An X-Ray Diffraction Study of Lattice Expansion and Phase Transformation in Electrochemically Loaded Palladium Hydrides

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Time resolved, in-situ, high-energy x-ray diffraction was performed on modified Fleishman-Pons electrolytic cells during electrochemical loading of palladium foil cathodes with hydrogen and deuterium. Concentrations of H and D up to 1:1 in 0.1 M LiOH/LiOD in H_2O/D_2O electrolytes were obtained with lattice constant data monitored throughout the range of concentrations. In addition to data on lattice constant versus H or D concentration and palladium hydride resistivity, some indication of the rapidity of loading and deloading of hydrogen from the Pd surface was obtained. The alpha-beta phase transformations were clearly delineated but no new phases at high concentration were definitively determined.

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In Situ Energy-Dispersive X-ray Diffraction Study of Thin Pd Foil at D/Pd and H/Pd ~1

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Motivation

• In situ XRD not performed for H/Pd > 0.76 in Fleischmann-Pons electrolytic cells

Possibility of learning

• Does a new γ phase was suggested by Tripodi et. al. for the electrochemically loaded palladium when the composition H/Pd approaching 1 exist?

• Does temperature coefficient of resistivity of PdH versus the concentration of H anomaly show up in Pd crystalline structure (Tripodi et. al.)?

• In the Pd-D system, new phases were found through deuterium thermal desorption spectra. Does anything show up on FPE system (Rybalko et. al.)?

• Report showing oscillating resistivity for palladium hydrides at some concentration range of H/Pd>0.9 (Miley et. al.).

• These proposed phase transitions are only based on indirect experimental data and have not been structurally determined.

Temperature Coefficient of Resistance

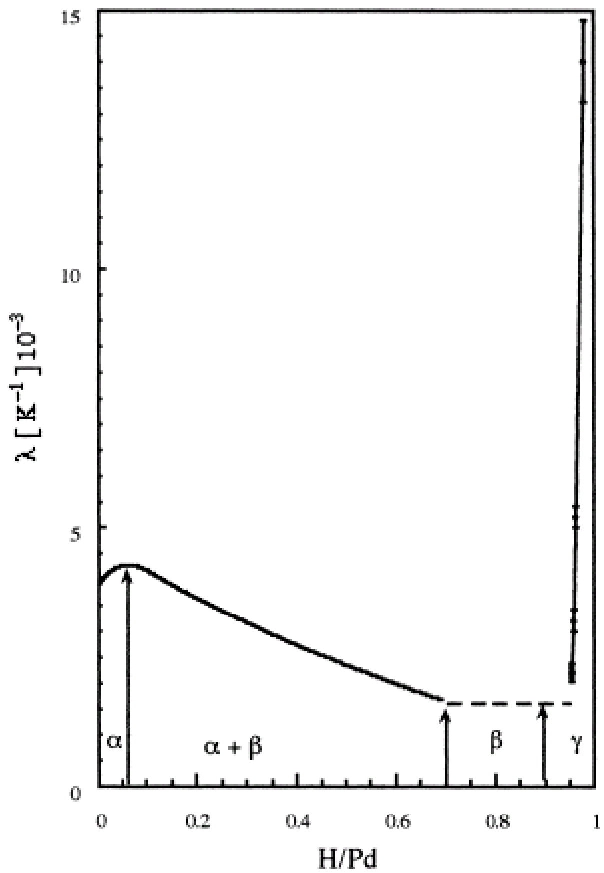


Figure 3: Temperature coefficient of resistivity λ for all phases. The dashed is the plateau value for λ.

Pd Foil Cathodes

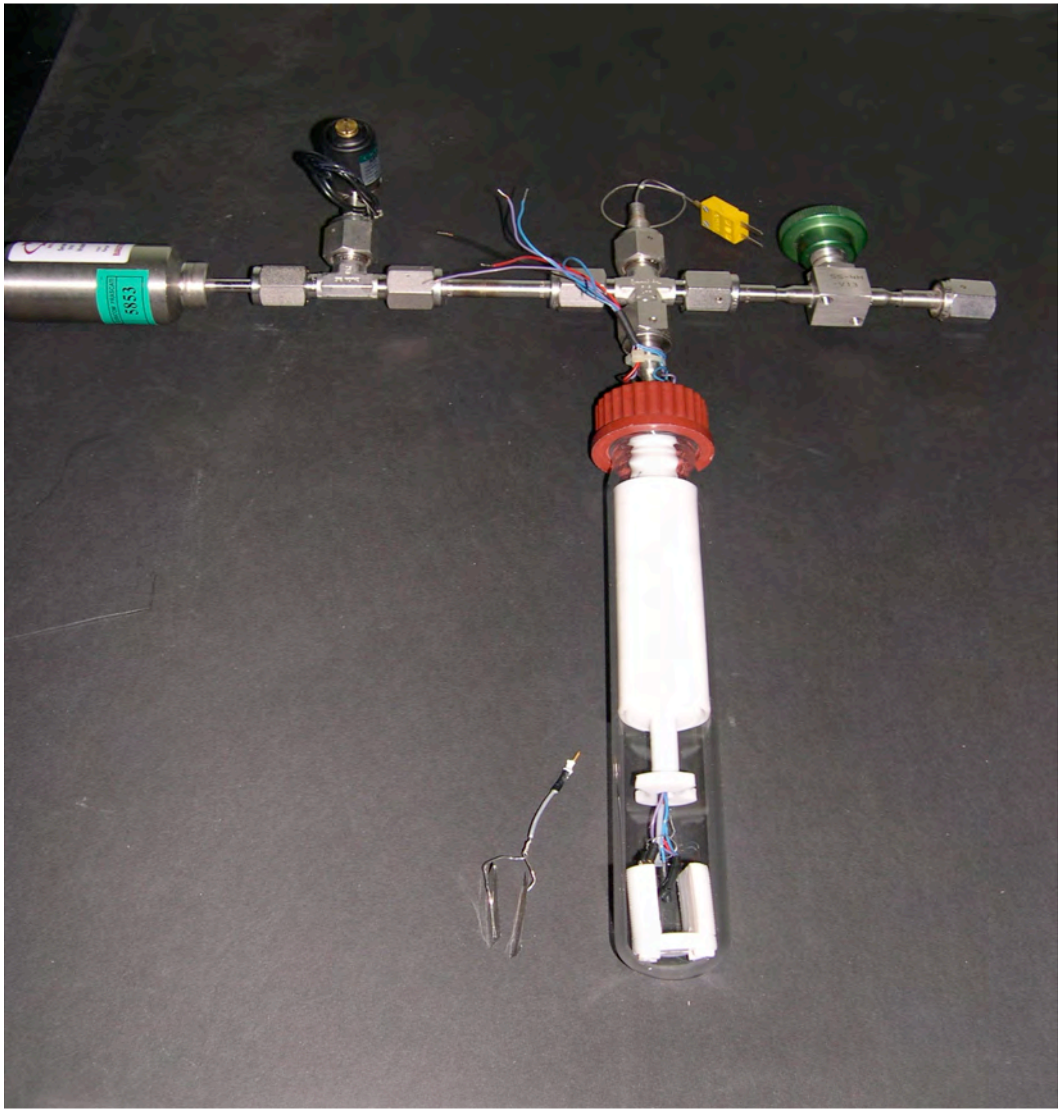
- Pd 0.9995 purity fabricated at ENEA by V. Violante

- Rolled from 1 mm thick bar to 50 μm thickness, annealed 850 C for 8 hours, etched in aqua regia for 2 minutes, cleaned in water and alcohol

