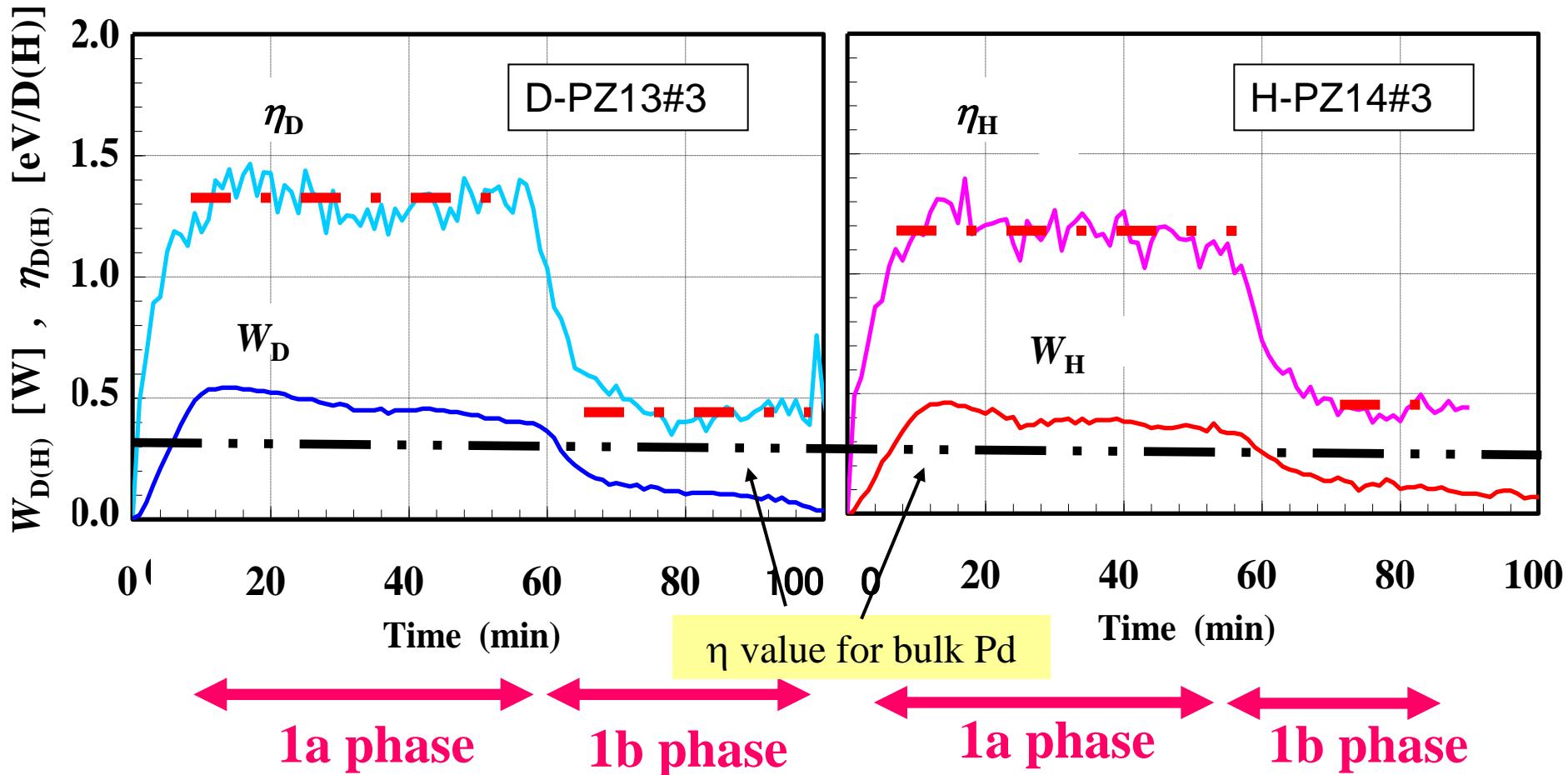
PdO/Pd(H₂) : 0.061



**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 1a Phases

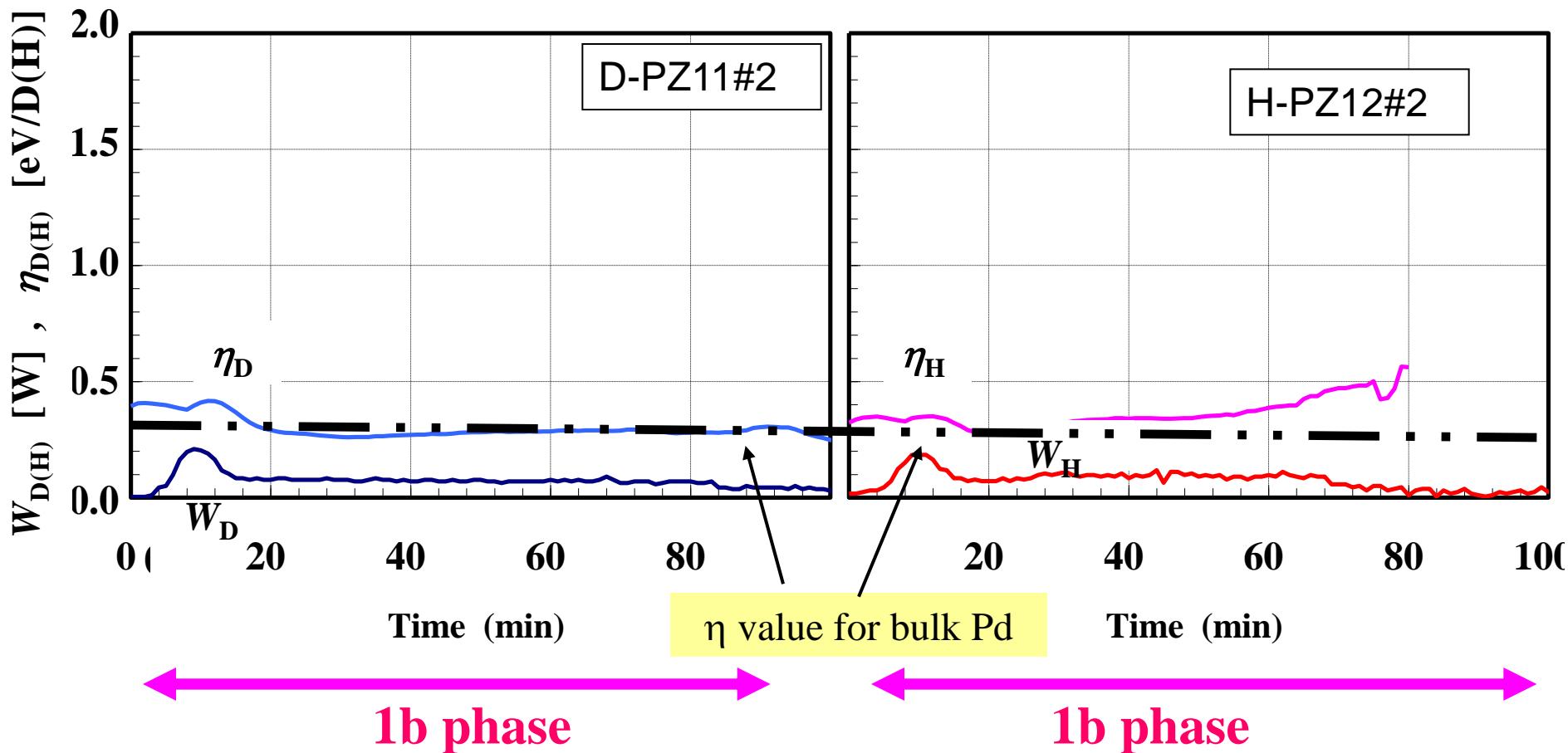
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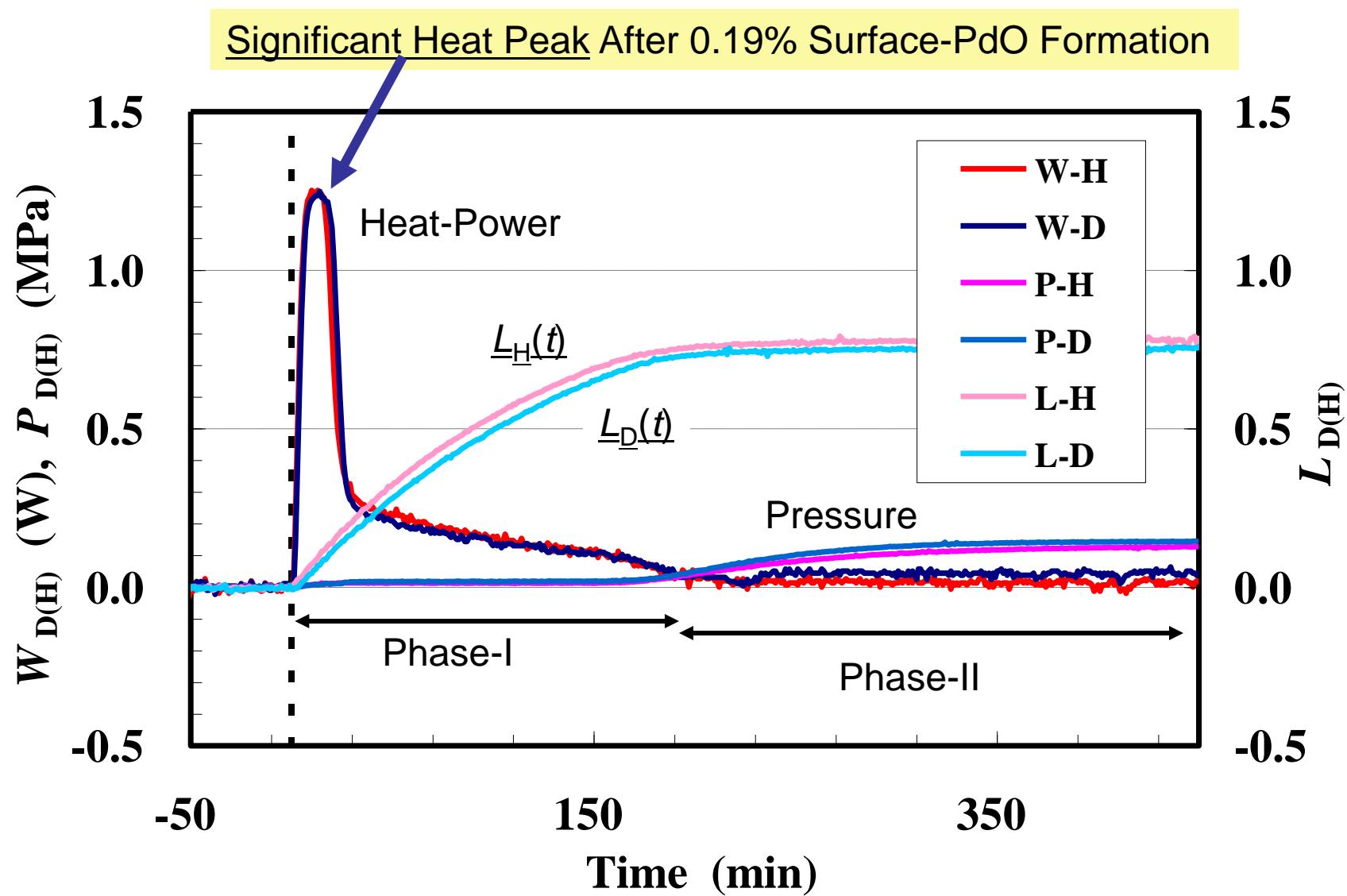
Typical variation of the specific sorption energy, η_D (η_H), compared with that of the power, W_D (W_H), in the #3 run for the PZ13(14) sample.

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

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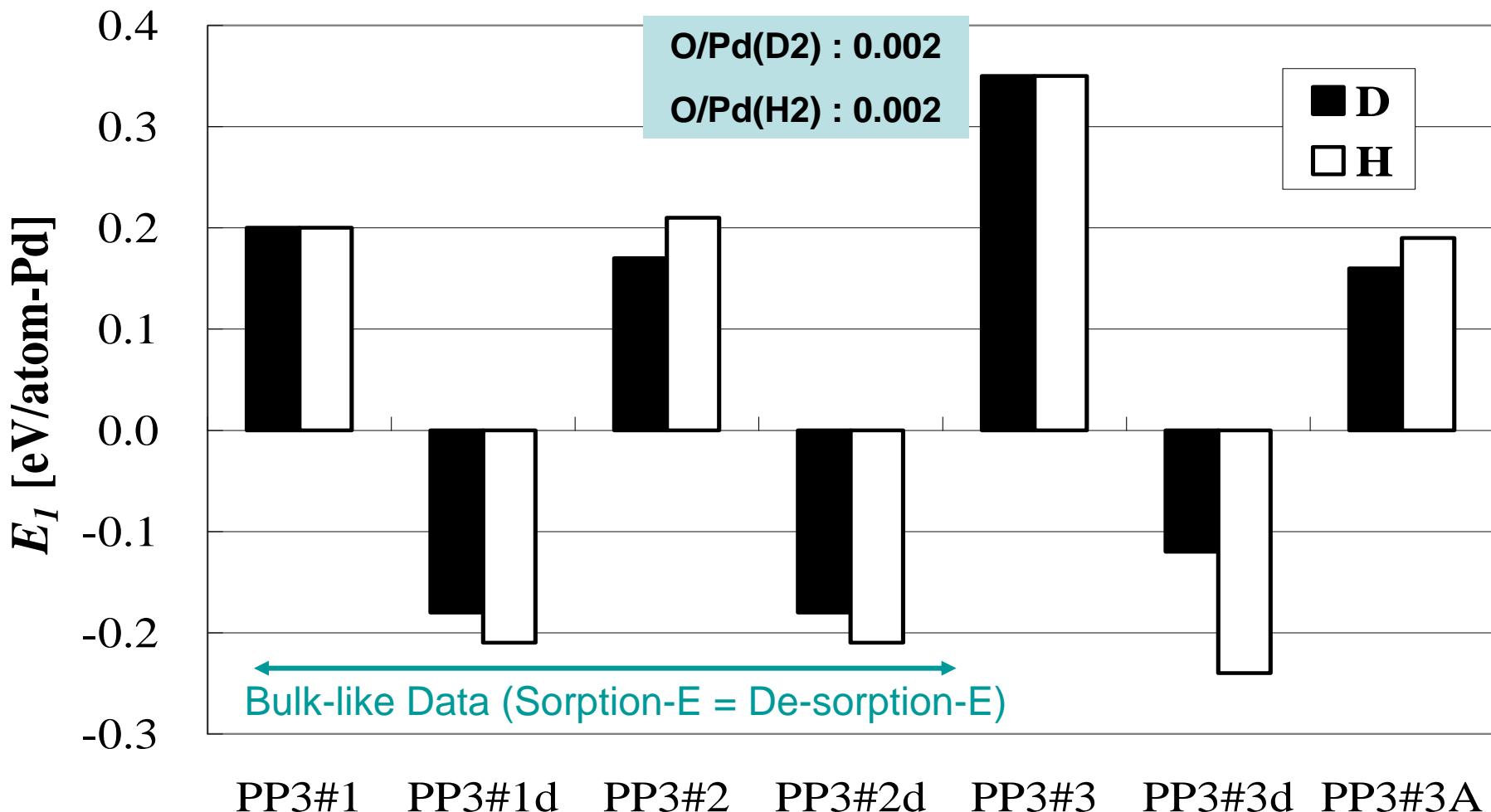
Typical variation of the specific sorption energy, η_D (η_H), compared with the power, W_D (W_H), in the #2 run for the PZ11(12) sample.



