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

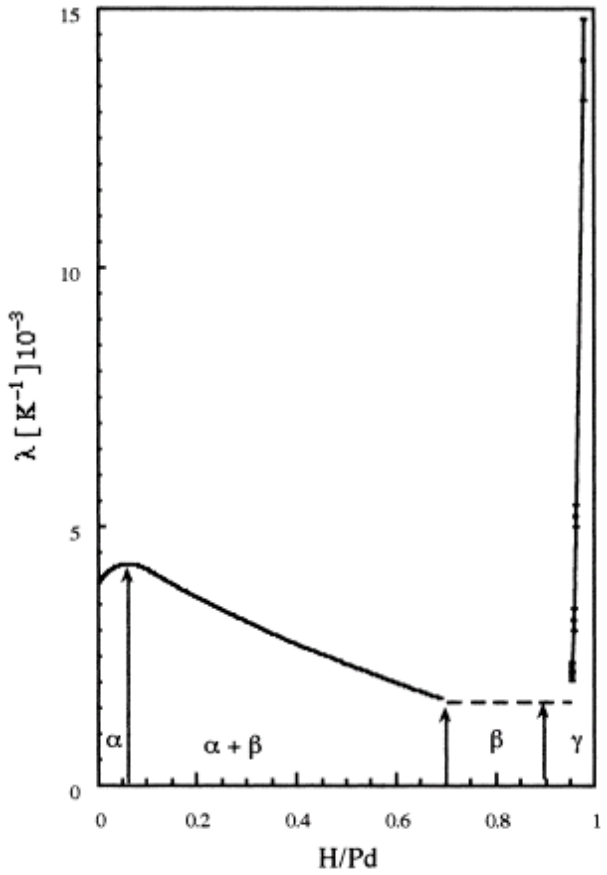


Figure 3: Temperature coefficient of resistivity λ for all phases. The dashed is the plateau value for λ.

Pd Foil Cathodes

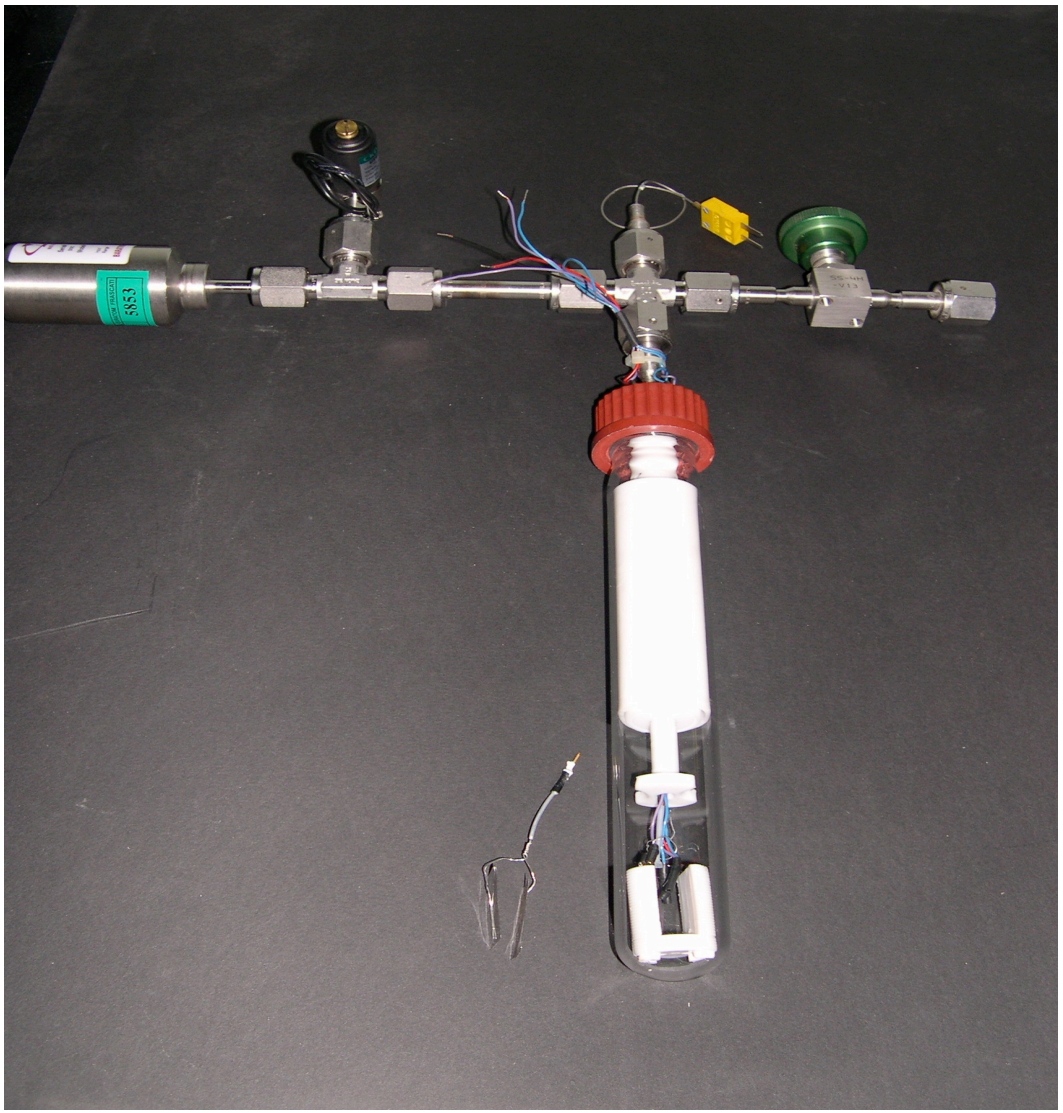
- Pd 0.9995 purity fabricated at ENEA by V. Violante