- 20 mm x 40 mm dimension

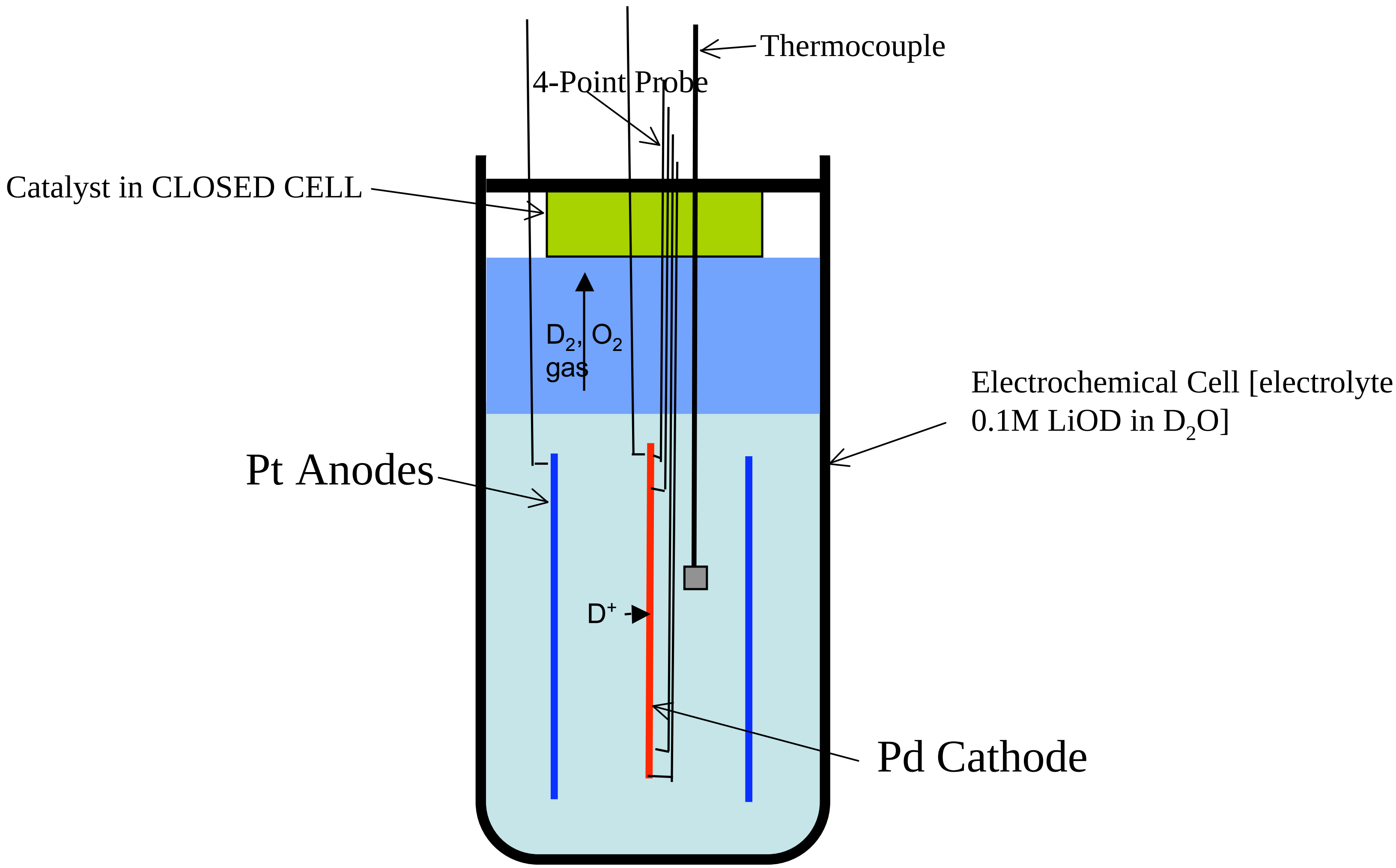
- ~100 μm grain size

Electrochemical Cell



- Designed and built by ENEA
- Dual Pt anodes

Electrochemical Cell



Experimental Measurements

Cell Measurements

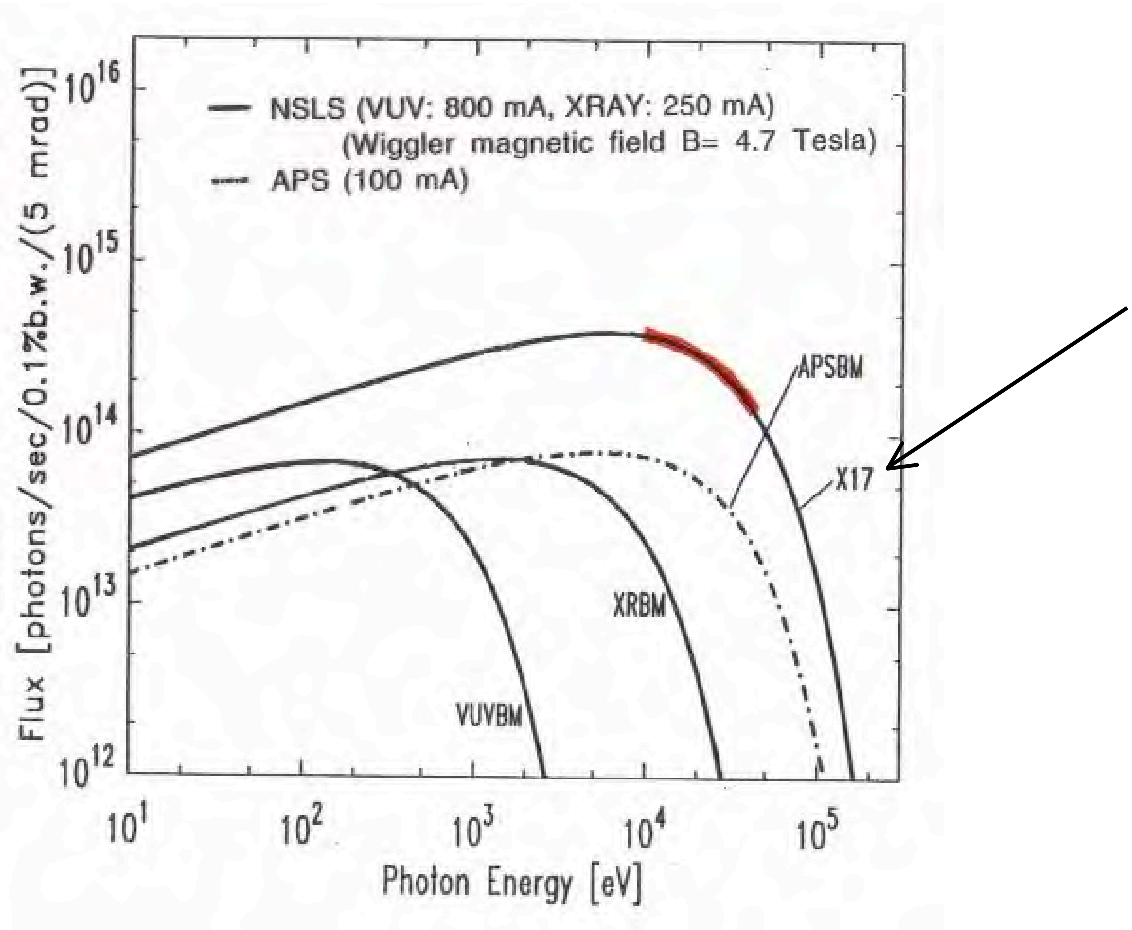
- Temperature
  - 1 thermocouple in electrolyte
  - 5 RTD's external to cell
- Electrolysis
  - Current
  - Voltage
- Cell Pressure
  - Baratron
  - Safety valve
- R/R_0
  - 4-point probe @ 1 kHz
- Time
- Data rate
  - 1/4 Hz

X-Ray Measurements

- 14 µm tall, 23-µm wide x-ray beam
- Diffraction spectra collection time ~5 minutes
- Ge high resolution detector

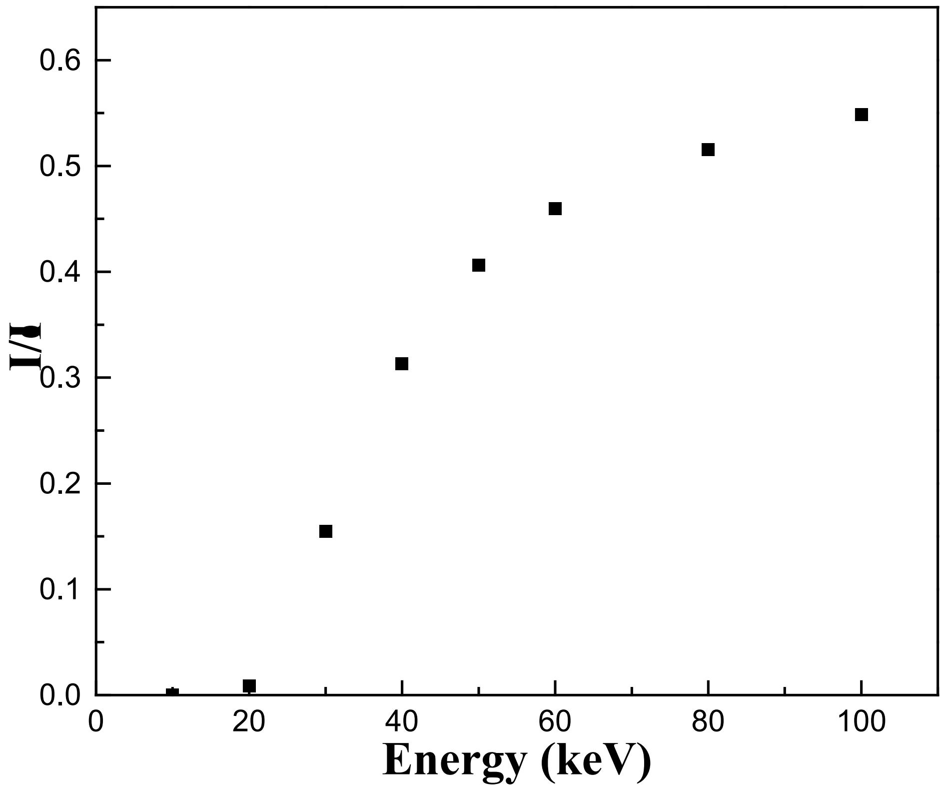
No Calorimetry!

Brightness of NSLS Beam Lines

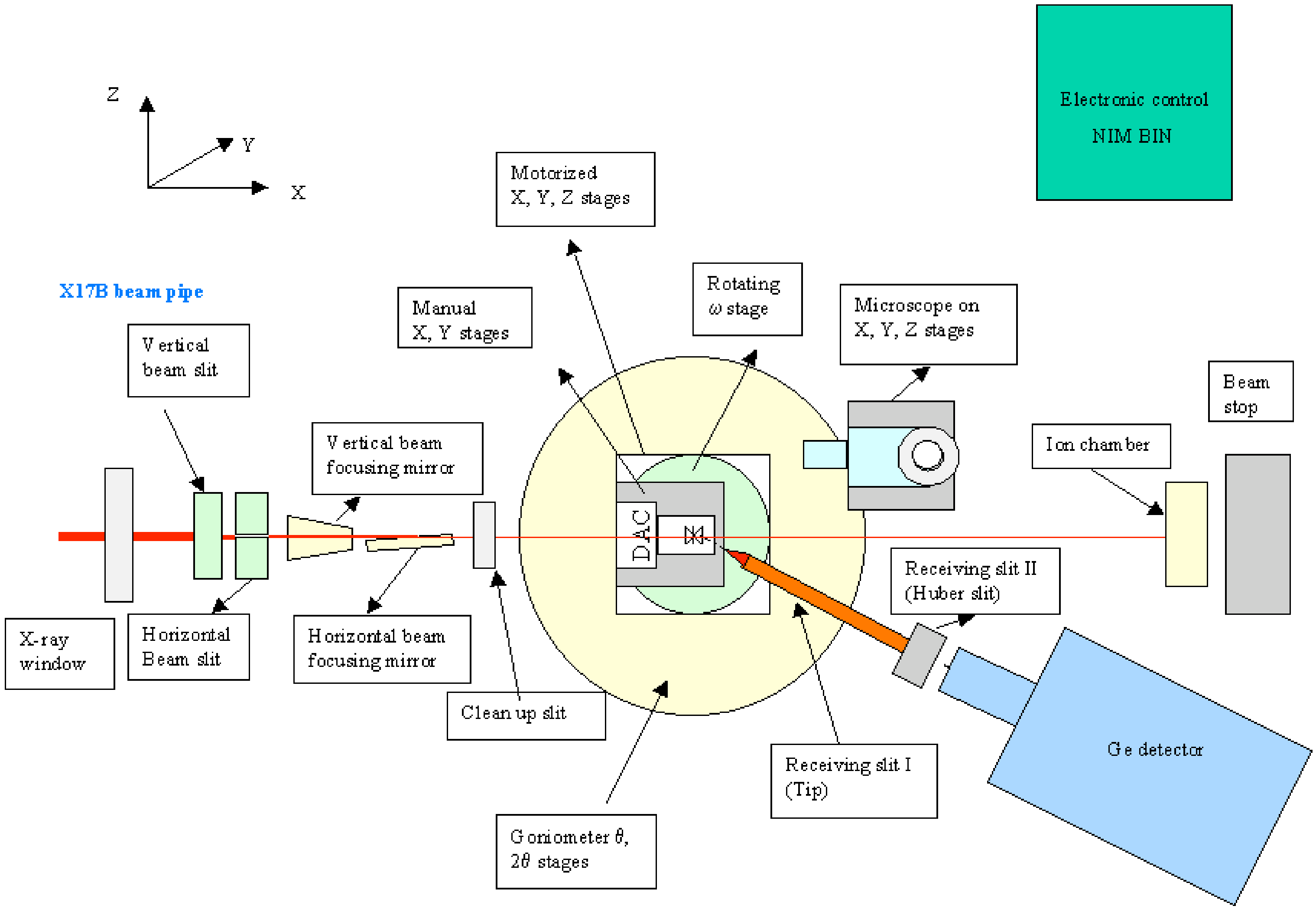


X-Ray Transmission through Electrochemical Cell

Absorption thru the Cell with 2.7 cms of H_2O and 0.3 cms of Glass with a density of 2.7 g/cm_3)