PP3,4 sample (100-nm ϕ Pd)

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; Show the similar (but smaller) effect of oxidization

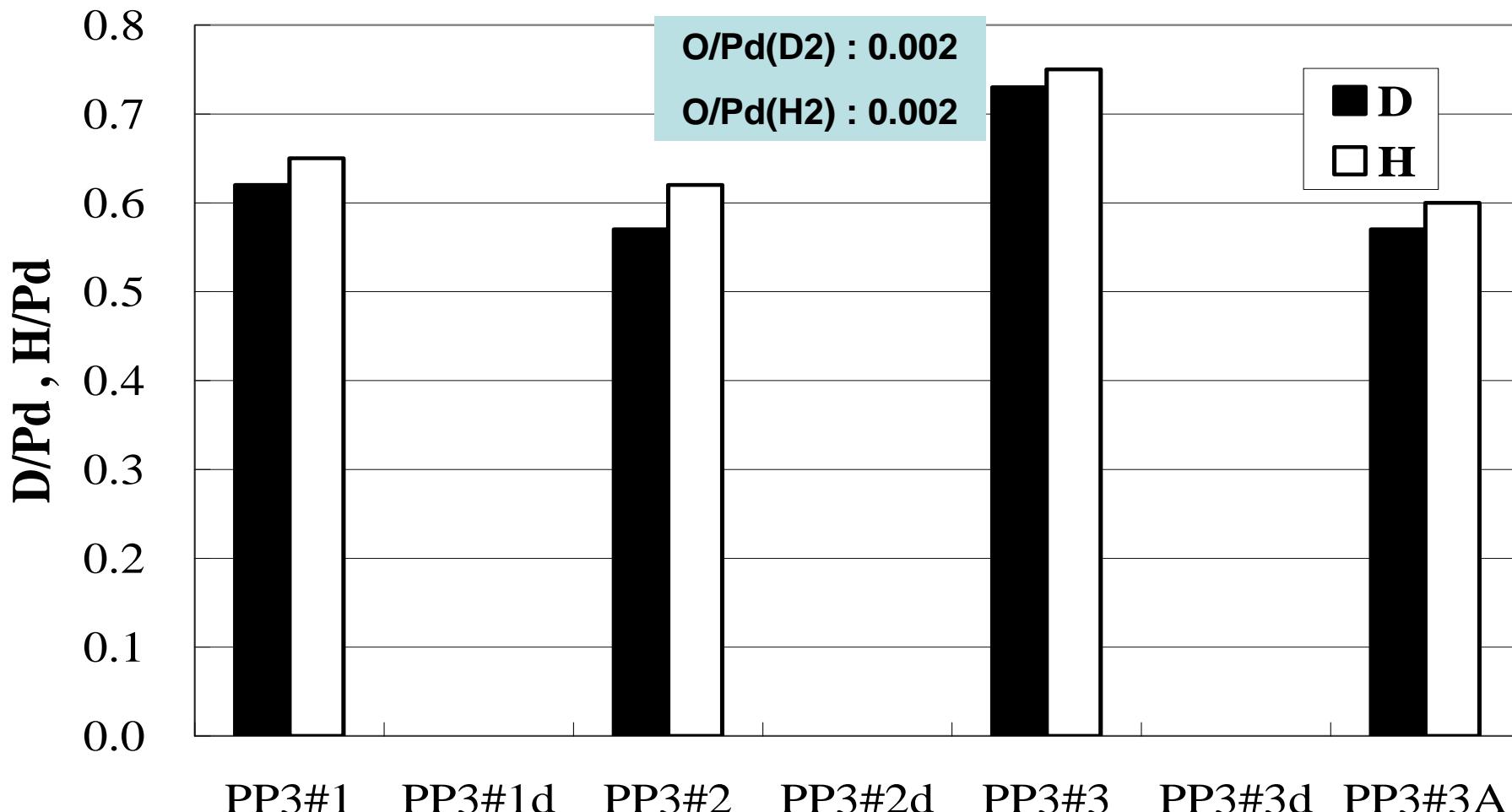


Comparison of the 1st-phase specific output energy E_1 for the runs D(H)-PP3(4)#1 through D(H)-PZ3(4)#3A

PP3,4 sample (100-nm ϕ Pd)

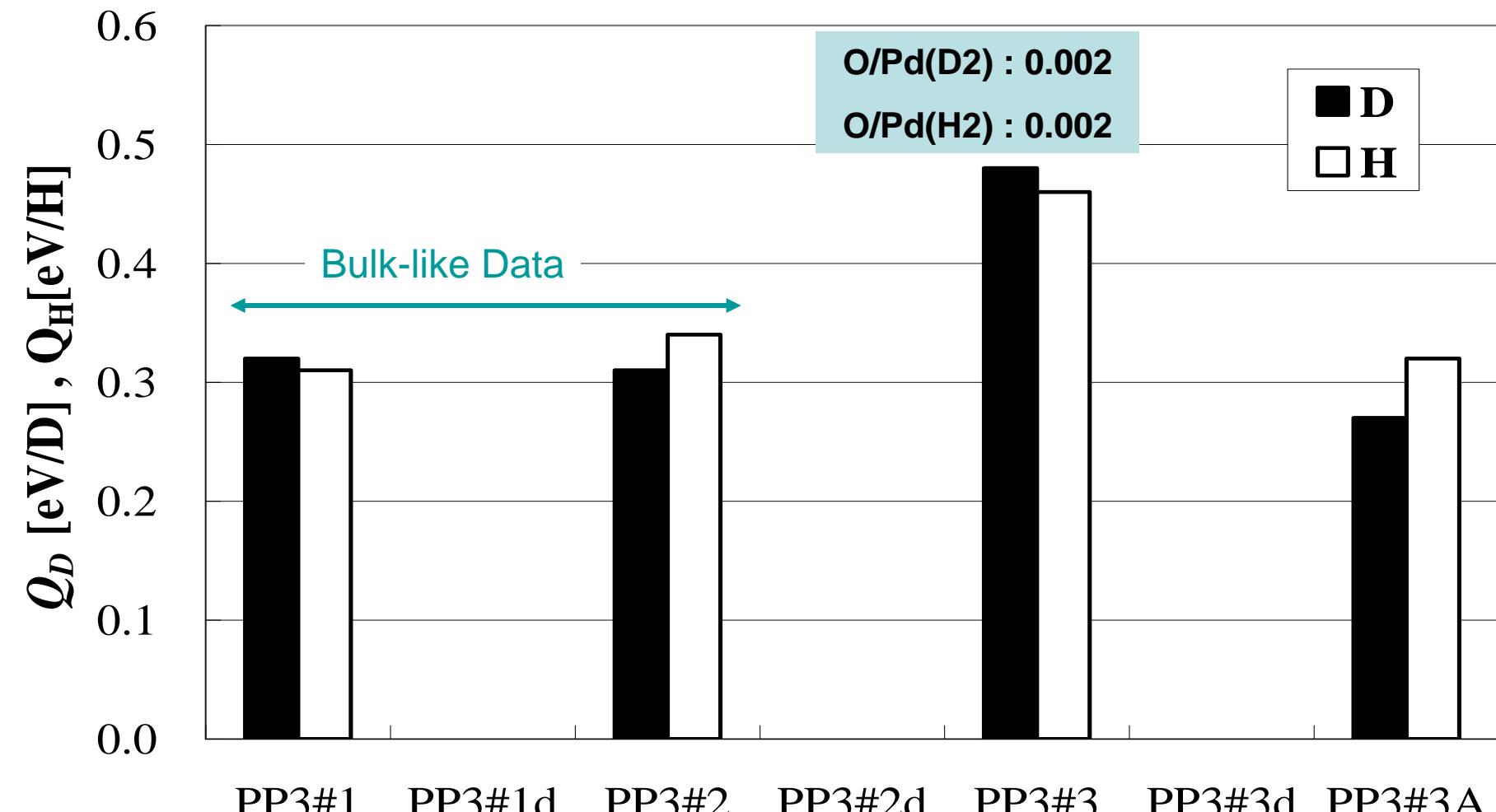
20

; 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

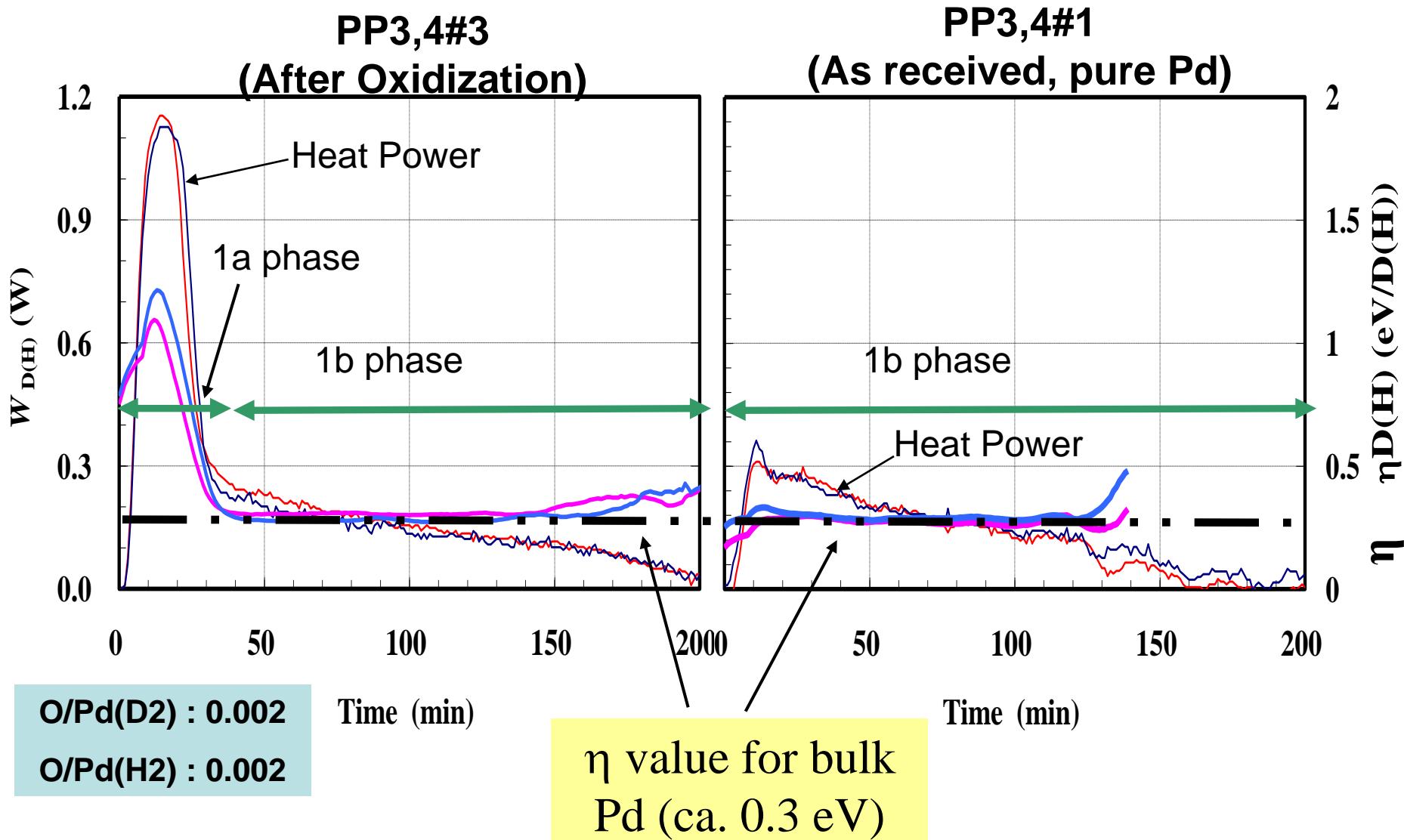
; Show the similar (but smaller) effect of oxidization



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

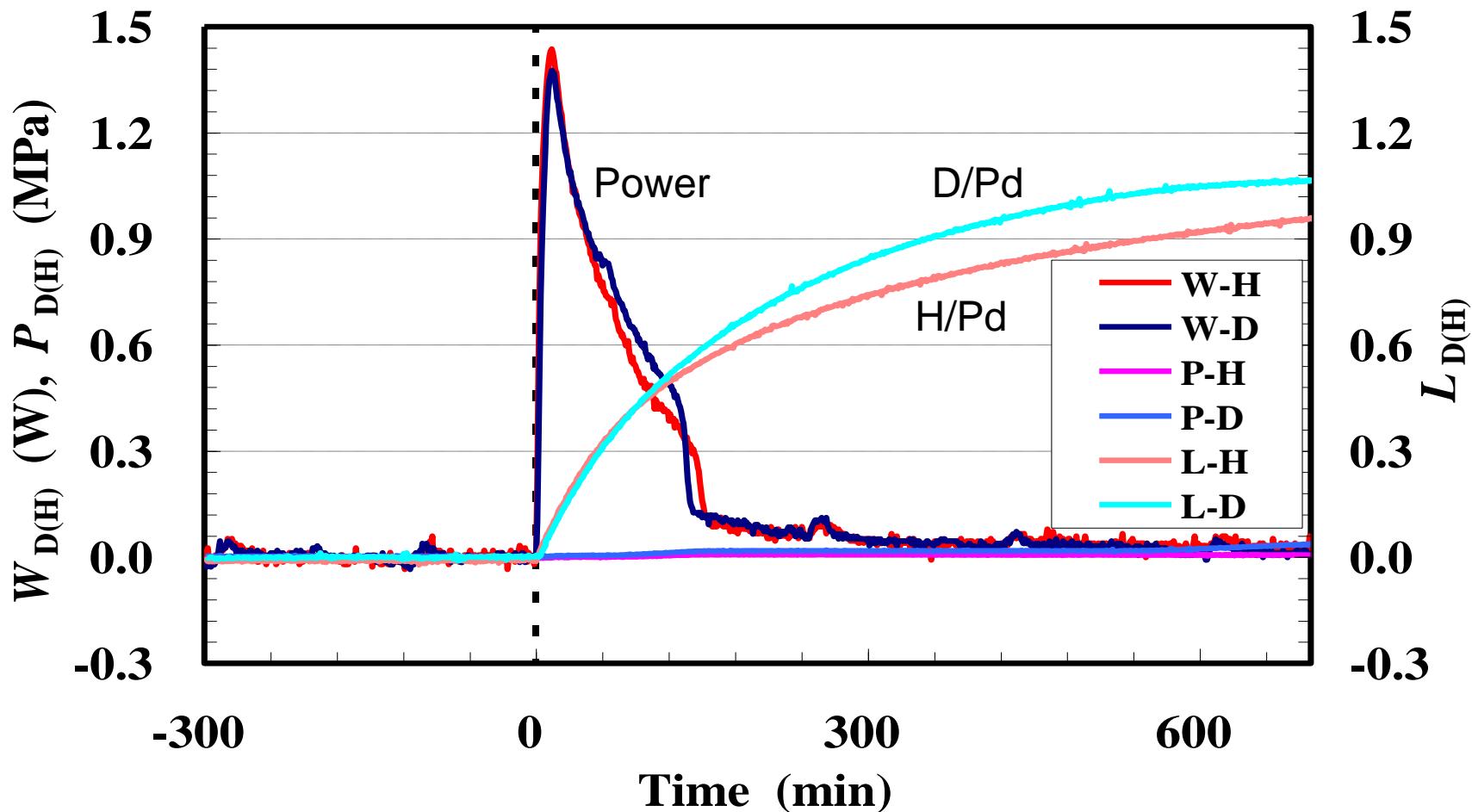
PP3,4 #1(right) and #3(left) (100-nm ϕ Pd):

Effect of slight PdO layer is great (Ia) cf. bulky (Ib).