BNL X17C Hutch Equipment



Bragg Condition
$2d \sin\theta = n\lambda$

$$E = h\nu, \quad \lambda\nu = c$$

$$2d \sin\theta = nch/E$$

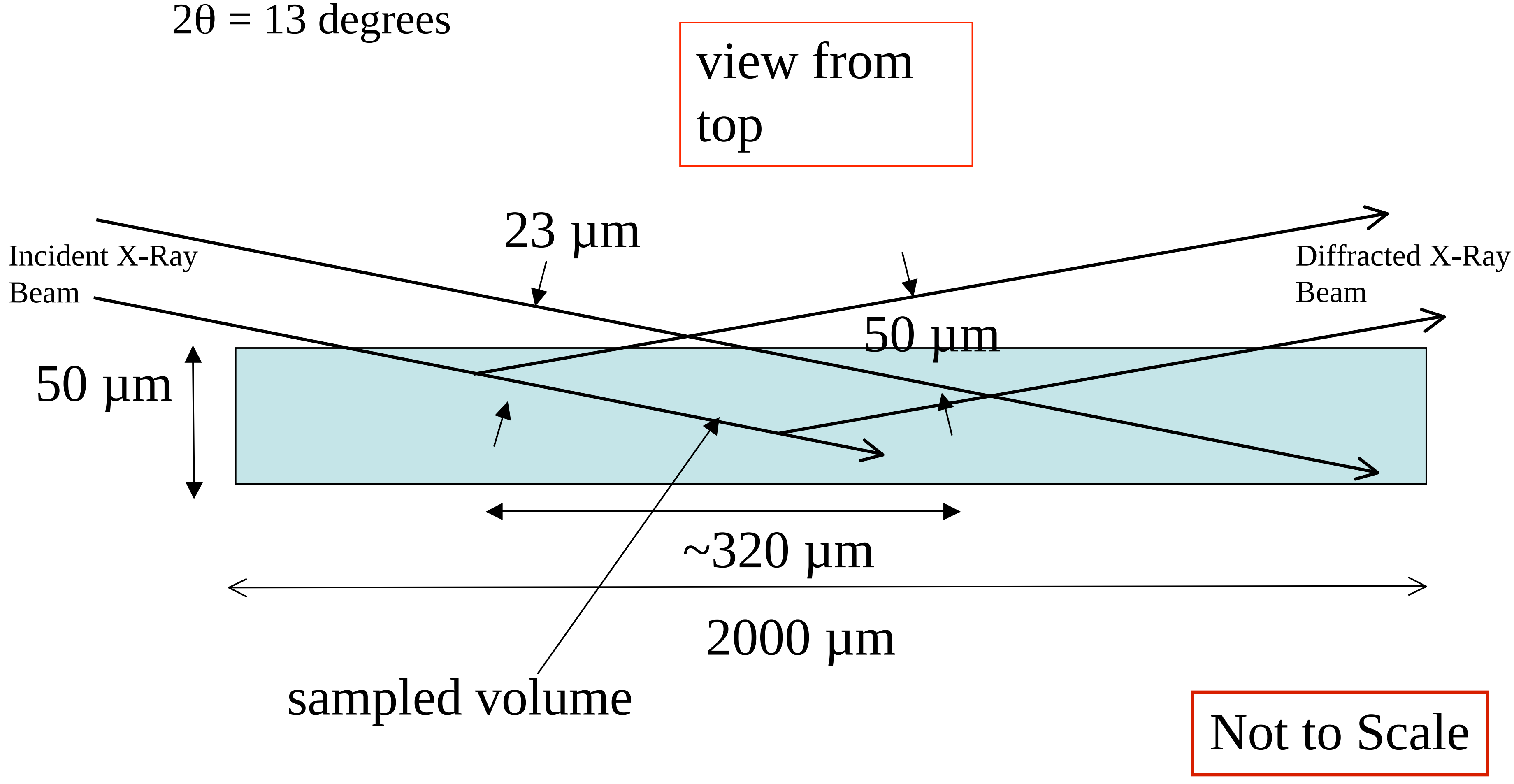
or

$$Ed \sin\theta = 6.1992n$$

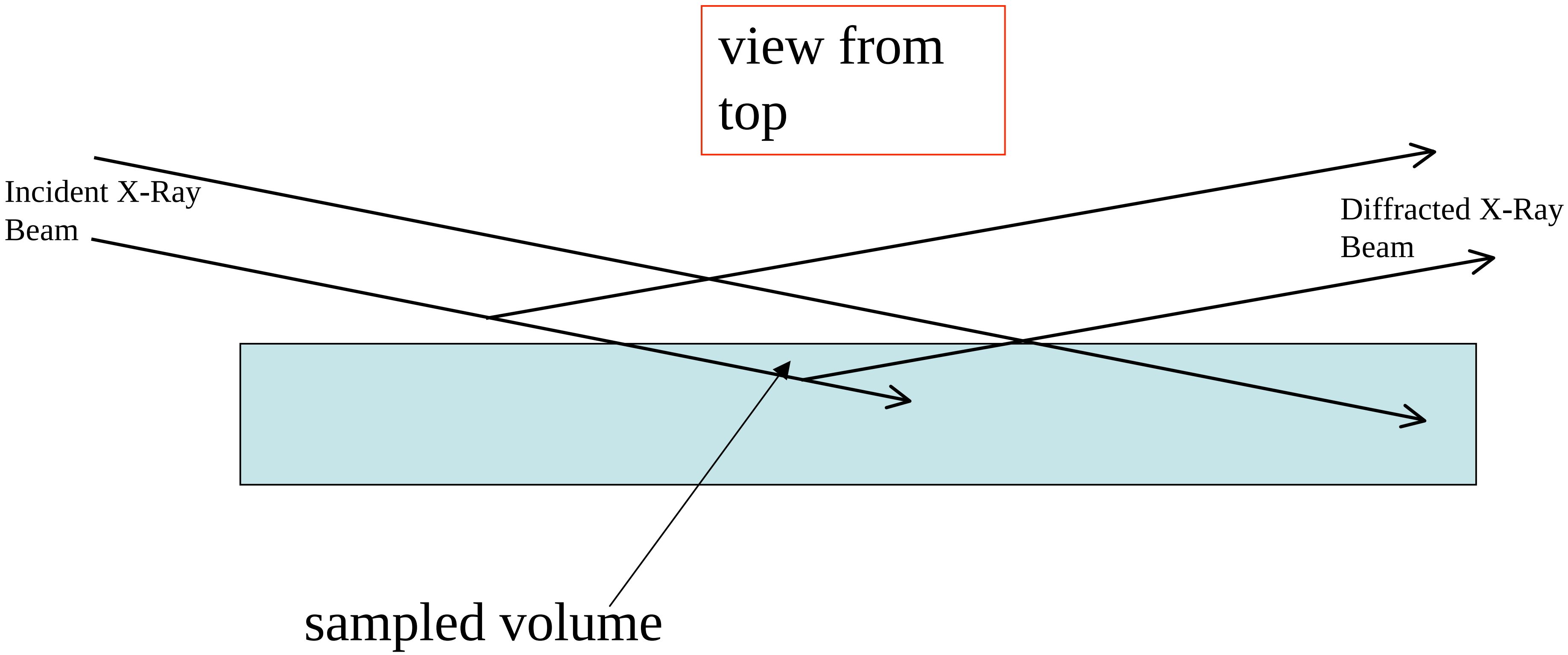
Continuous energy picks out d for properly oriented planes

Detection Volume - 1.6 x 10^{-12} m^3

collimated X-ray beam is 23 µm wide x 14 µm tall
collimated diffracted beam is 50 µm wide x 500 µm tall
2θ = 13 degrees



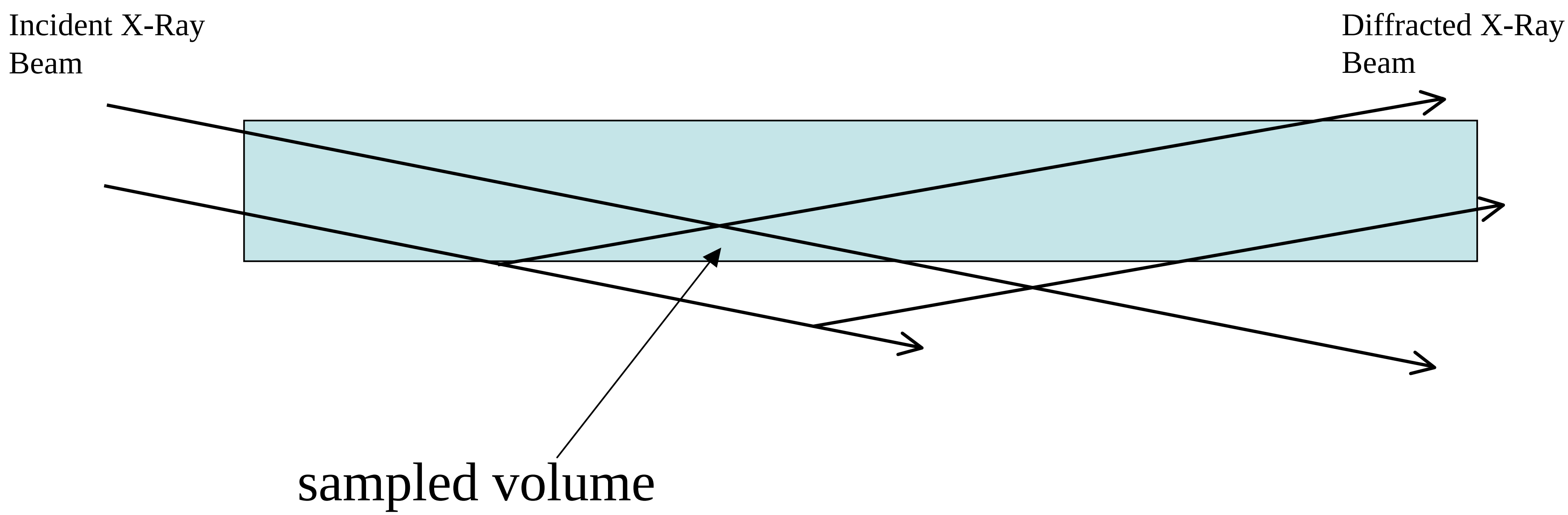
Detection Volume



Near surface sampling (Pd x-ray fluorescence observed)

Detection Volume

view from top



Bulk sampling (No Pd x-ray fluorescence observed)

Unexpected Challenges & Observations

• Control of geometry difficult due to movement of foil from stresses caused by 13% volume change as cathode was loaded with hydrogen.

•Since beam covered only a few grains, diffraction condition often had to be found by x-y-z position scanning.

• When cell abruptly turned off at high loading fraction, electrolyte turned black and then clarified in ~ 60 seconds. Presumably this was caused by rapid removal of impurities plated on the cathode surface that then dissolved into the electrolyte.

• Observation of spontaneous deloading under current control.

• Observation of highest loading fractions early in loading cycle.

Cathode Loading Descriptions

Cathode	Electrolyte 0.1M LiOD in	R0 mOhm	Total Time	Total Charge (C)	Total Energy (kJ)	Maximum H/Pd Ratio fr resistivity	Maximum (H,D)/Pd Ratio fr lattice const.
NRL#2	D_2O	3.69	46:15	6337	22.14	0.85	0.89
L23	D_2O	3.82	30:15	5974	18.32	0.87	0.93
B2	D_2O	10.08	48:22	110947	783.24	0.95	1.02
L5	H_2O	5.24	09:56	4354	18.19	0.97	1.01

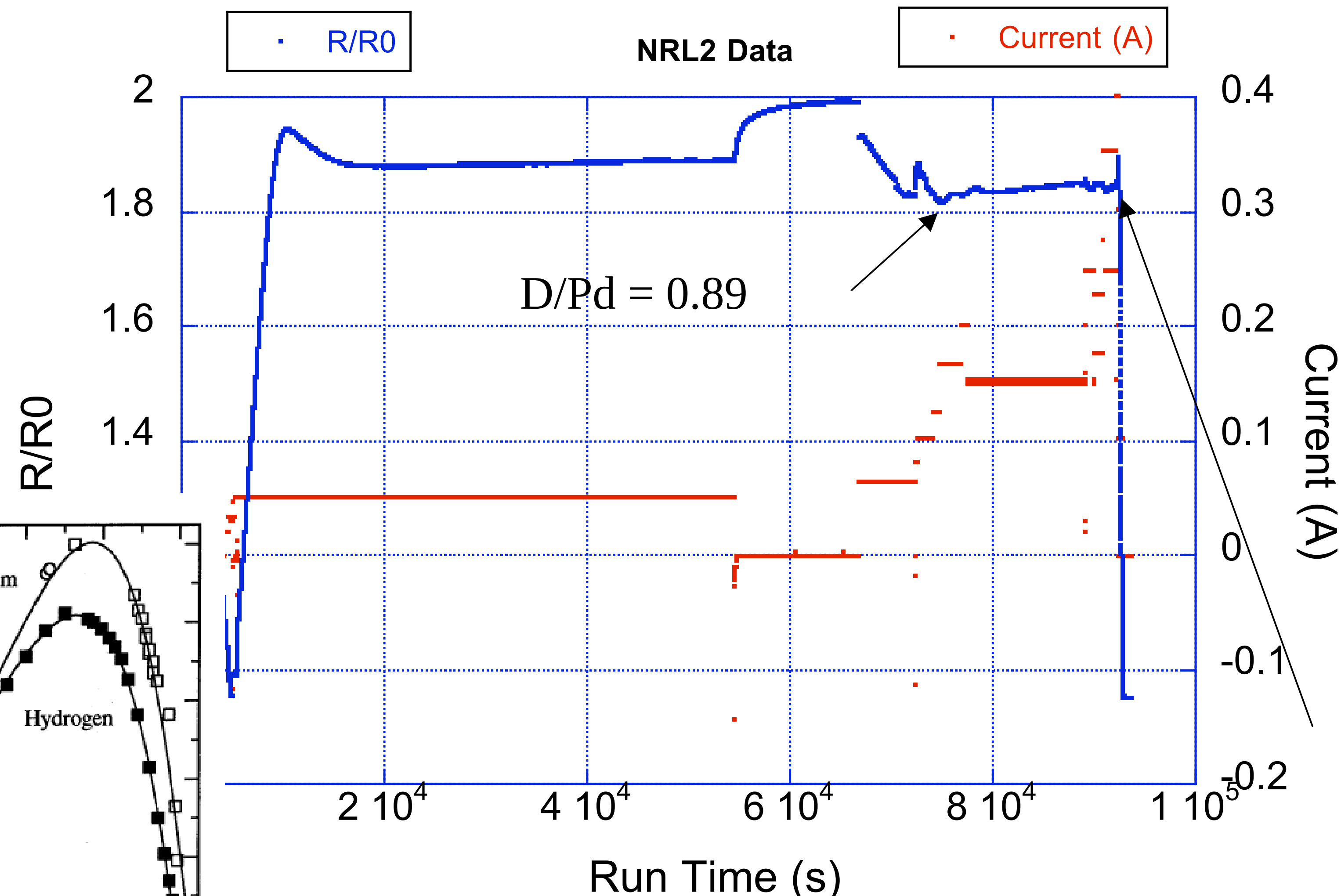
<u>Tentative observations:</u>

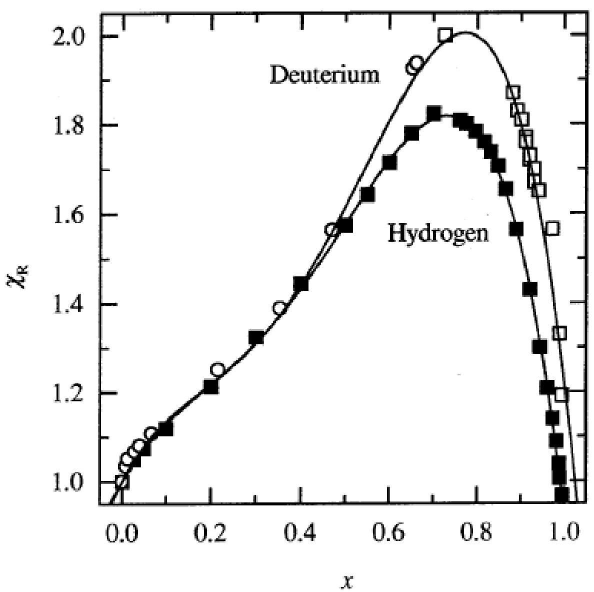
•R/R0 four point probe underestimates loading ratio