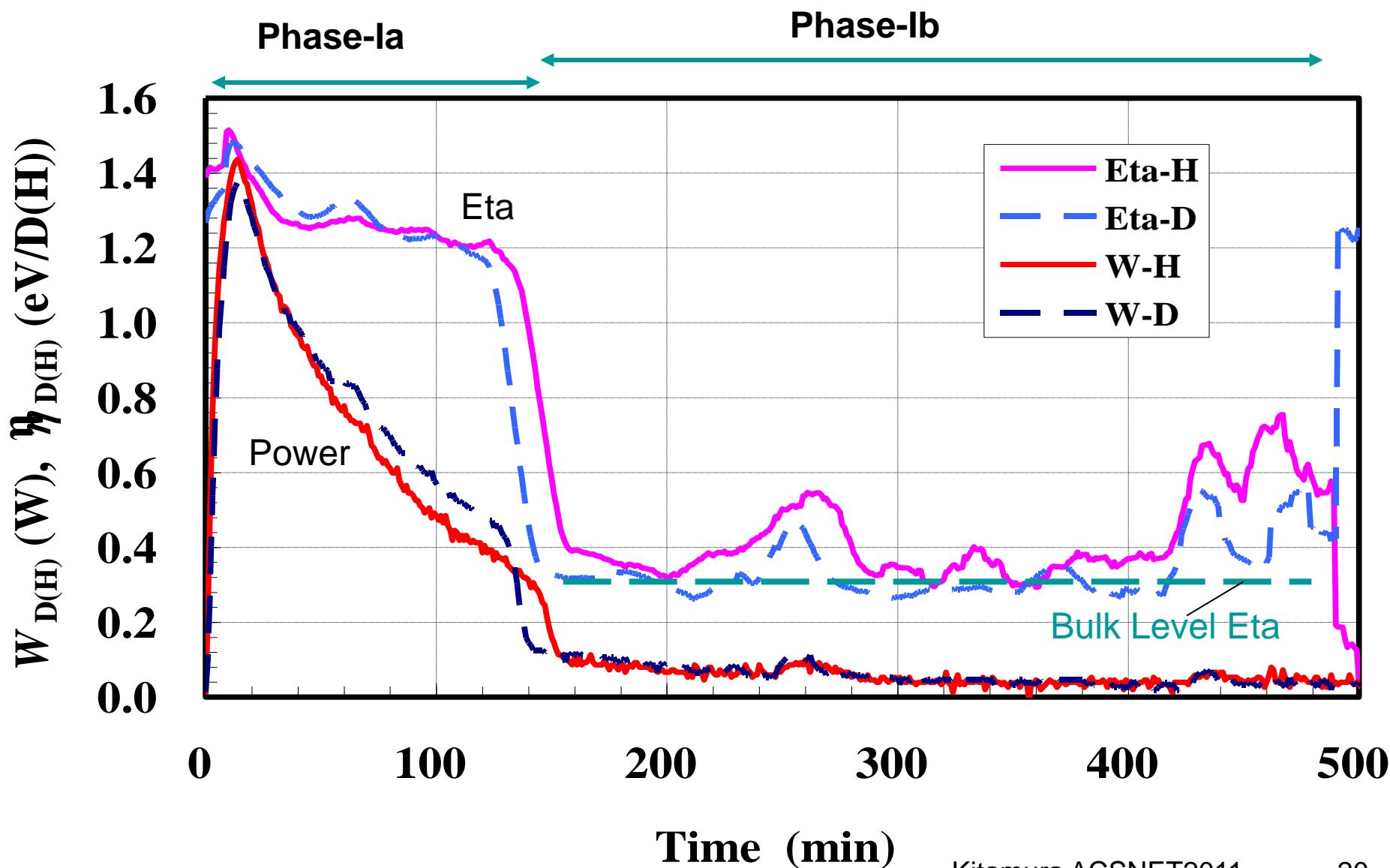


Palladium Black Samples

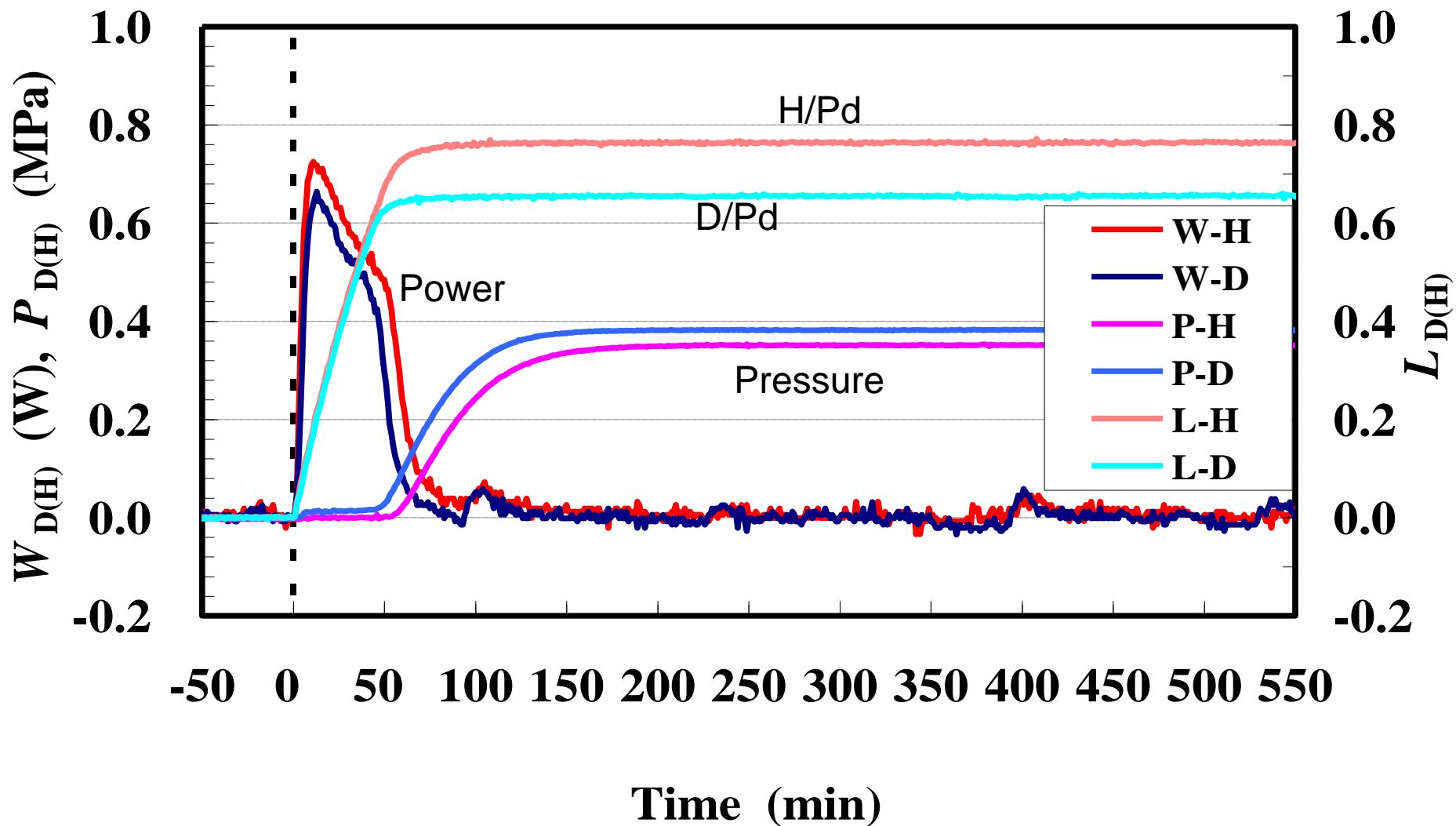
PB5,6#1: Virgin Runs (10g each)



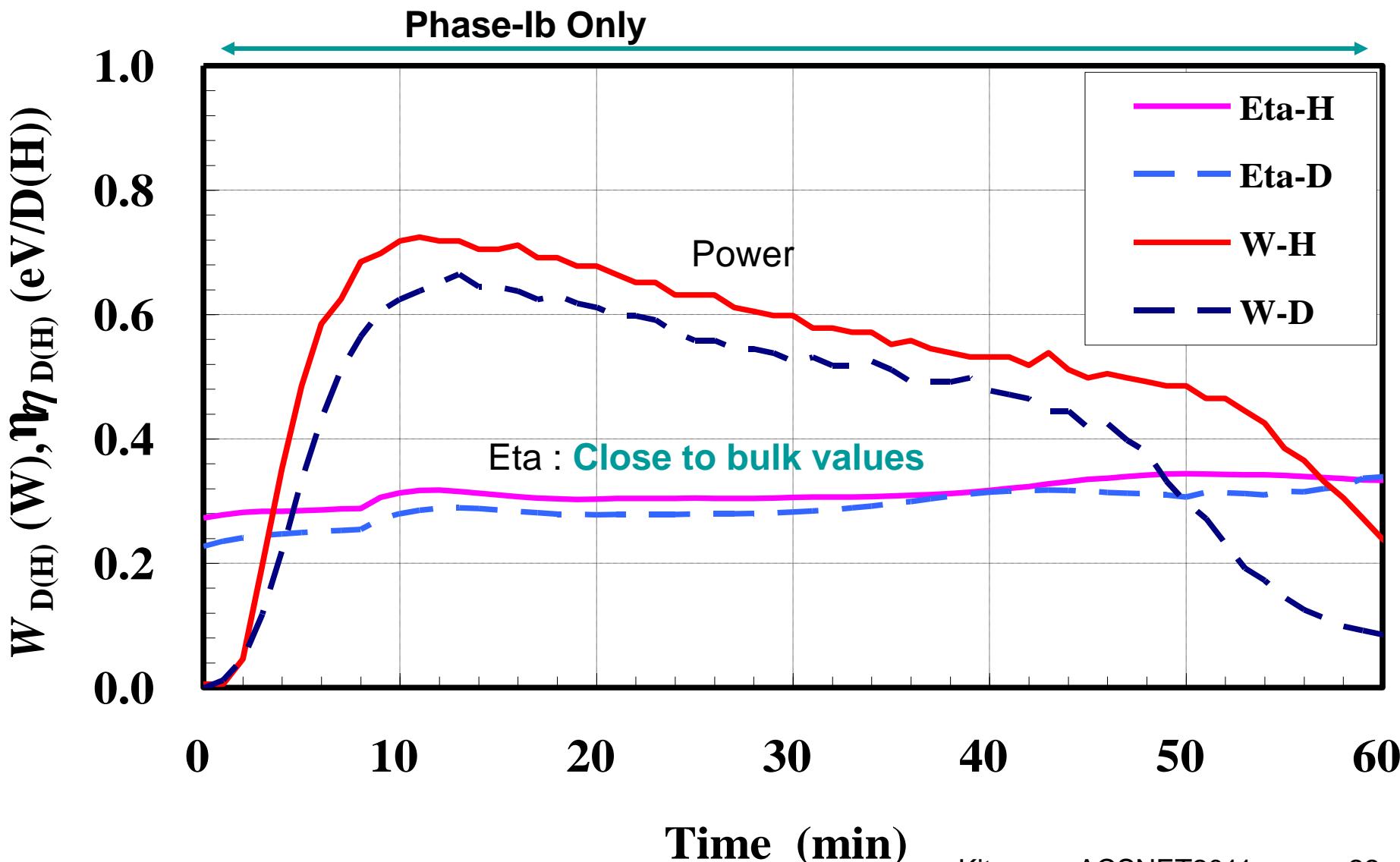
PB5,6#1; η -values vs. power



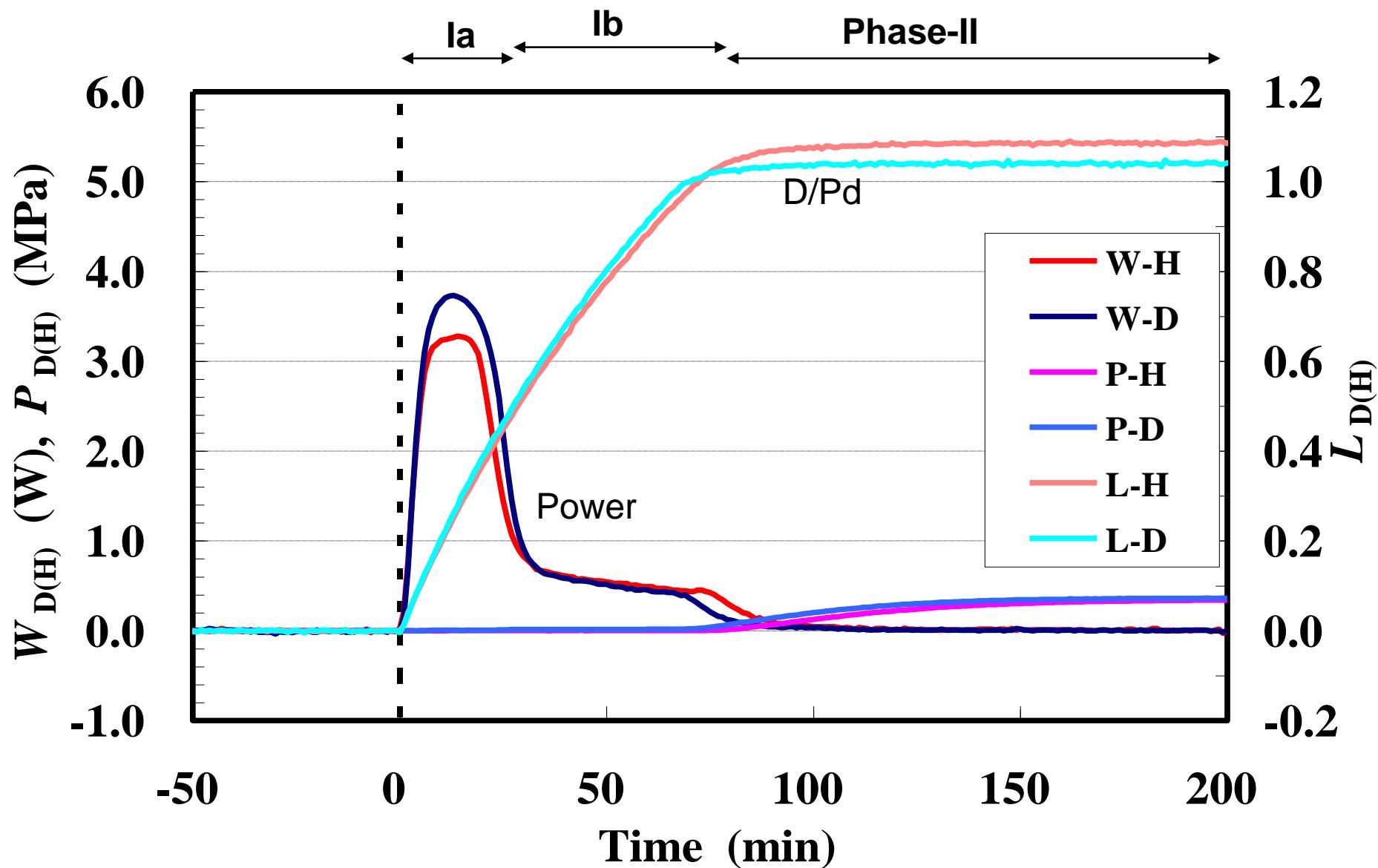
PB5,6#2; After Forced De-Oxidization



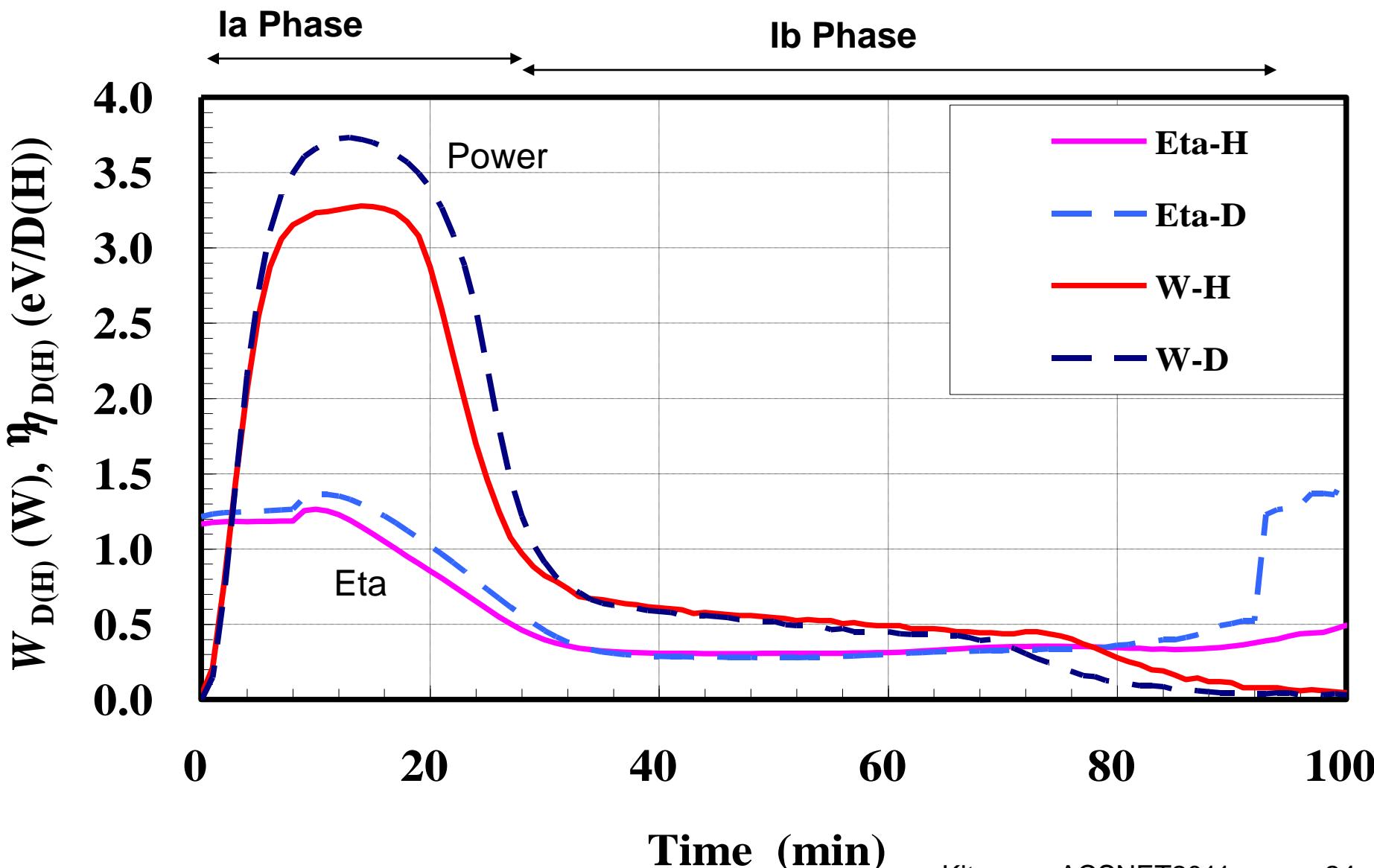
PB5,6#2 η -values vs. powers after De-oxidization



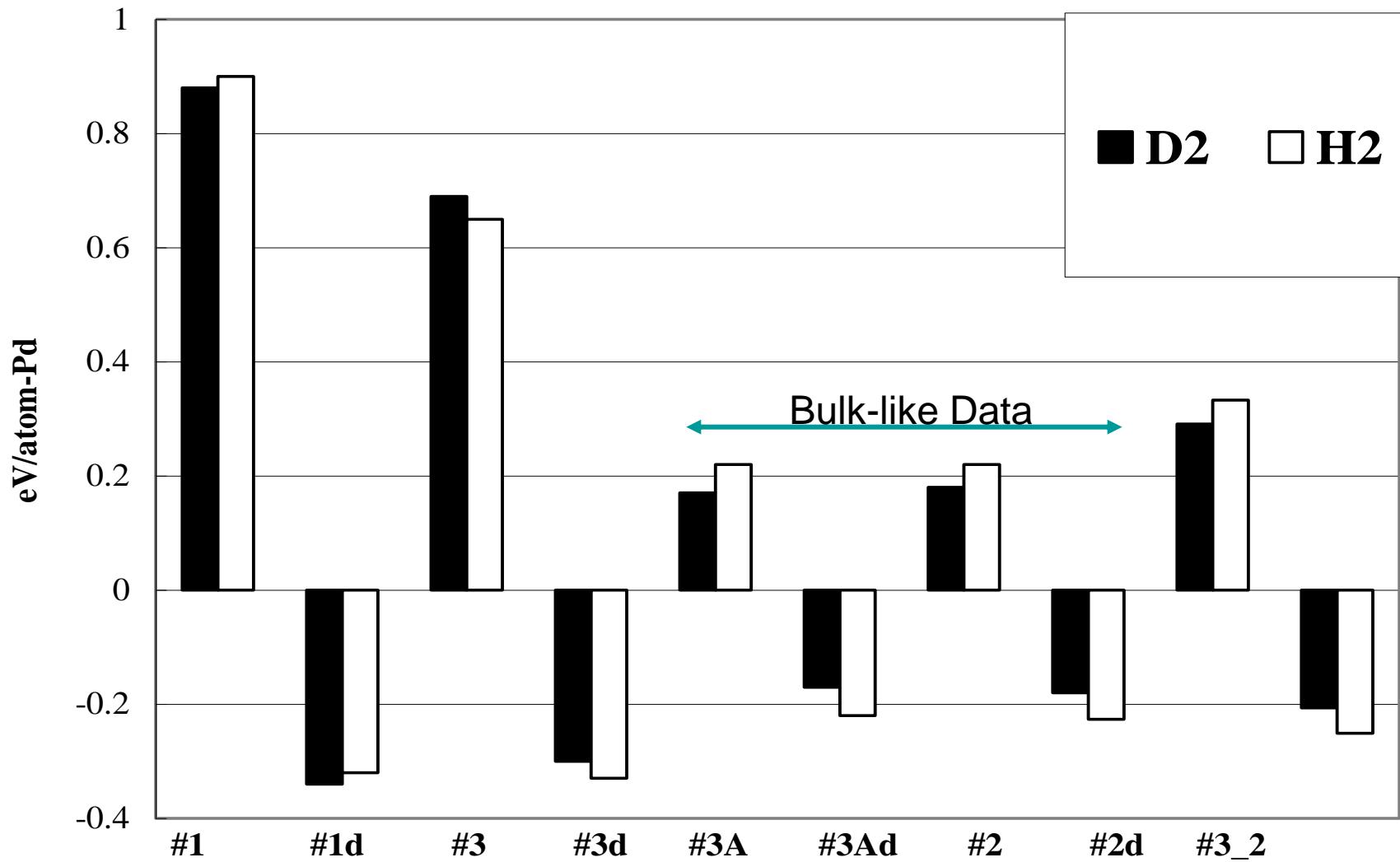
PB5,6#3: 2(D)-1.7(H)%PdO/Pd, After Oxidization



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

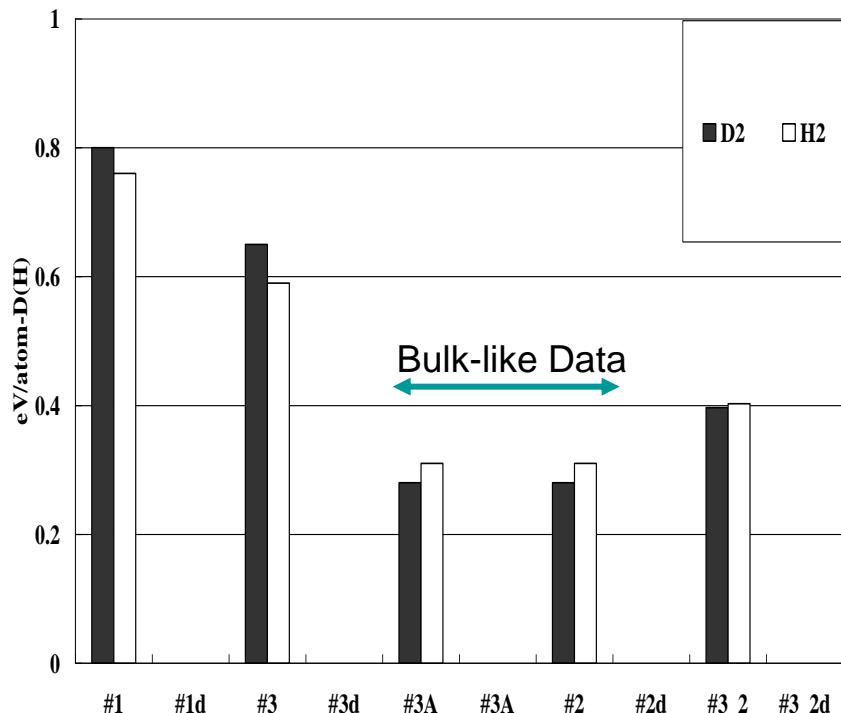


Integrated Heat Data for PB5,6 E_1

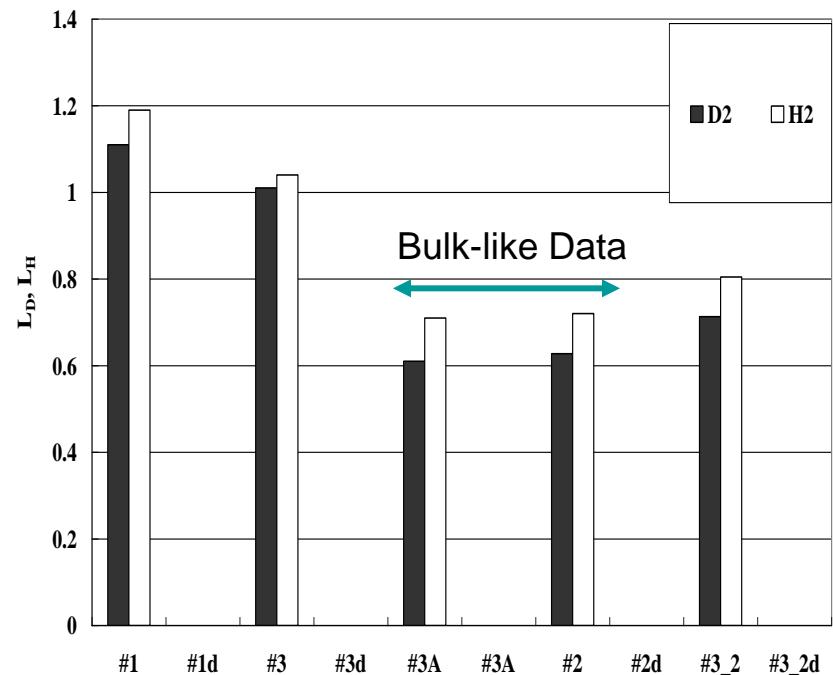


Integrated Data for PB

Absorption Energy per D(H)



Saturated Loading Ratios



Summary-1

PZ: 8-nm ϕ 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 $D(H)/Pd \sim 2.0$,
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-nm ϕ 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