•R/R0 is a good in situ qualitative guide for loading ratio

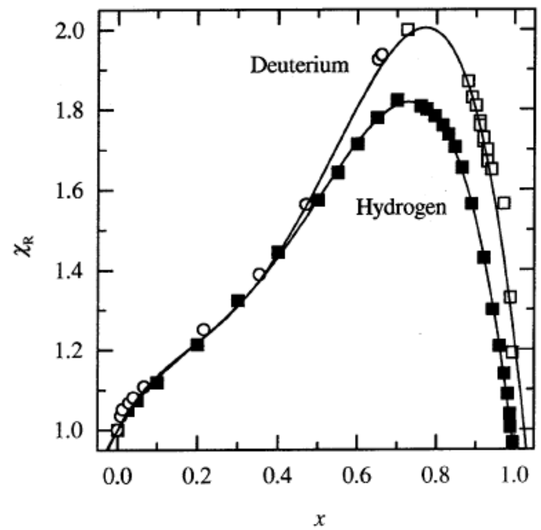
•Thinner foils loaded to higher ratio

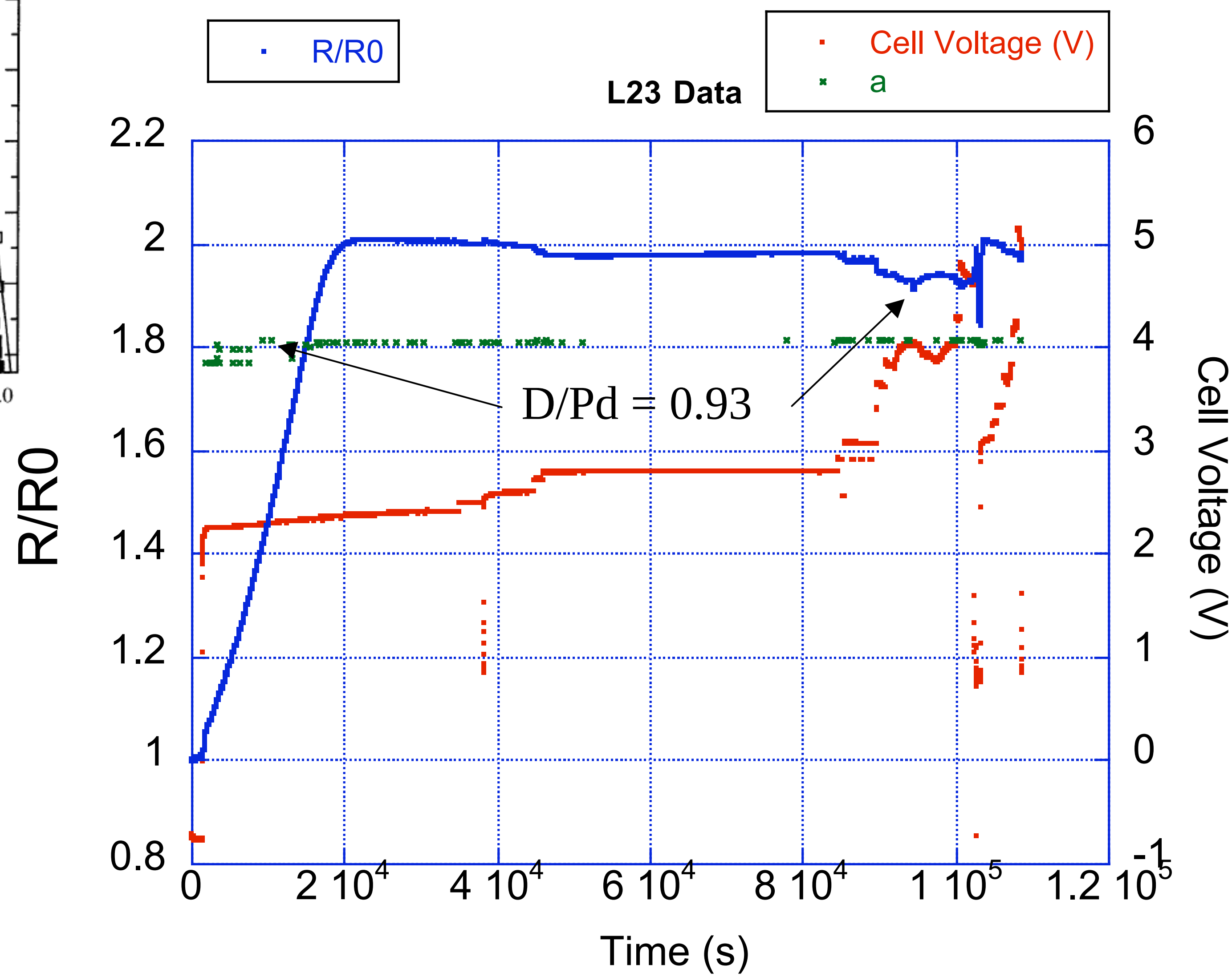
Observation of Spontaneous Deloading



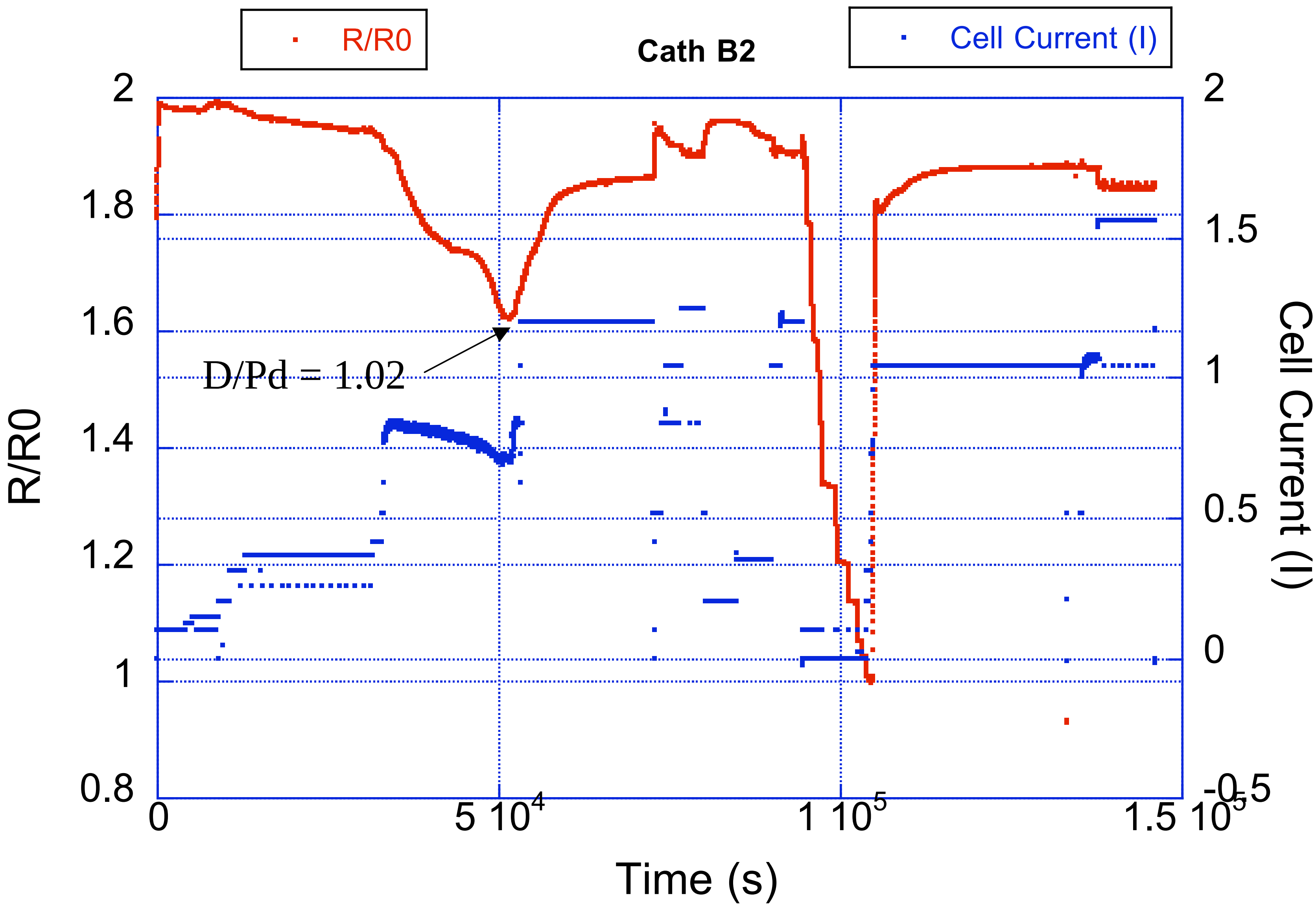


Electrochemical History

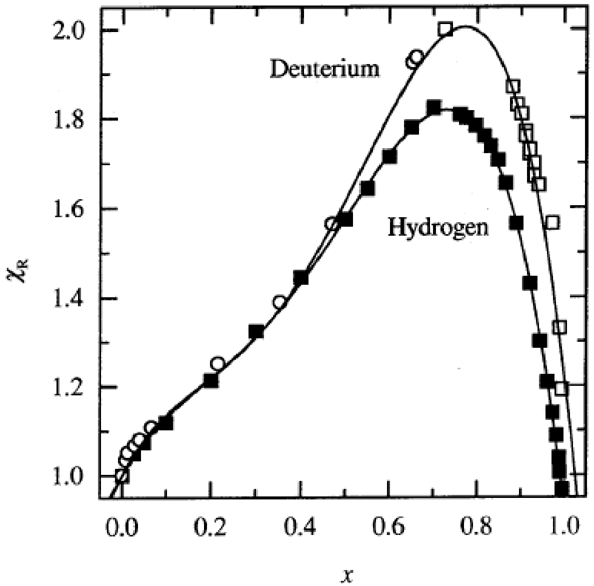


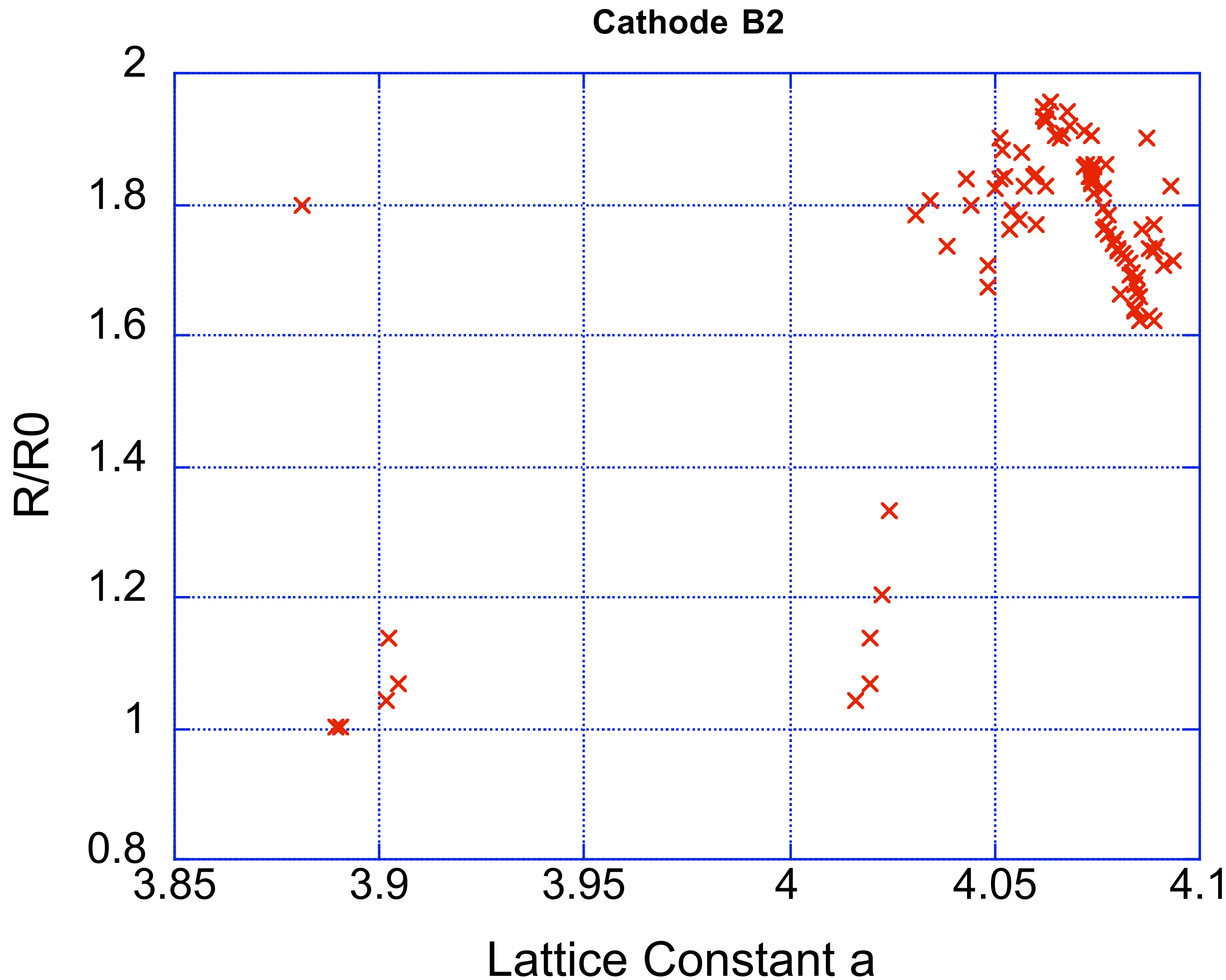


Electrochemical History

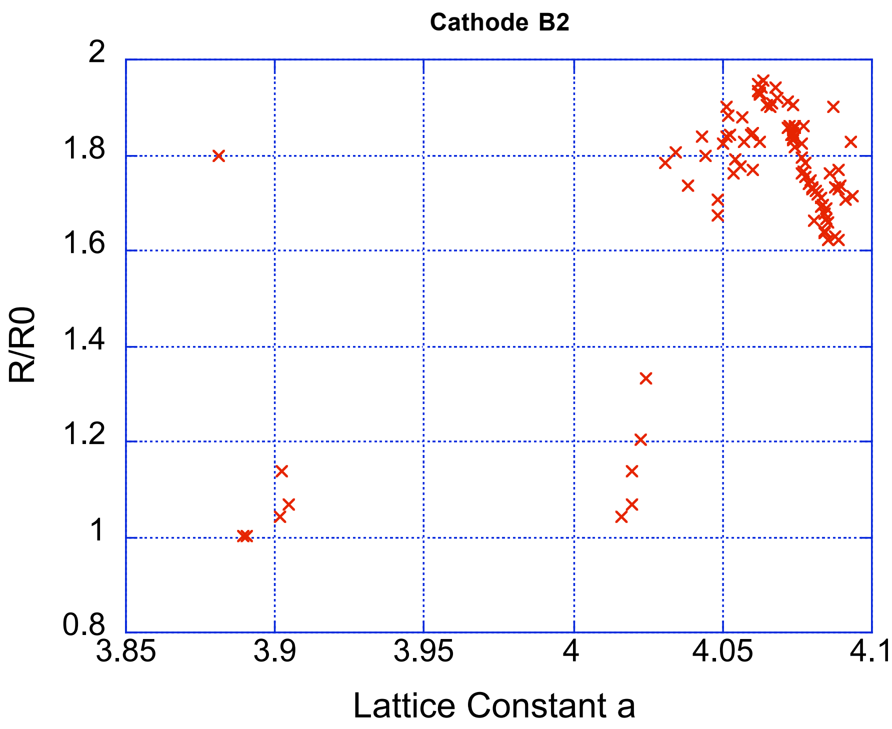


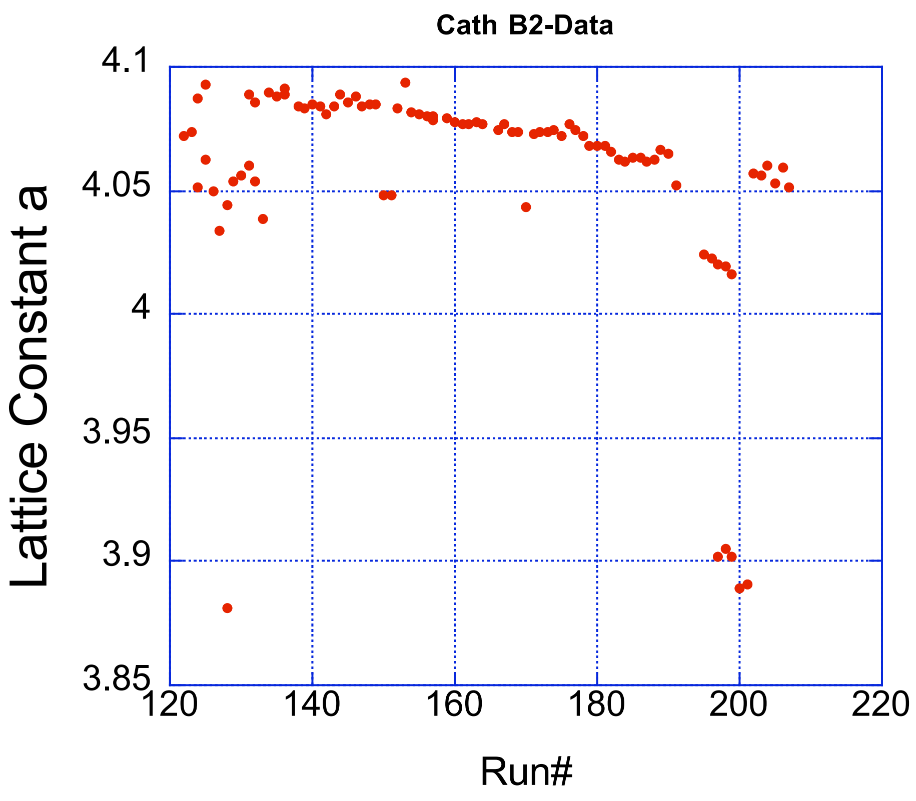
Systemmatics of Loading



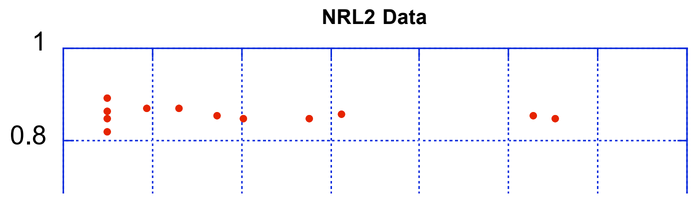


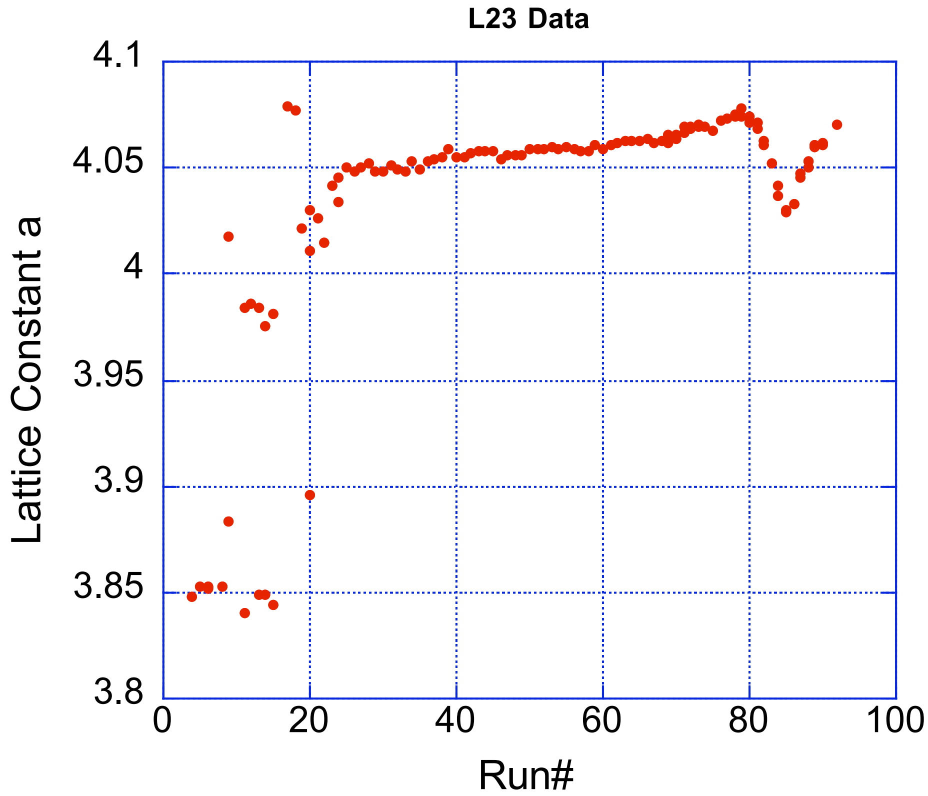
Systemmatics of Loading

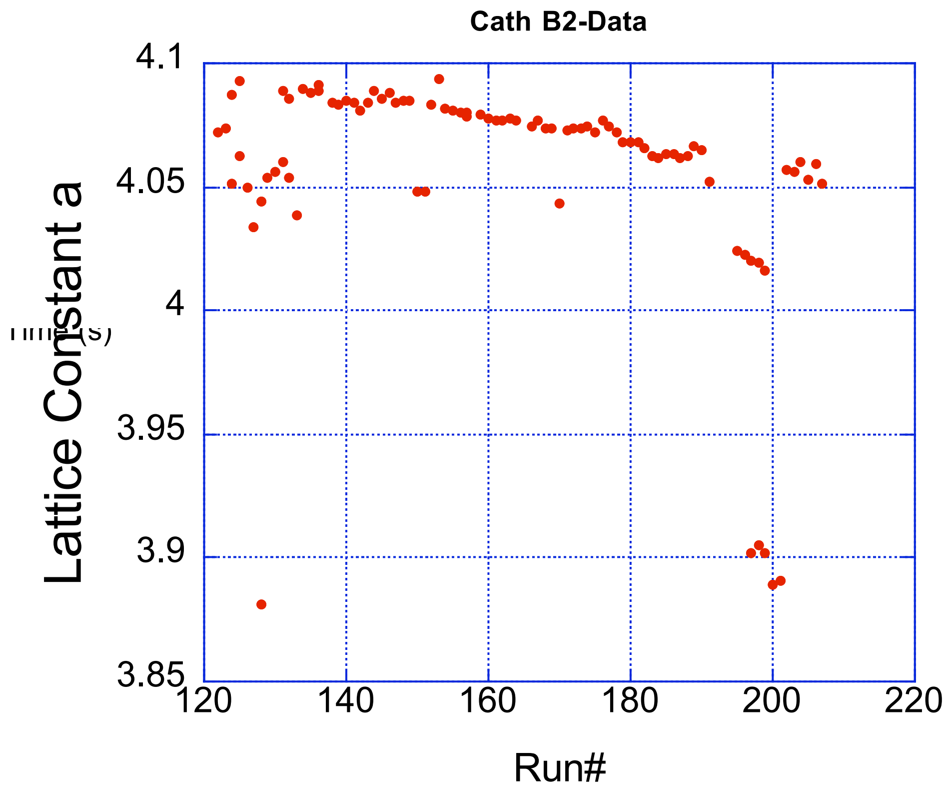




High Loading Fractions at Early Time

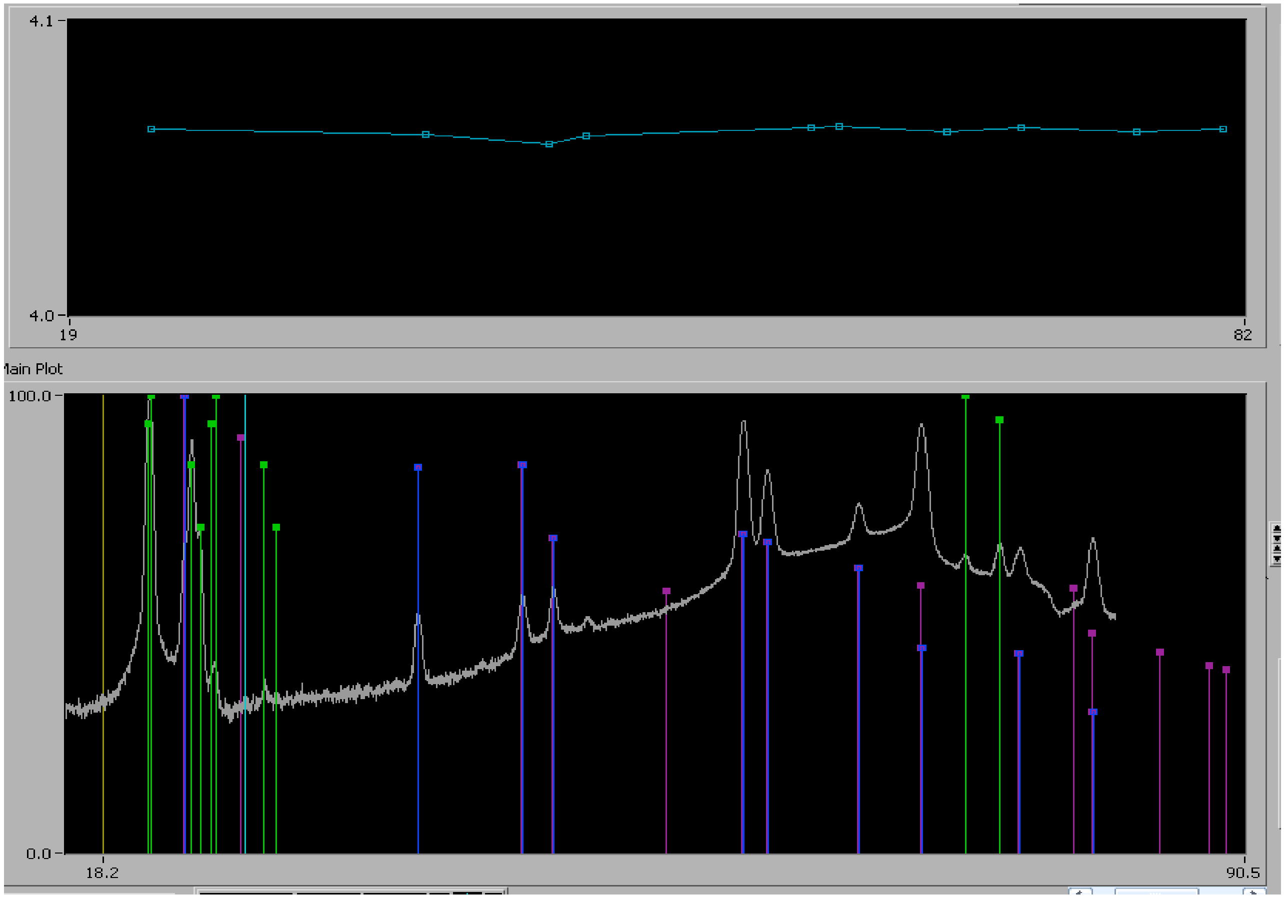






Typical X-Ray Spectrum

Semi-Log Plot

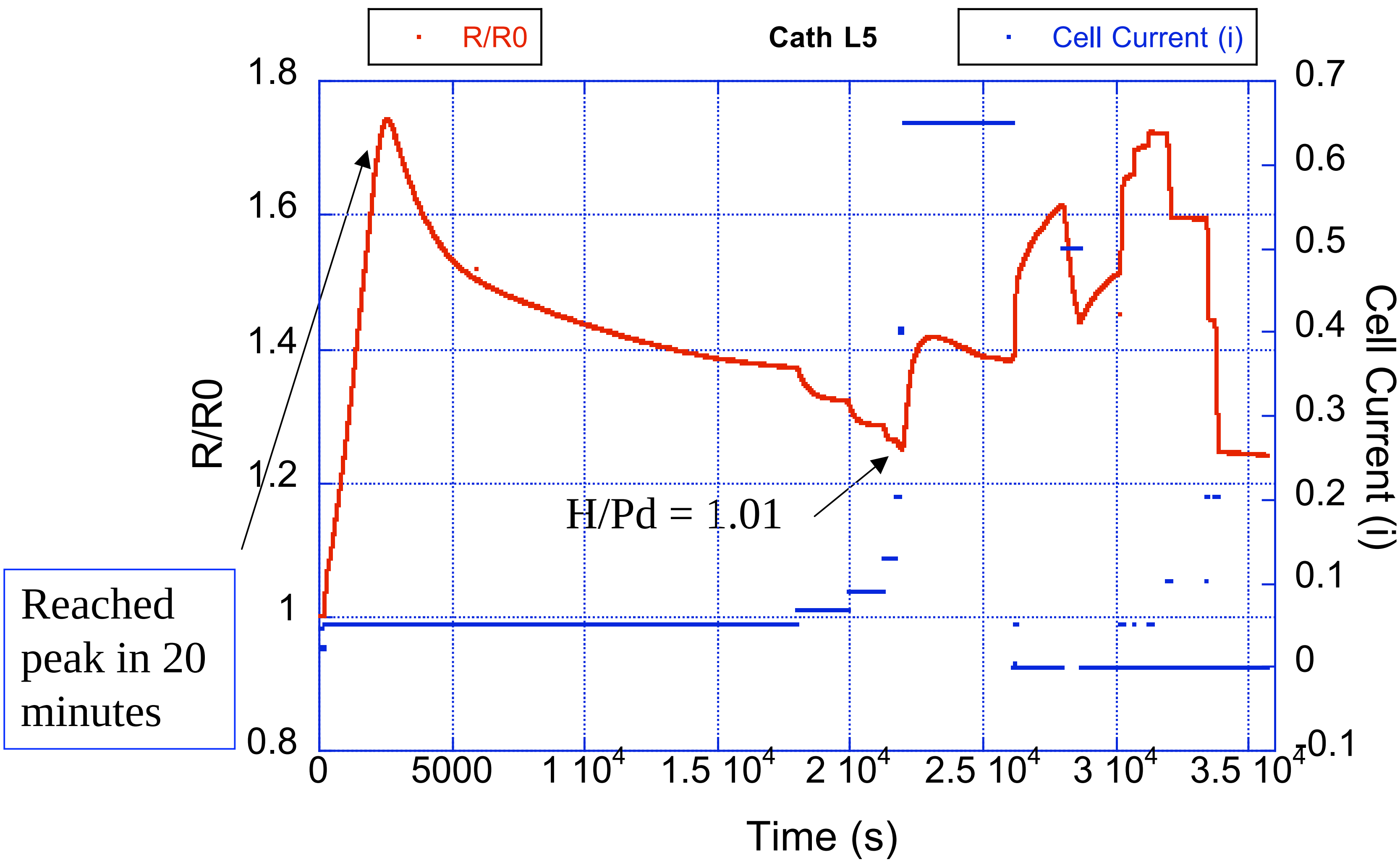


- Intensity falls off at low E due to absorption in electrolyte
- Pd K-edge absorption below 23 keV
- Intensity falls off at high E due to x-ray beam intensity fall-off
- In this spectrum, 10 x-ray diffraction peaks fit well

- Fluorescence peaks for Pb and Sn appear during all cell runs
- Pd fluorescence used to monitor surface

- Only a few instances where Alpha and Beta diffraction seen simultaneously. Therefore, within ~ 3-5 min intervals, the phase change is complete
- Only several grains interrogated