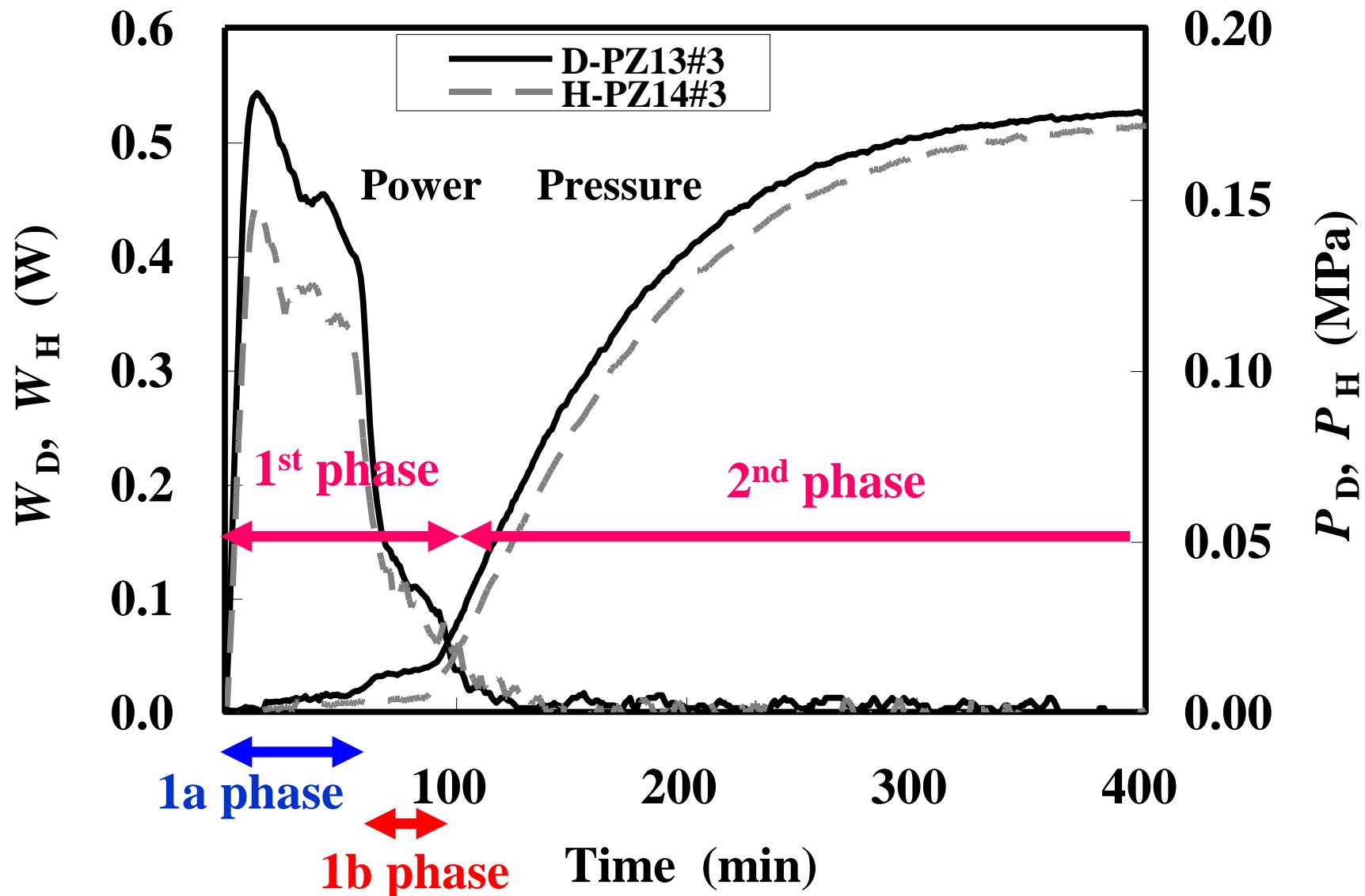
	Pd	Ni	Zr	O	Supplier	Anomalies observed?
100nm ϕ -Pd PP	995%, 100nm ϕ	---	---	---	Nilaco Corp.	[1],[2] No, bulk metal data, but PdO
Pd-black PB	99.9%, 300mesh	---	---	---	Nilaco Corp.	[1],[2] Yes, a little large heat & D/Pd
8-10nm ϕ -Pd PZ	0.346	---	0.654	(1.64)	Santoku Corp.	[1],[2],[3], discussed Yes,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

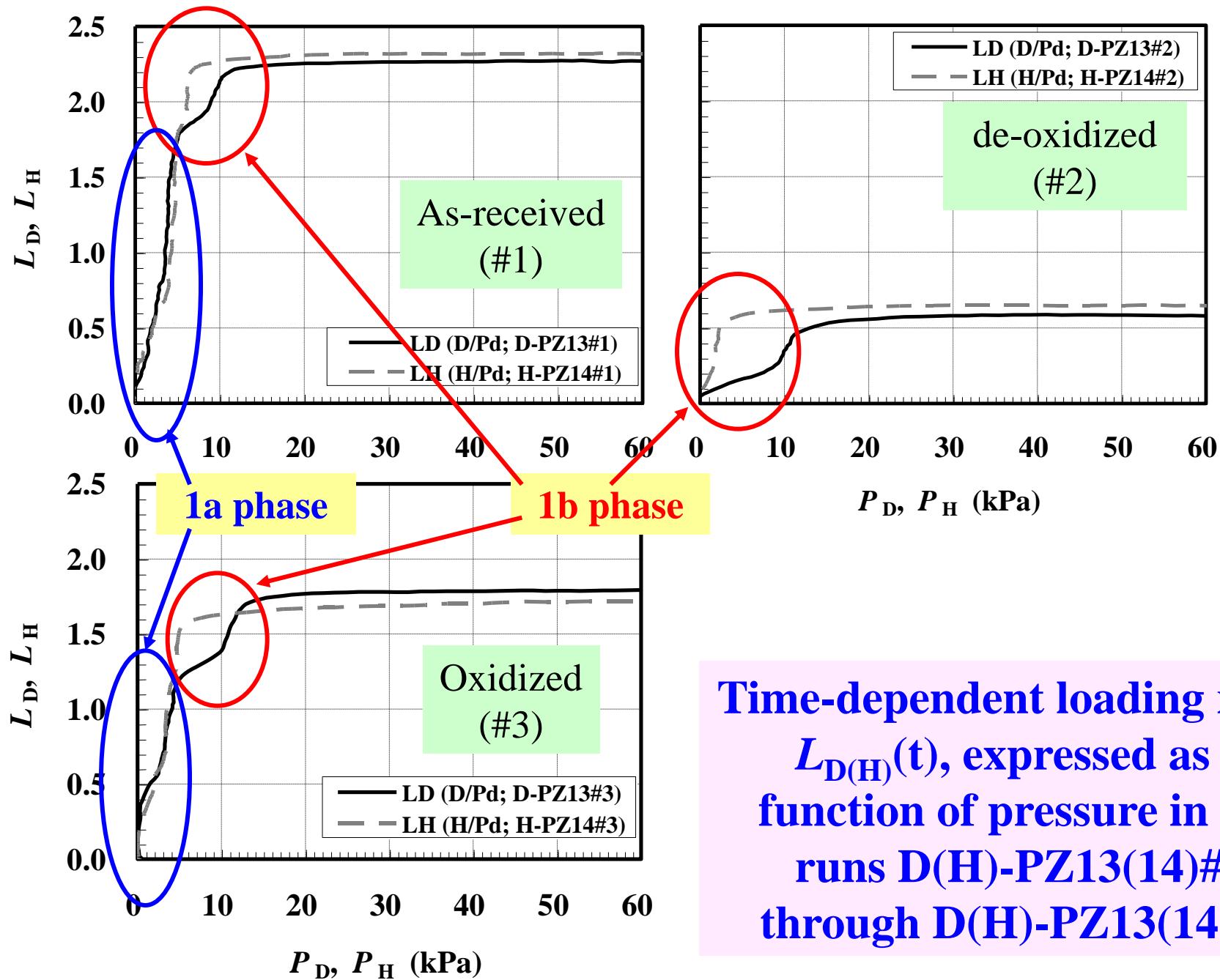
[1] Phys. Lett. A, 373 (2009) 3109-3 Drastic change happens by Meso-Catalyst! **Why?**

[2] **Low Energy 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





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,** or differential heat of hydrogen uptake, defined as the **output energy per one hydrogen isotope atom absorbed/adsorbed**,

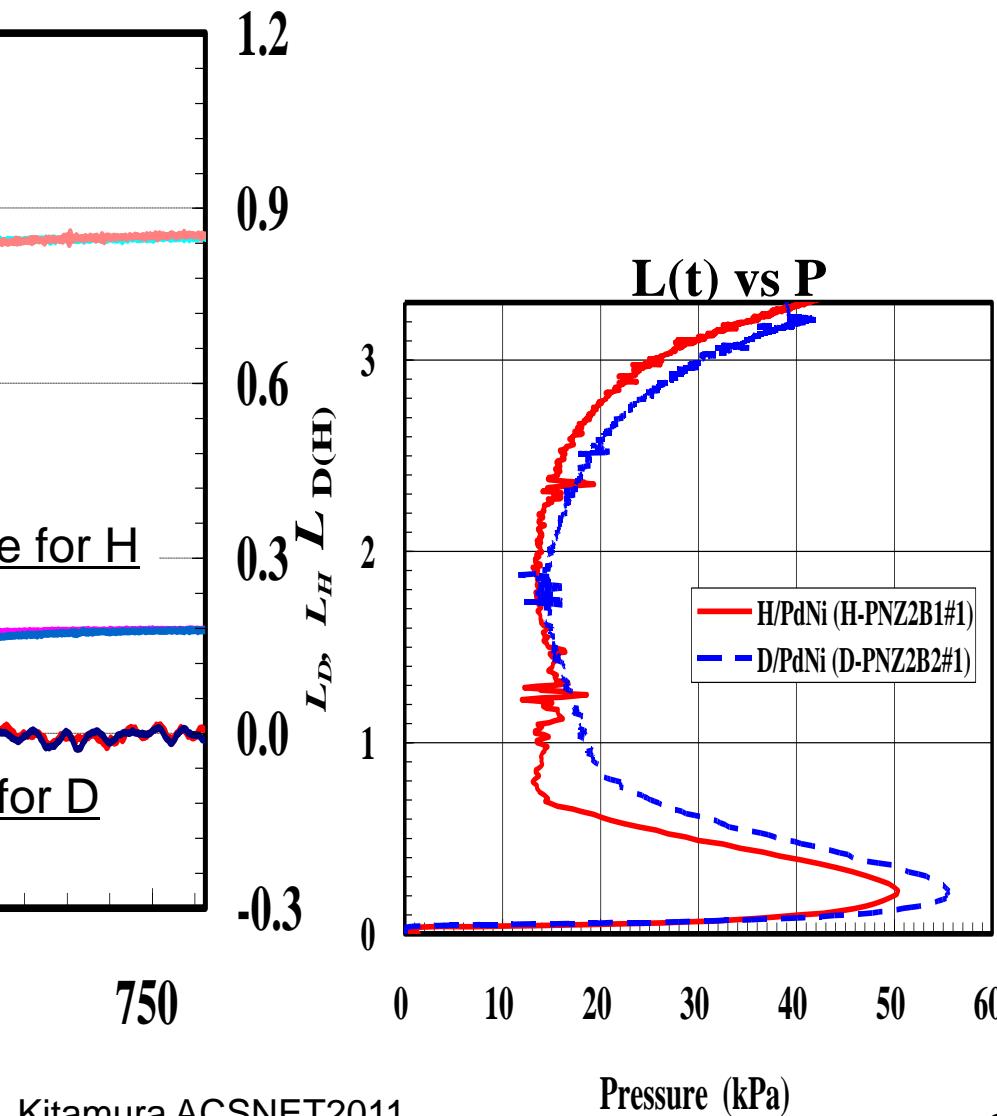
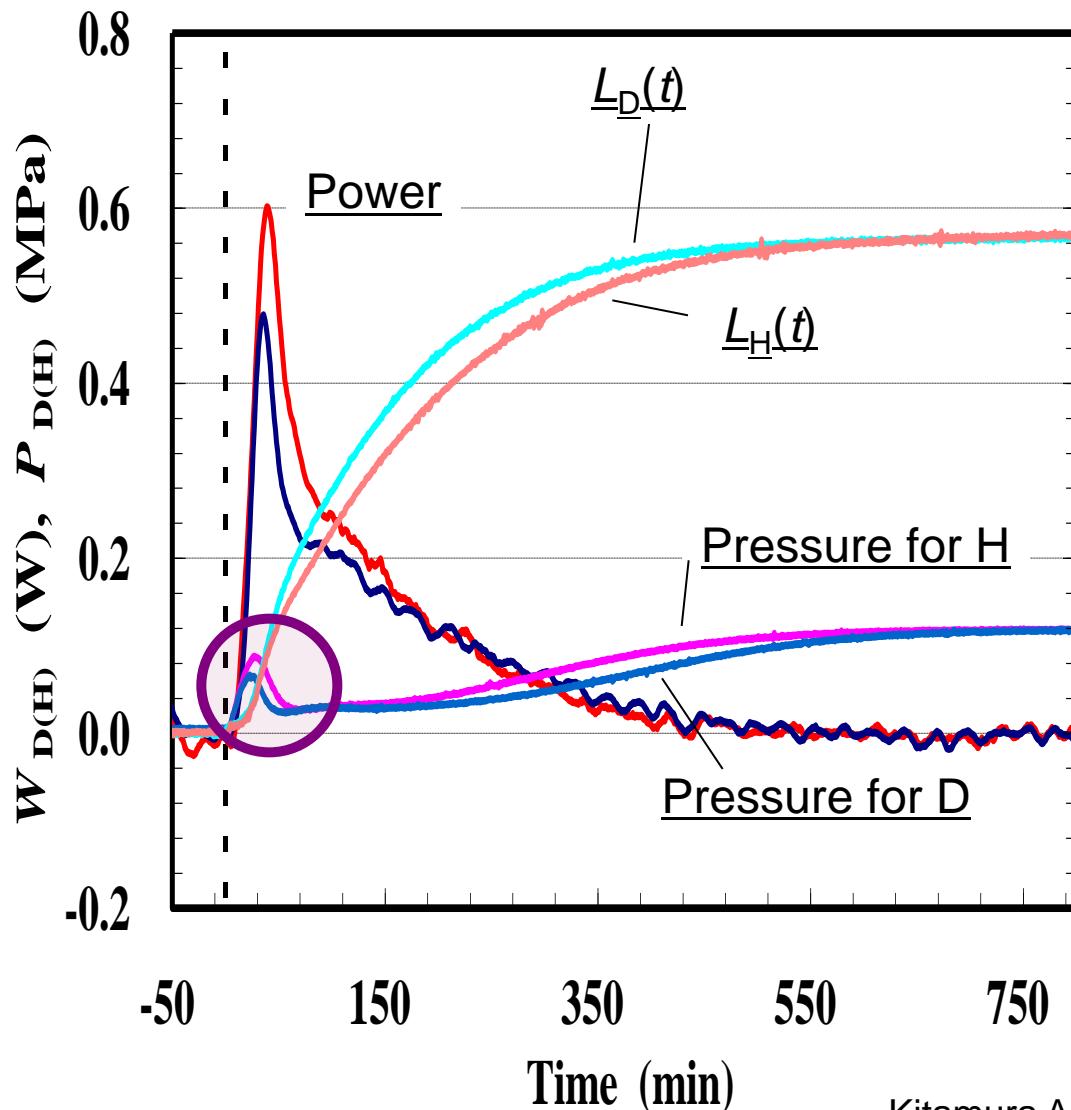
$$\eta(t) \equiv \frac{\int_t^{t+\Delta t} W_{\text{true}}(t) dt}{L(t + \Delta t) - L(t)}$$

$$\eta(t) \approx \frac{\int_t^{t+\Delta t} \overline{W(t, \tau)} dt}{L(t + \Delta t) - L(t)},$$

$$\overline{W(t, \tau)} = \frac{\int_t^{t+\tau} W_{\text{meas}}(t) dt}{\tau}$$

- The values of $W_{\text{true}}(t)$ should be de-convoluted from the measured output power $W_{\text{meas}}(t)$, which has an indicial delay with a time constant of τ , and is approximated here by $W(t, \tau)$ 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.

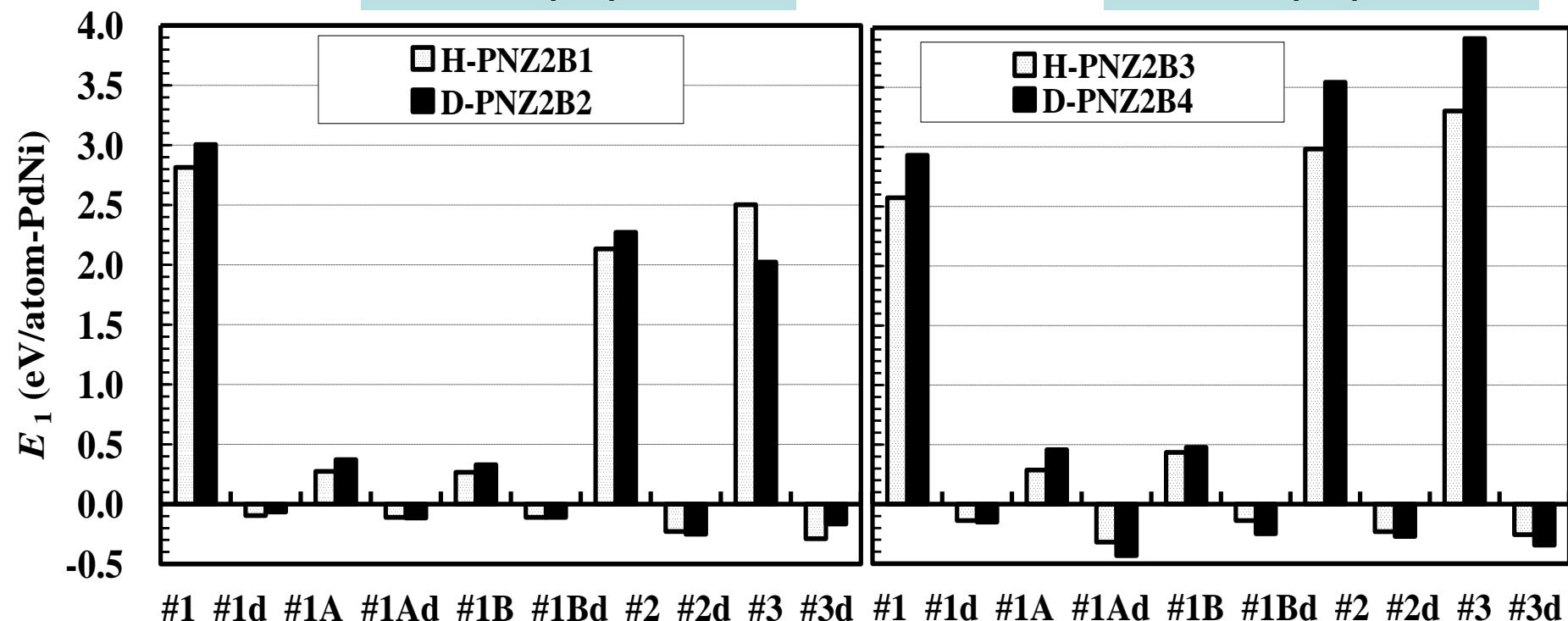
Pd	Ni	Zr	O	Supplier
0.04	0.29	0.67	(1.67)	Dr. B. Ahern



; Deoxidization works as well as oxidization

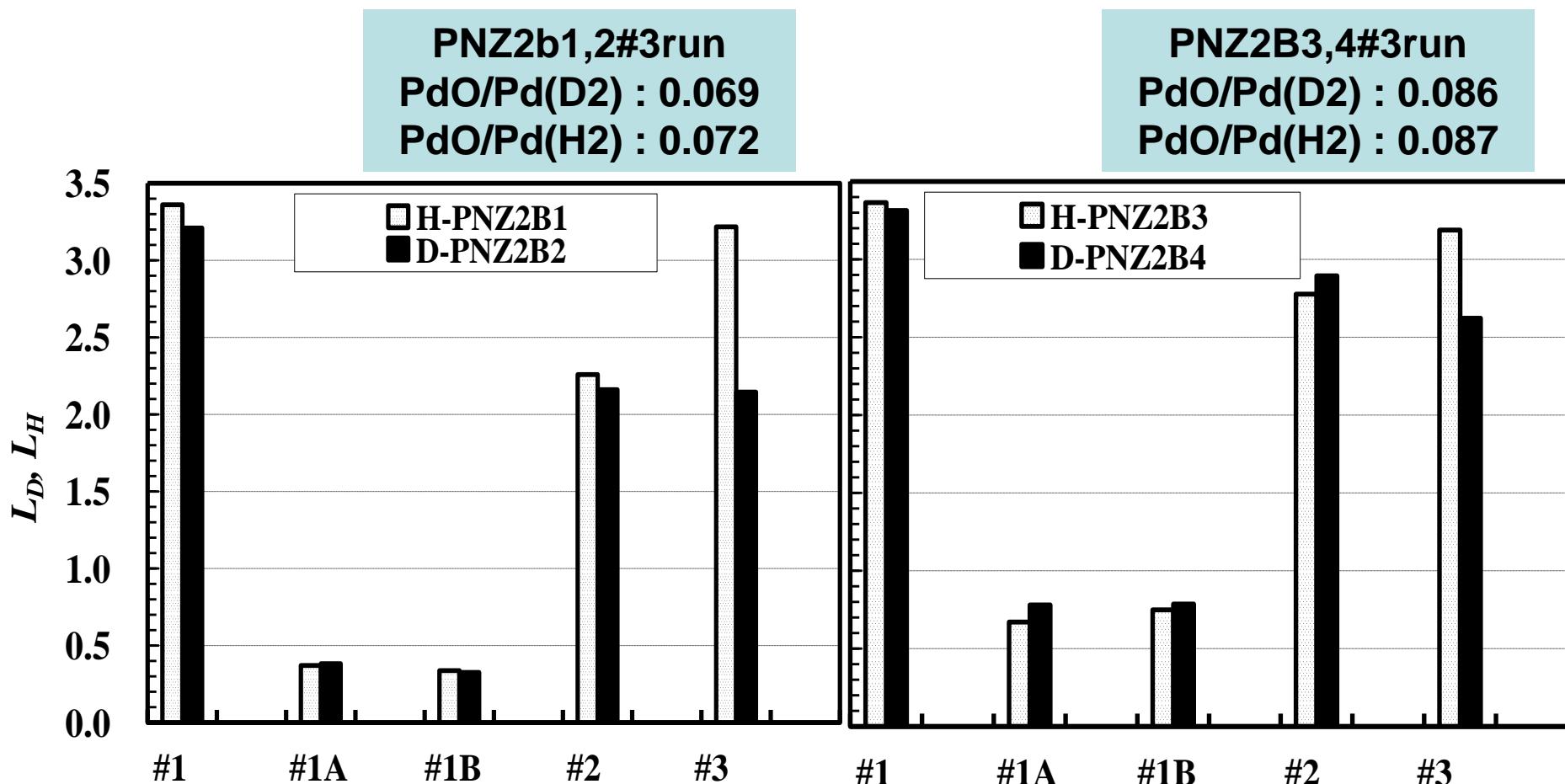
PNZ2b1,2#3run
PdO/Pd(D2) : 0.069
PdO/Pd(H2) : 0.072

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



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

; Deoxidization works as well as oxidization



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

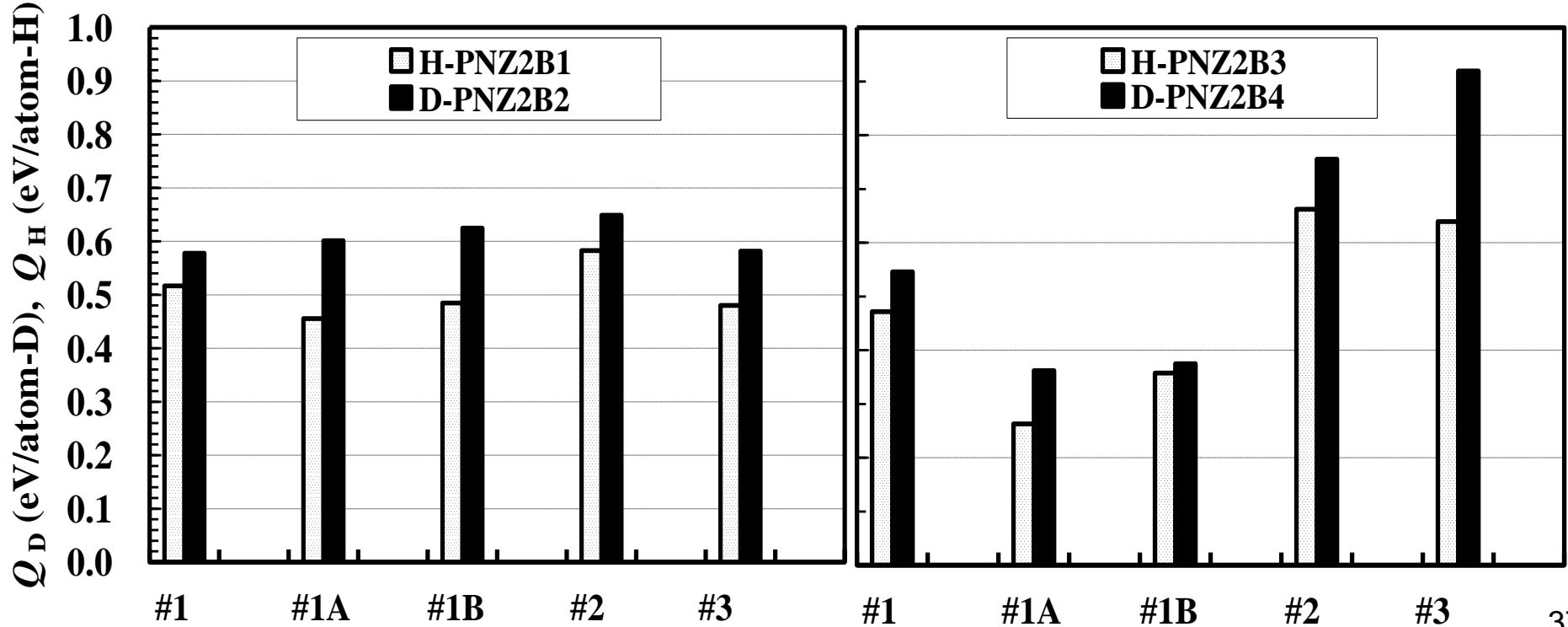
; Deoxidization works as well as oxidization

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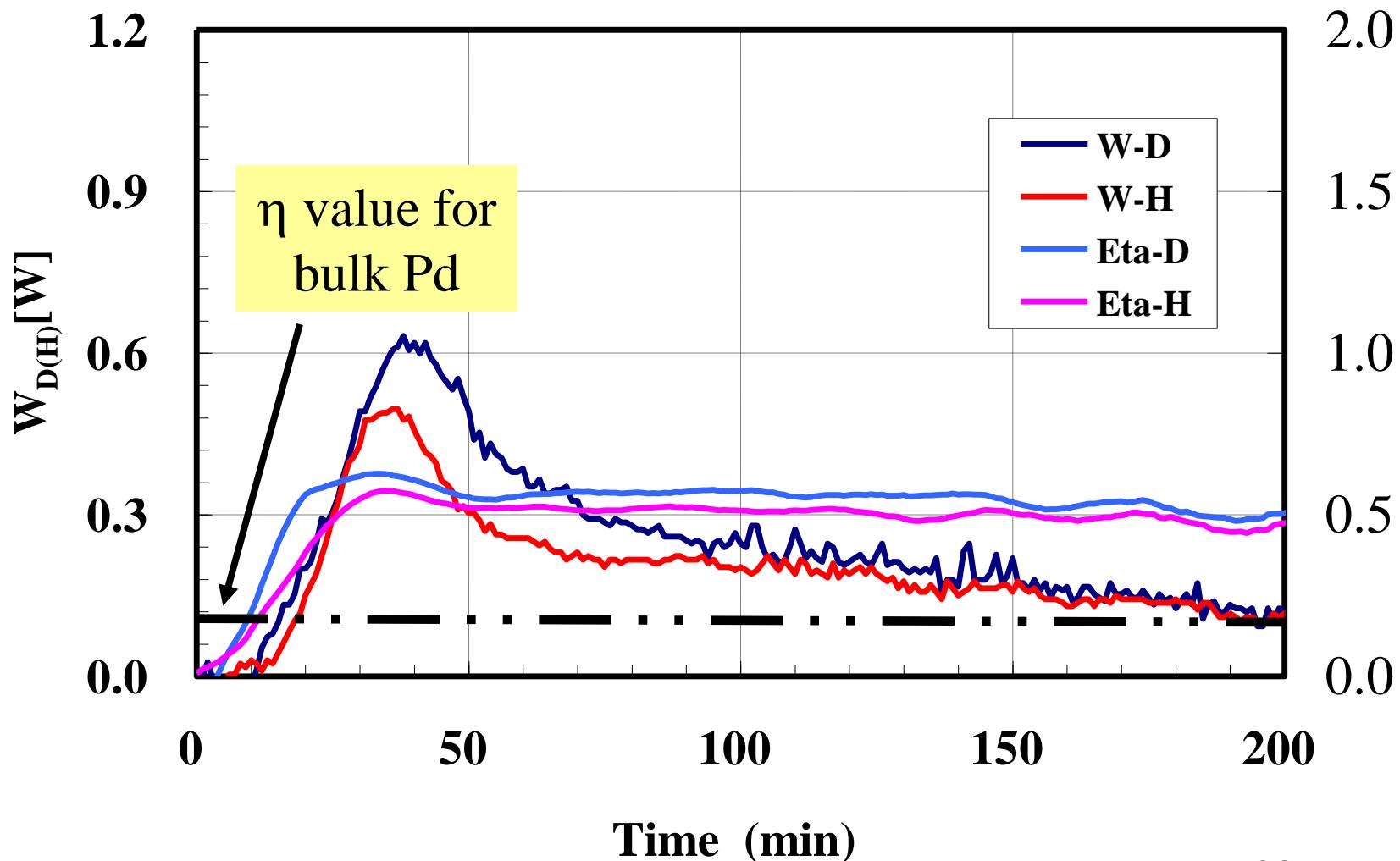
Larger energy $Q_{D(H)}$ for the D-runs
D(H)-PNZ2B2(1)#1 through D(H)-PNZ2B4(3)#3