Cathode Loaded with Hydrogen



Summary - Electrolysis of 4 Cathodes

Observations consistent with literature

More difficult to load D than H

Spontaneous deloading under current control

Evidence of large amount of deposited impurities on surface

R/R0 in situ resistivity measurement is a good *qualitative* guide to loading ratio

Once a cathode has been loaded to high a ratio, it can not be loaded a second time

Tentative new observations

Higher starting resistivity foils (thinner foils) loaded to higher D/Pd ratio

Highest loading ratios occur at early time in loading cycle

All four ENEA-prepared cathodes loaded to high D/Pd ratios

Summary - X-Ray Diffraction

Observations consistent with literature

alpha-beta phase change

Tentative new observations

Rapid surface deloading and reloading

Very few x-ray spectra with both Alpha and Beta phases present suggests that within multiple grains, the transformation from Alpha to Beta is very rapid (within the 3-5 minute time resolution of the data)

Highest D/Pd ratio early in loading cycle

New observations

High D content by x-ray diffraction (D/Pd = 1.02)

R/R0 measurement consistently underestimates the loading ratio

No obvious new phase at high loading fractions (for Pd sublattice only)

First time x-ray diffraction performed in FPE cell at concentrations greater than D/Pd > 0.76

Conclusions

- Time resolved, in-situ, high-energy x-ray diffraction was performed on modified Fleishman-Pons electrolytic cells during electrochemical loading of palladium foil cathodes with hydrogen and deuterium.

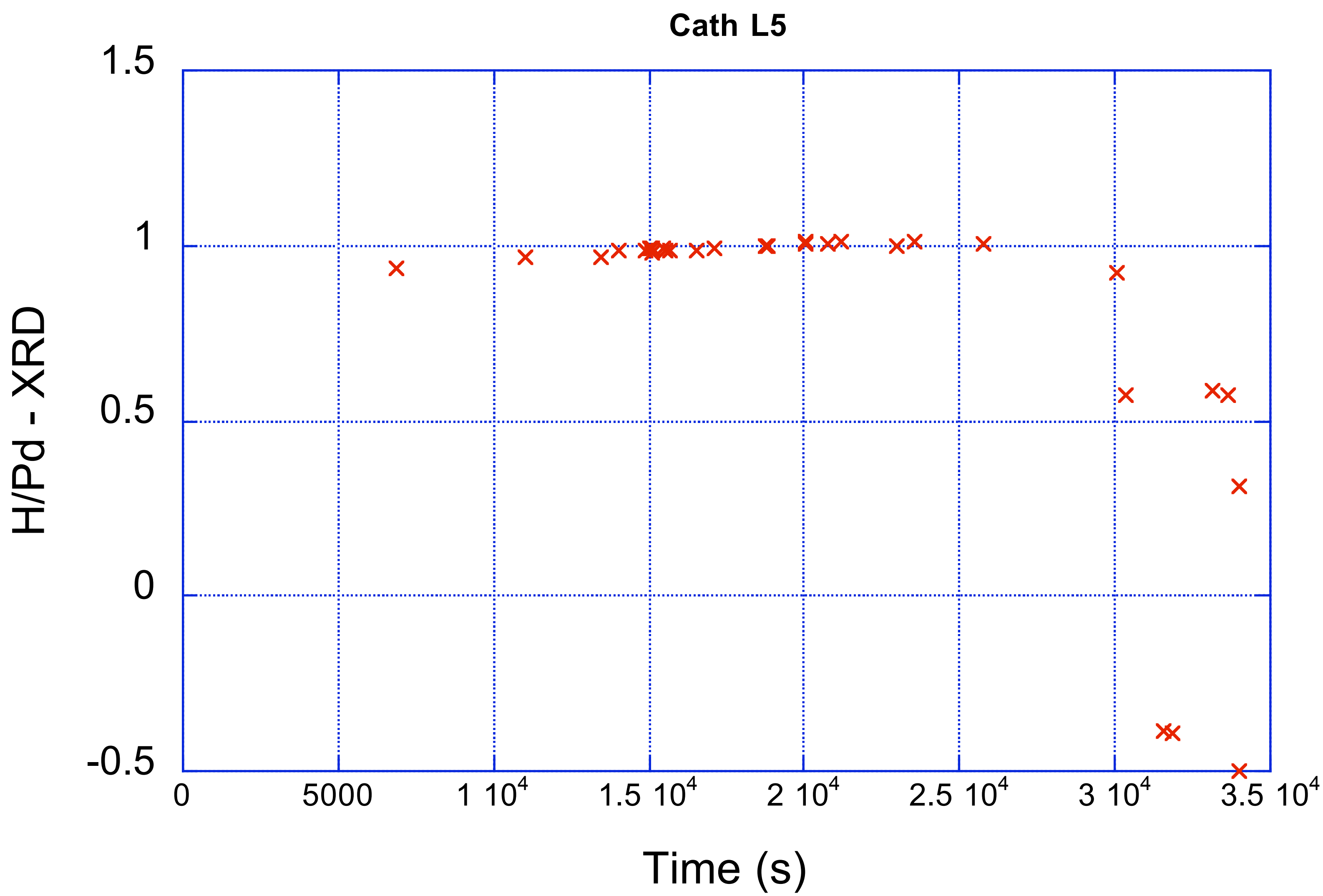
- Concentrations of H and D up to 1:1 in 0.1 M LiOH/LiOD in H_2O/D_2O electrolytes were obtained.

- While very interesting data in its own right, no new anomalous behavior was observed that identifies a mechanism of FPE.

Table I: Maximum Electrolytic Loading Ratios Achieved in the Pd-H and Pd-D systems.

System	Loading Ratios	Loading Conditions and/or Sample Preparation	In Situ X-Ray or Neutron Diffraction	Year	Ref
Pd-D	0.72	0.1 M LiOD	x-ray diffraction	1998	27
Pd-D	0.92-0.96	1M LiOD, stepwise changed current density; 0.96 if etched with aqua regia, 0.92 if polished with diamond grit	none	1997	12
Pd-H; Pd-D	0.78-0.82	0.1 M/1M LiOH or LiOD, 50 mA/cm^2	none	1996	13
Pd-H; Pd-D	**0.76**	0.1 M LiOD	x-ray diffraction	1995	14
Pd-H;Pd-D	0.85-0.90	1 M LiOH and LiOD	none	1995	15
Pd-D	0.91-0.93	Pd was vacuum annealed and acid etched.	none	1994	16
Pd-D	0.55	0.1 M Li_2O in D_2O	neutron diffraction	1990	66

High H Content



Pd-H Phase Diagram

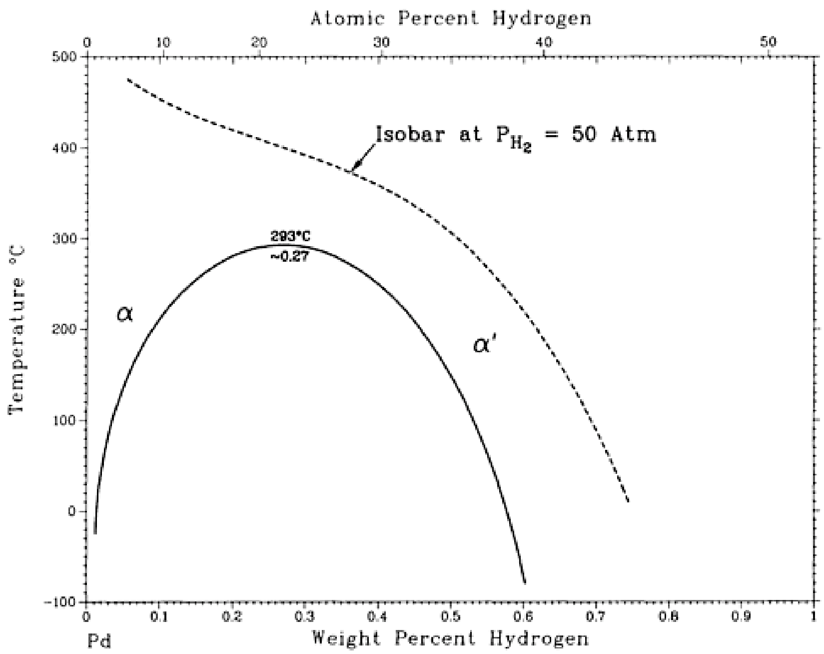


Figure 1: The phase diagram of Pd-H system.