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

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

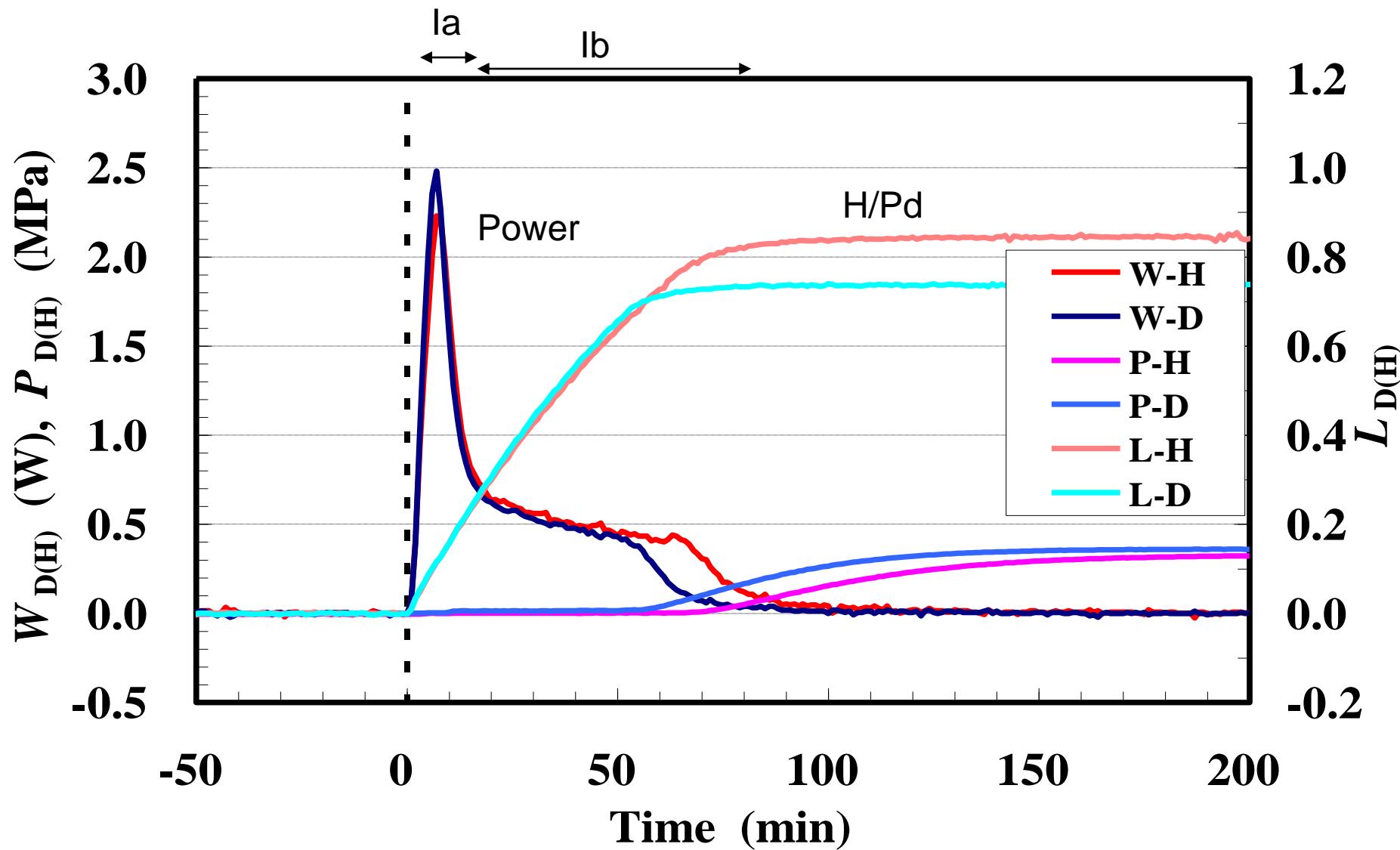


Absorption / desorption energies are constant and anomalously large, while Ni does not absorb D(H) at all at room temperature.

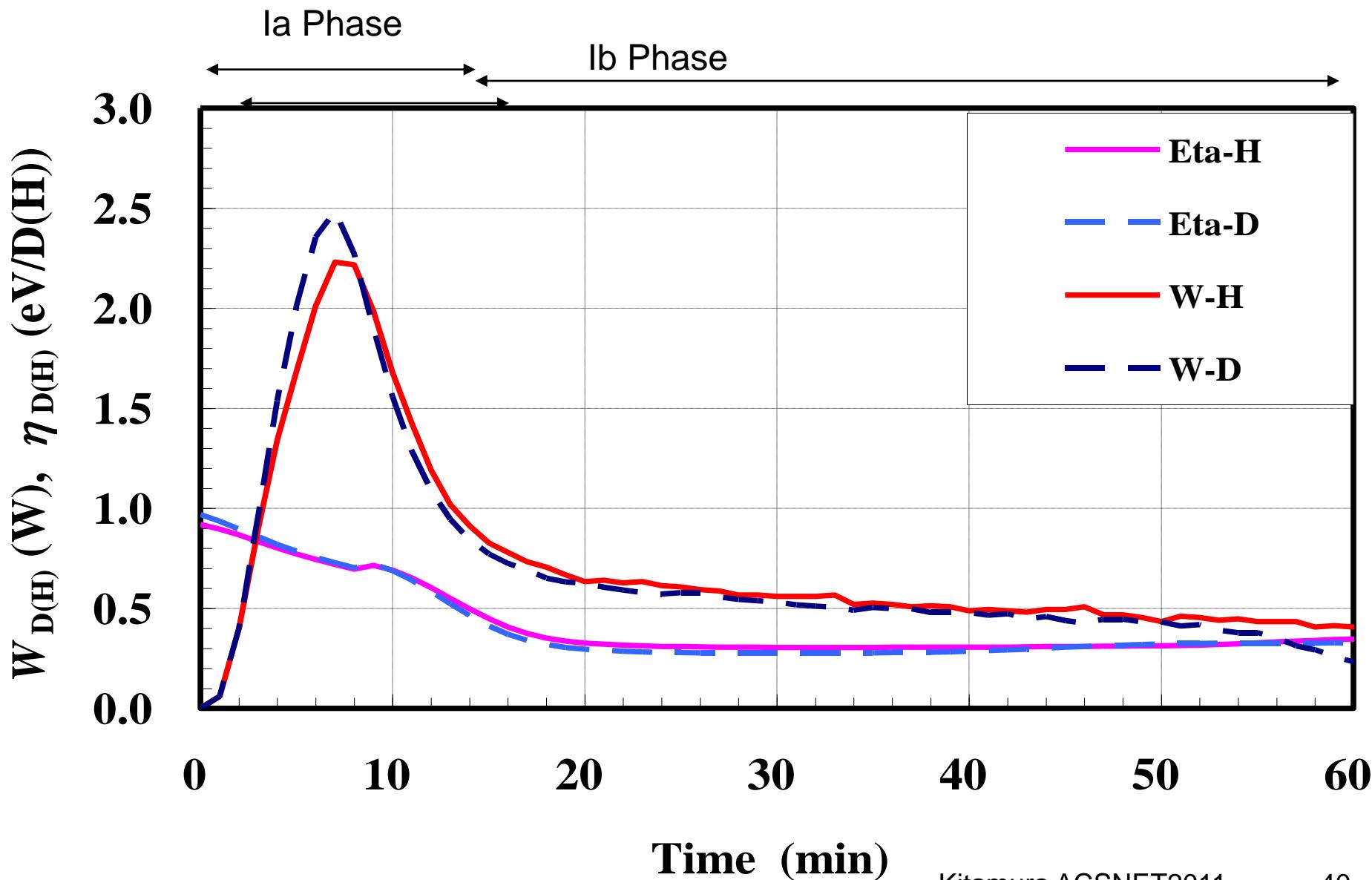


PB5,6#3_2: 0.47%PdO/Pd

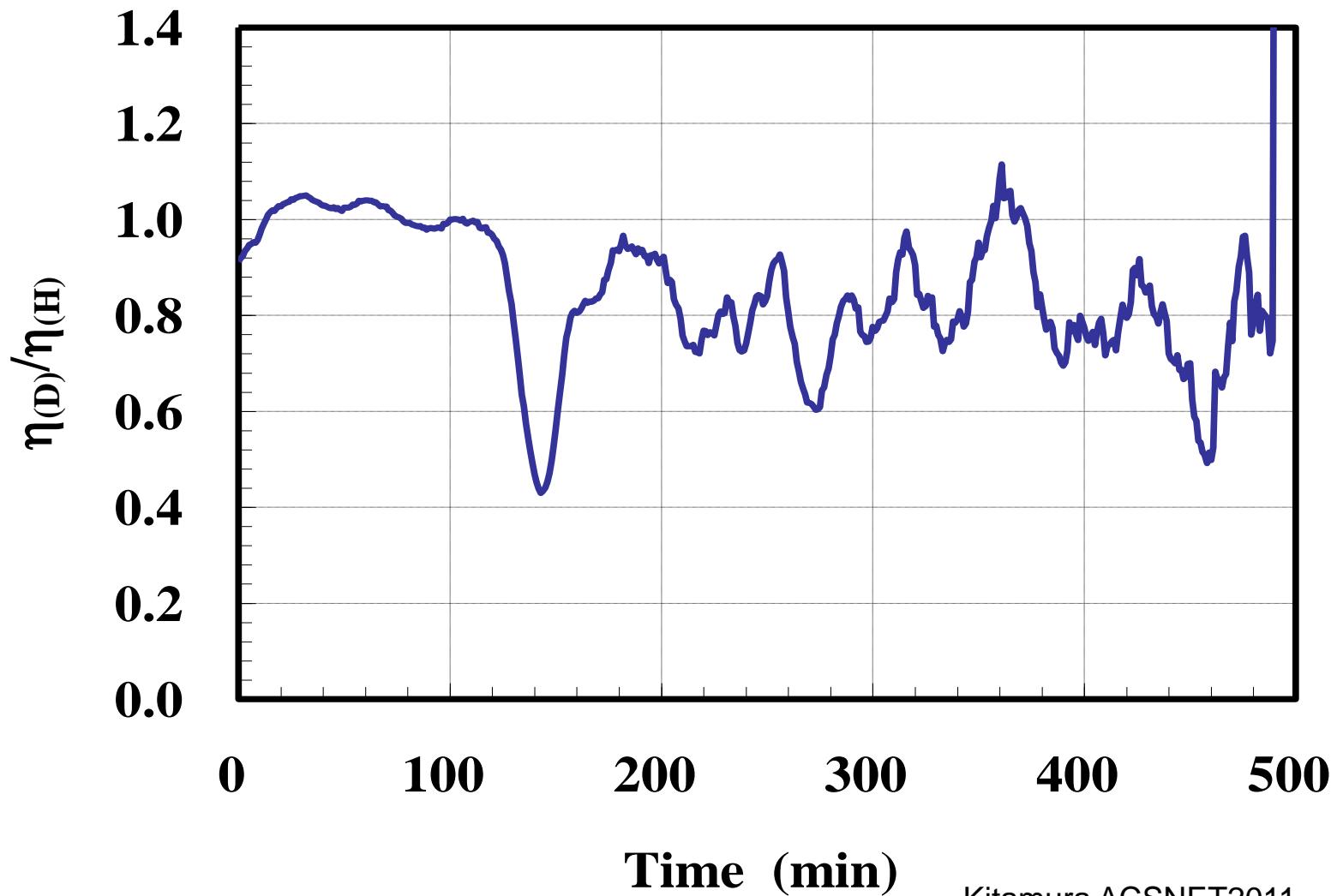
The second forced-oxidization runs gave smaller la phase.



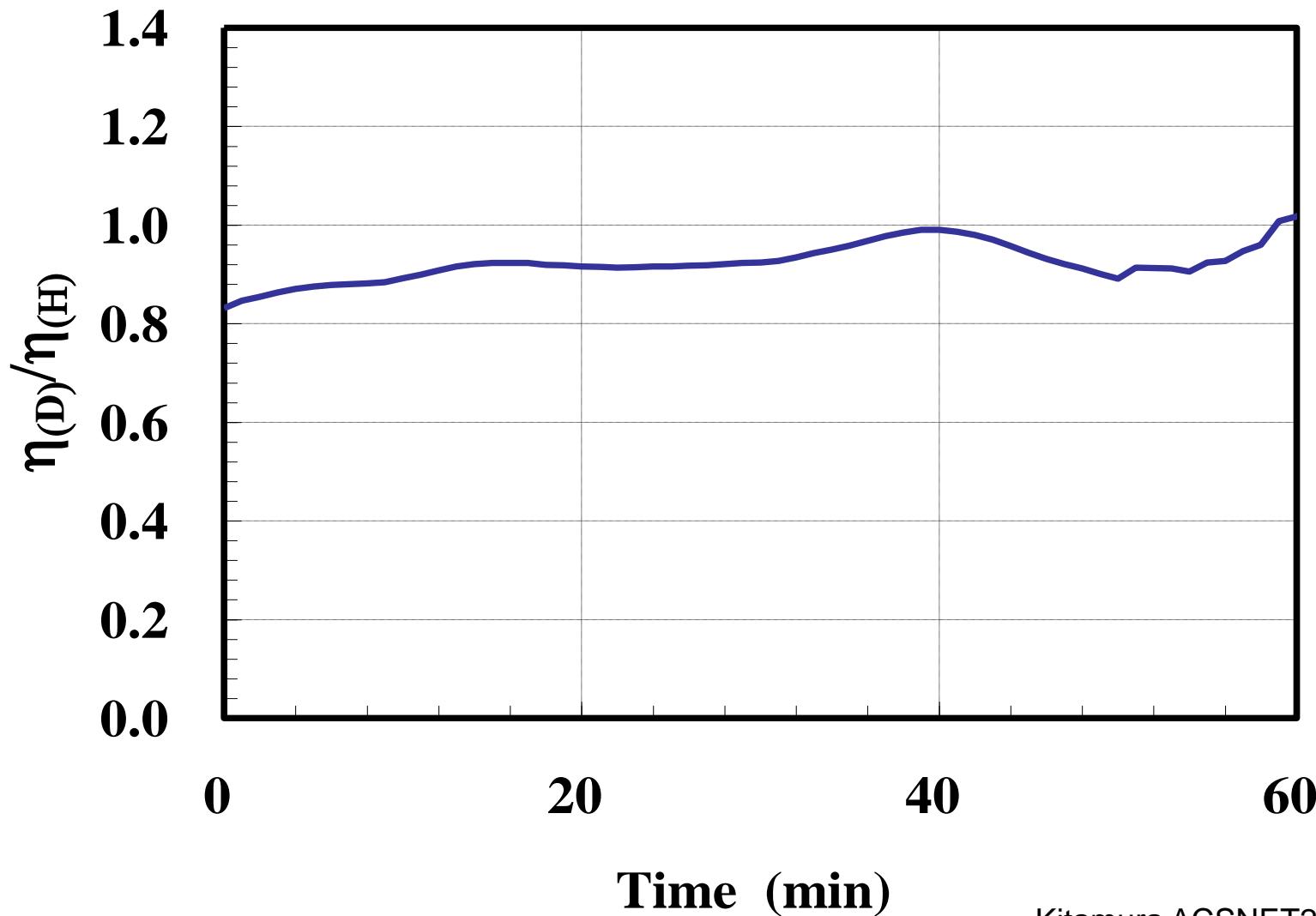
PB5,6#3_2 η



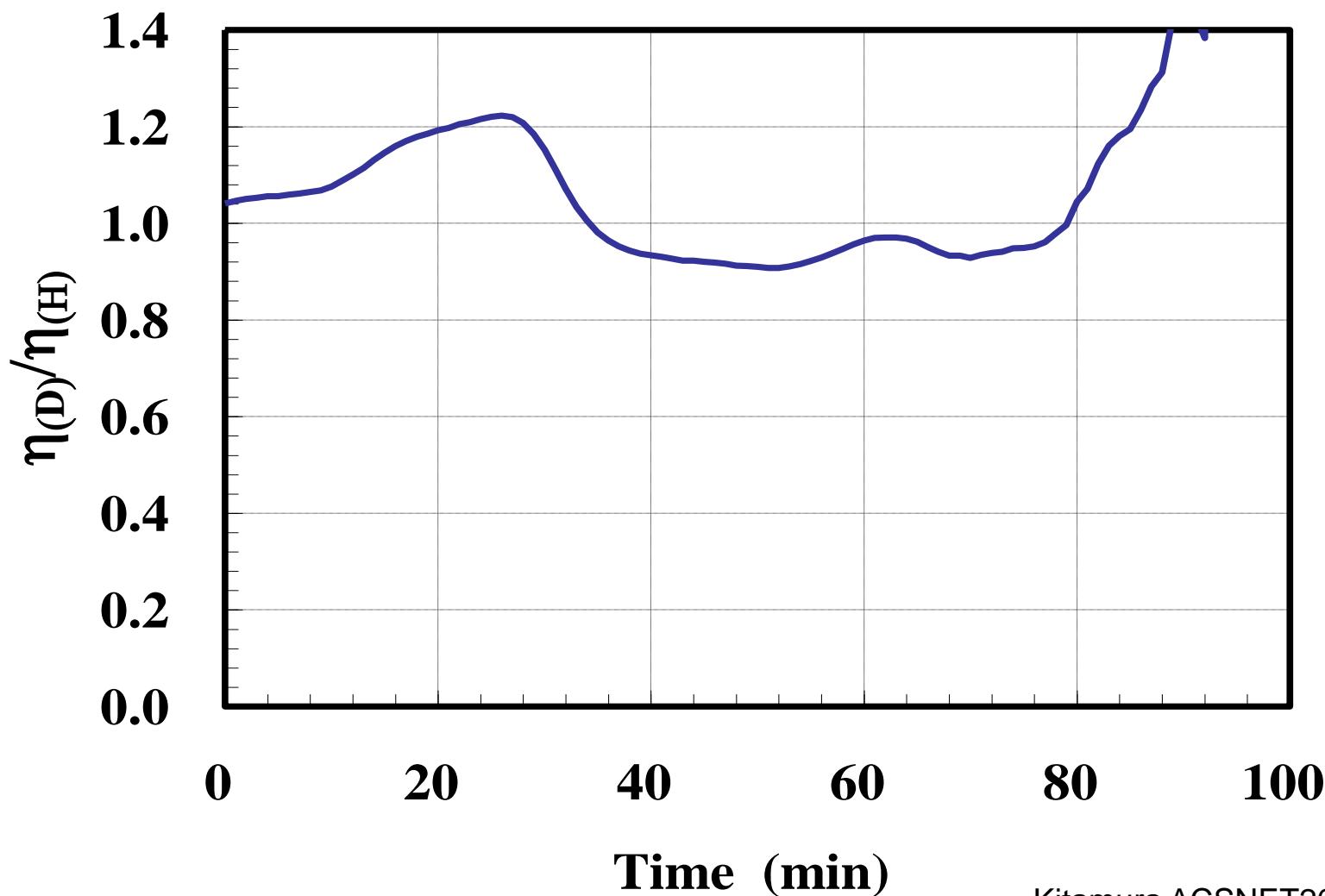
PB5,6#1 η_D/η_H



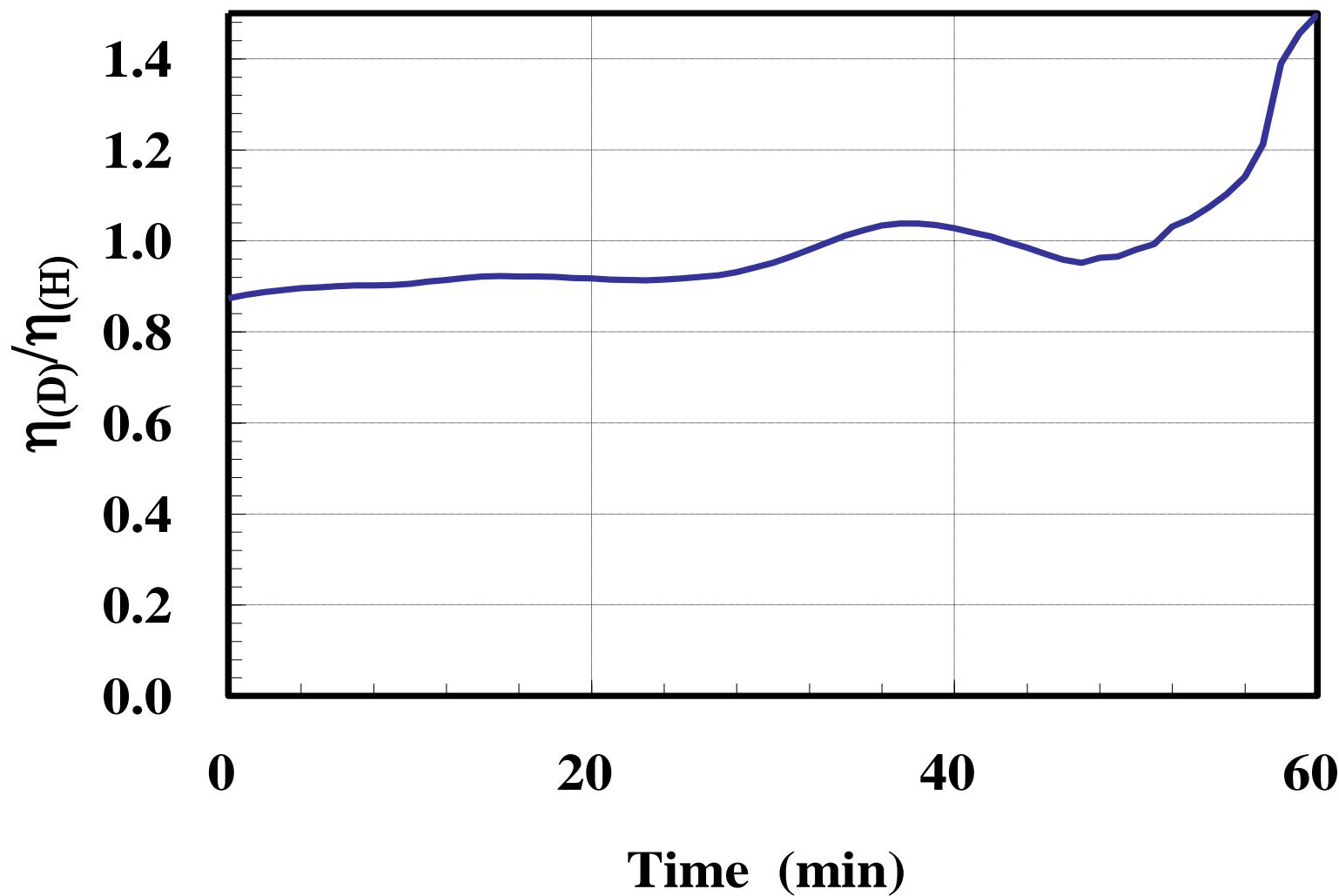
PB5,6#2 η_D/η_H



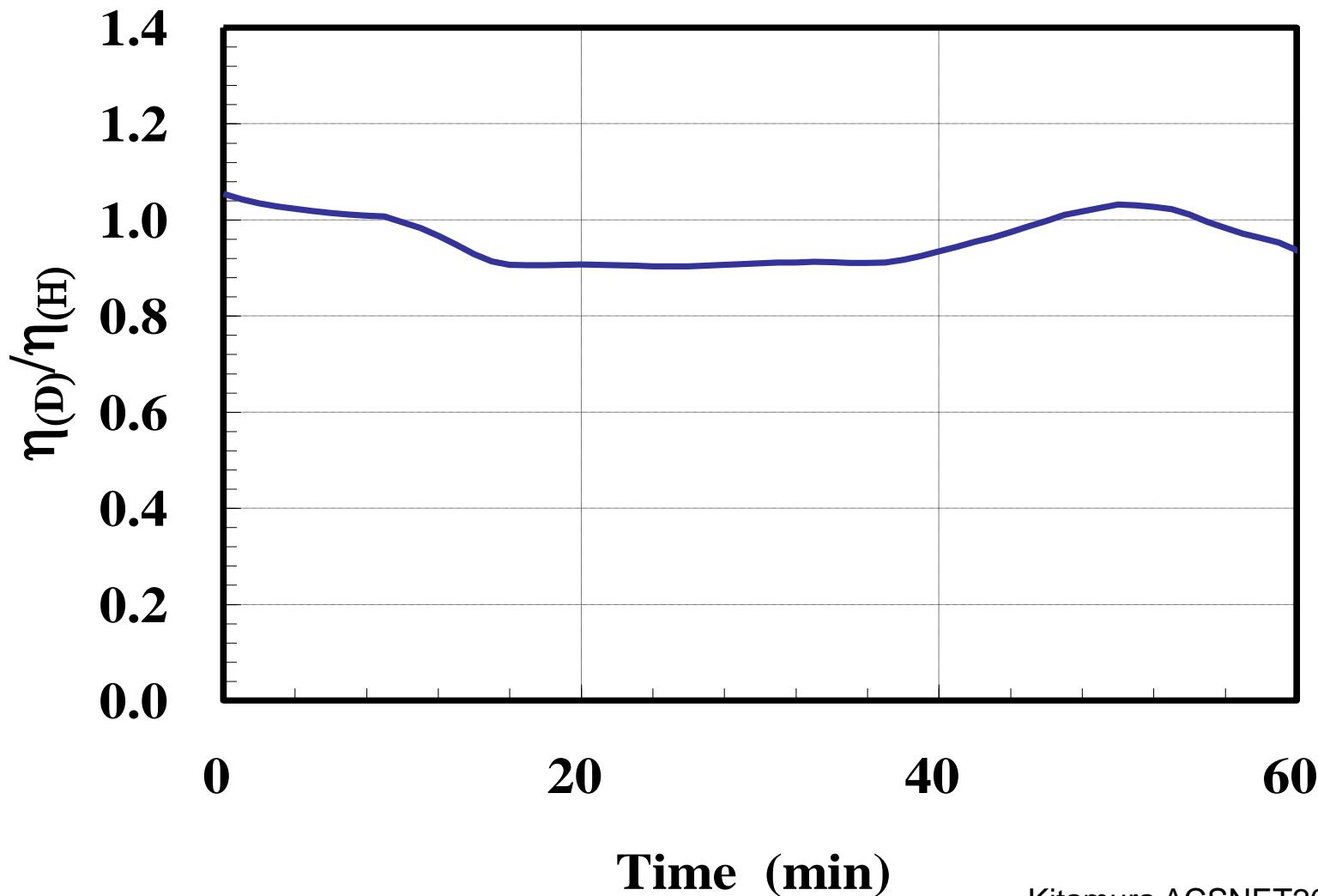
PB5,6#3 η_D/η_H



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; $\text{Pd}_{36}\text{Zr}_{64}$)

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

(2) PP sample (Nilaco; $0.1\text{-}\mu\text{m}\phi$)

- $E_1 \sim 0.2 \text{ eV/Pd}$, $D(\text{H})/\text{Pd} \sim 0.6$, $Q_{\text{D}(\text{H})} \sim 0.3 \text{ eV/D(H)}$,
- less prominent 1a-phase, and less effective enhancement by oxidization.

(3) PB sample (Nilaco; Pd-black)

- intermediate characteristic values.

(4) PNZ (Santoku; $\text{Pd}_{11}\text{Ni}_{25}\text{Zr}_{64}$, $\text{Pd}_2\text{Ni}_{44}\text{Zr}_{54}$) and NZ ($\text{Ni}_{36}\text{Zr}_{64}$)

- absorption in proportion to Pd content.

(5) PNZ2B (B.Ahern; $\text{Pd}_4\text{Ni}_{29}\text{Zr}_{67}$; melt spinning)

- absorption occurs at R.T. with $E_1 \sim 2.0$ (1.8) eV/atom-[Pd-Ni] ,
- $D(\text{H})/[\text{Pd-Ni}] \sim 3.3$ (3.3),
- $Q_{\text{D}(\text{H})}$ (and η) ~ 0.55 (0.50) eV/atom-D(H) ,
- 1a-phase / 1b-phase ; indistinguishable,
- modest deterioration after absorption runs.