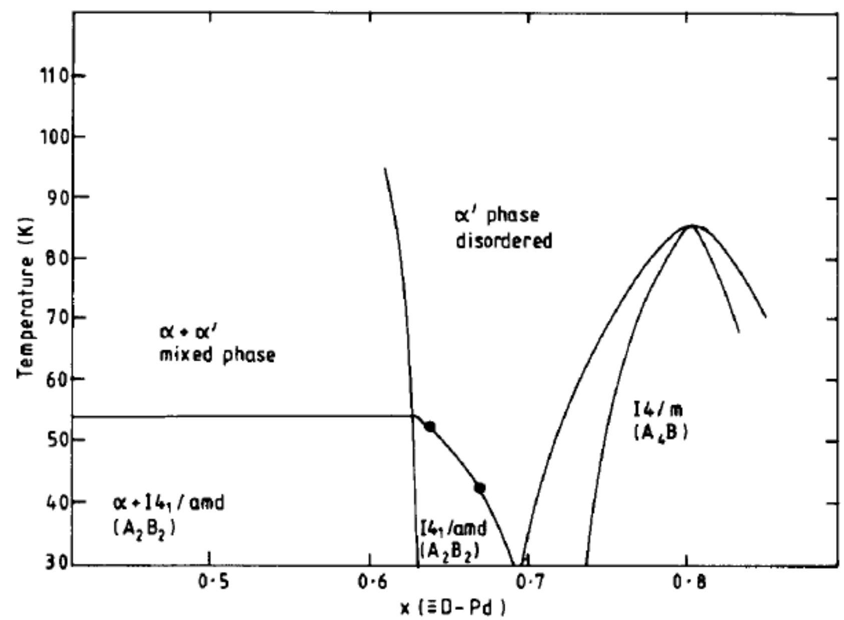


Figure 2: The phase diagram of Pd-D system (Here, α’ phase means β) at low temperatures.

Shifts in XRD peaks with time

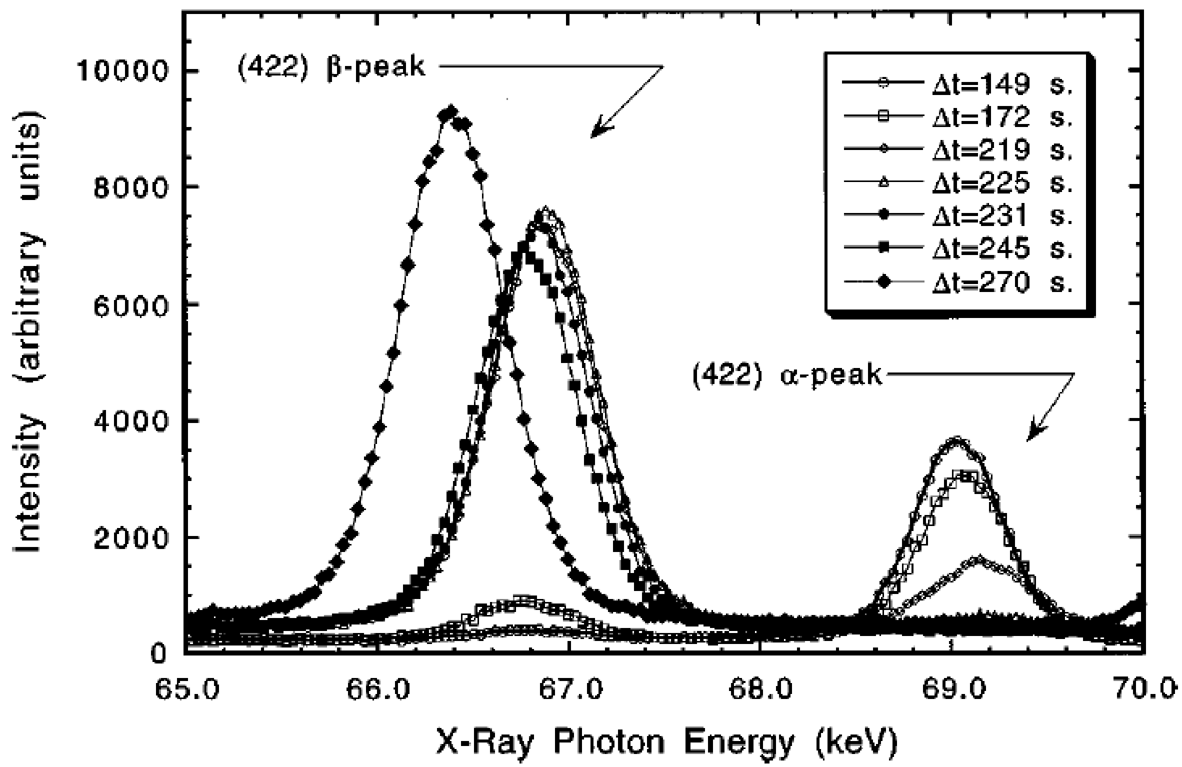
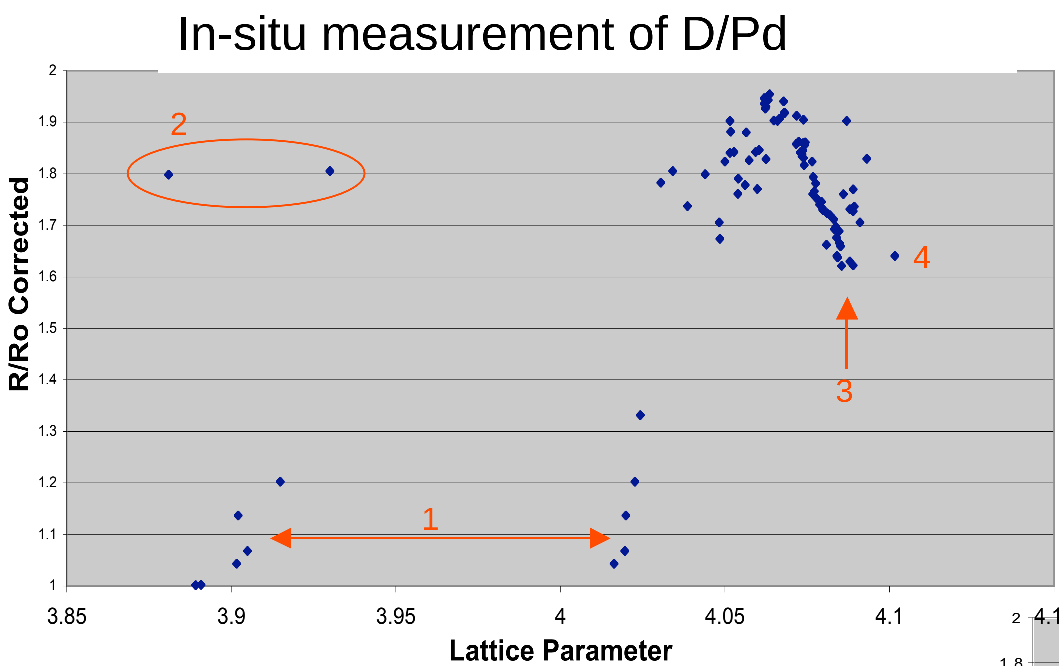
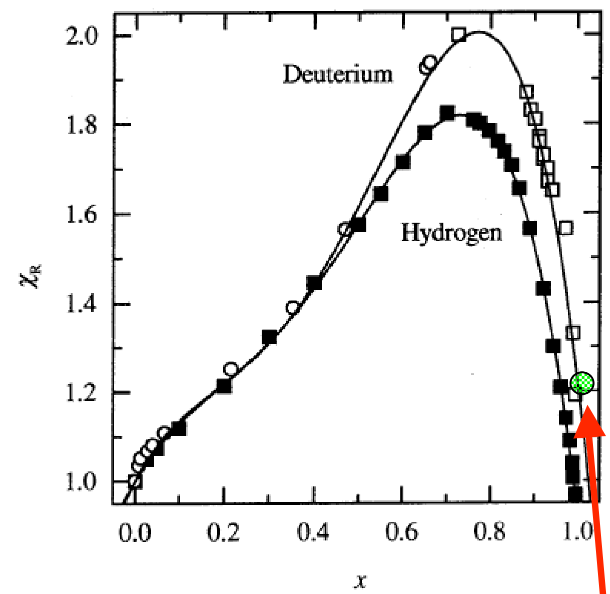
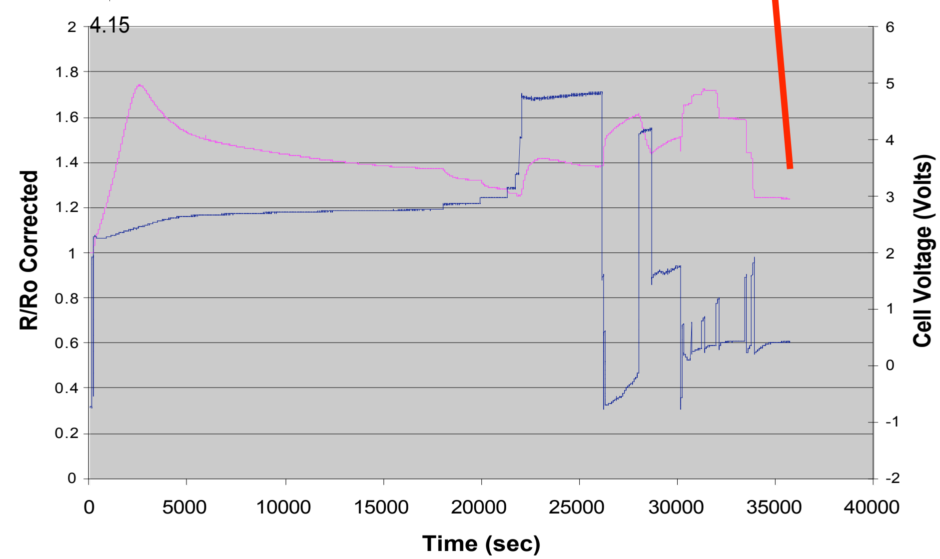


Figure 5: Temporal dependence of the intensity of (422) diffraction peaks of α and β phases.

D/Pd > 1







1 alpha-beta phase change

2 rapid surface deloading

3 high D content

4 suggestion of phase change