- 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

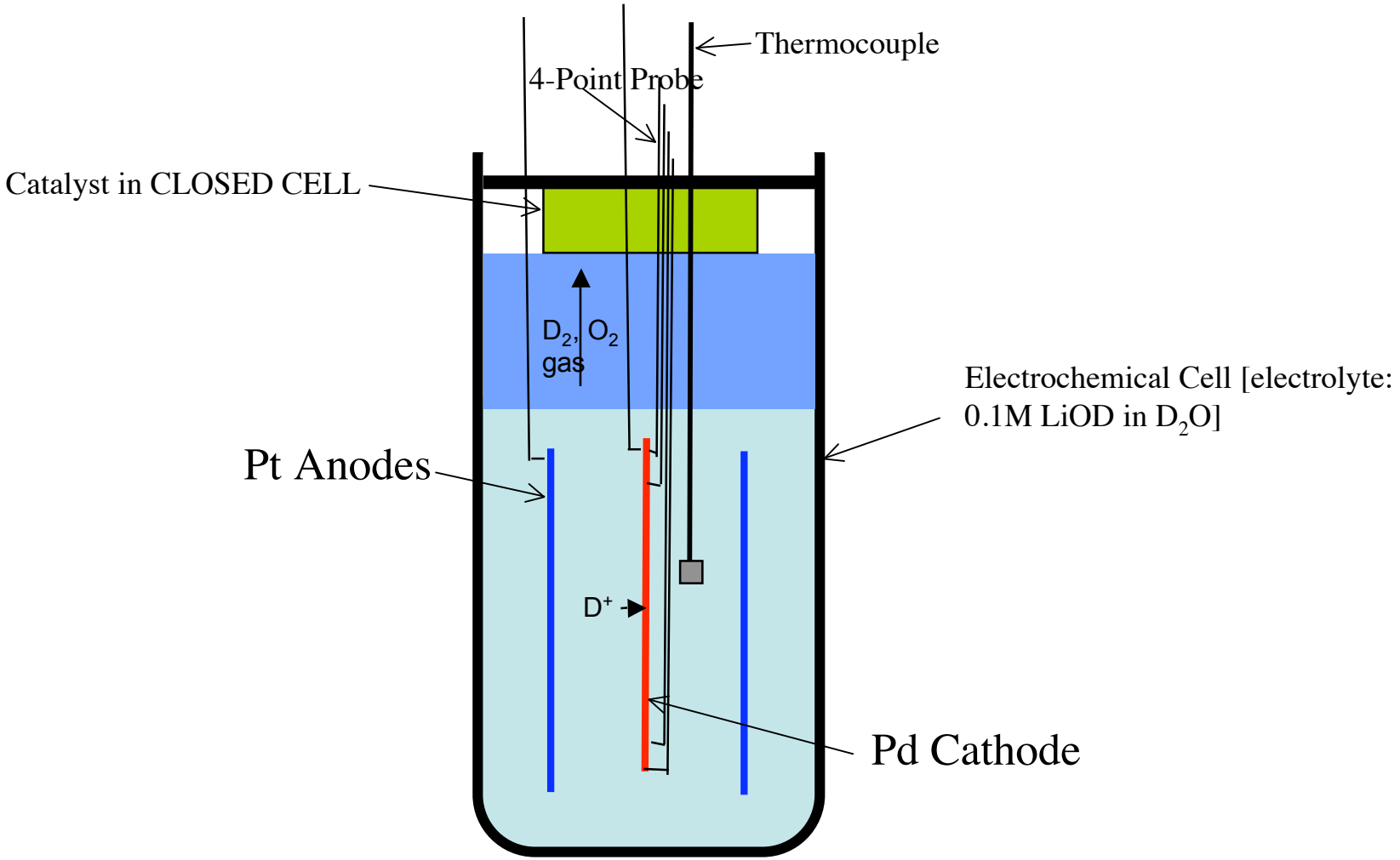
- ~100 μm grain size

Electrochemical Cell



- Designed and built by ENEA
- Dual Pt anodes

Electrochemical Cell



Experimental Measurements

Cell Measurements

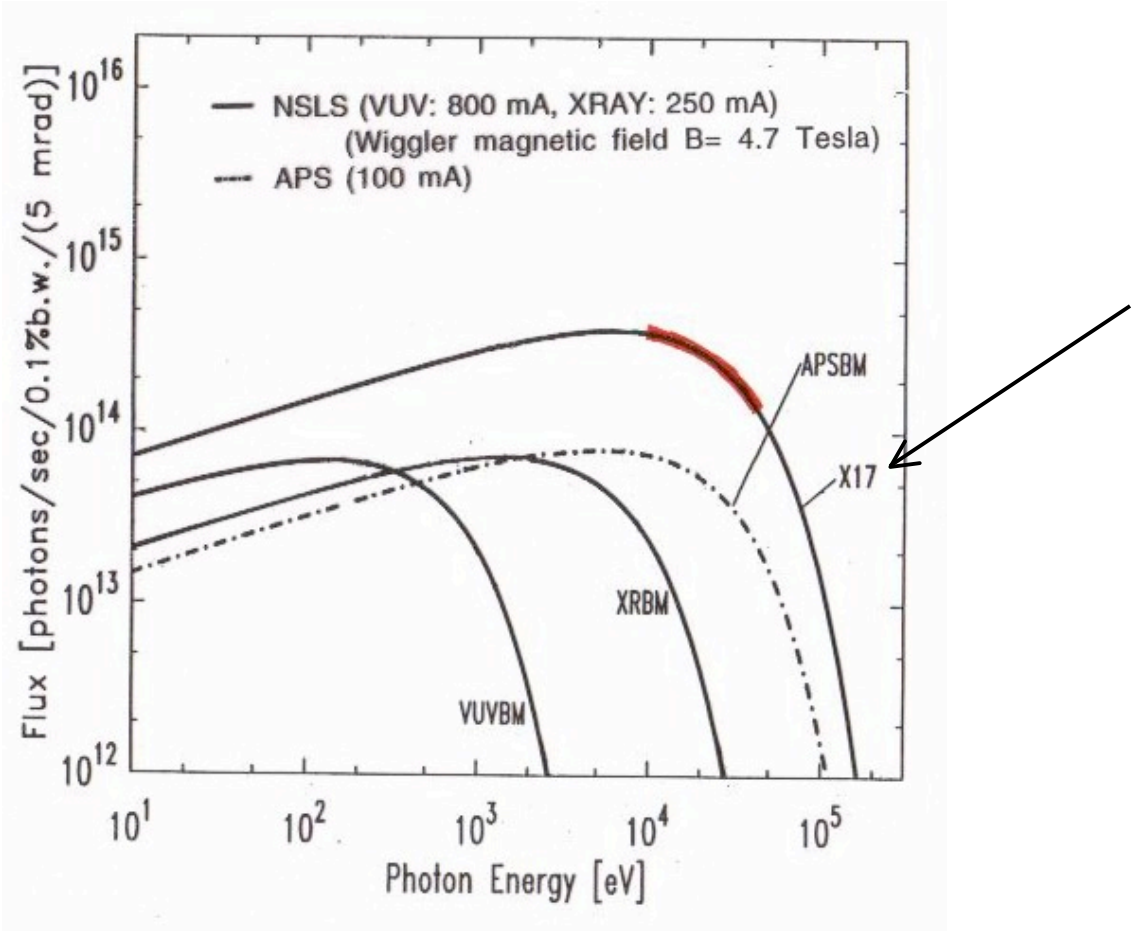
- Temperature
  - 1 thermocouple in electrolyte
  - 5 RTD's external to cell
- Electrolysis
  - Current
  - Voltage
- Cell Pressure
  - Baratron
  - Safety valve
- R/R_0
  - 4-point probe @ 1 kHz
- Time
- Data rate
  - 1/4 Hz

X-Ray Measurements

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

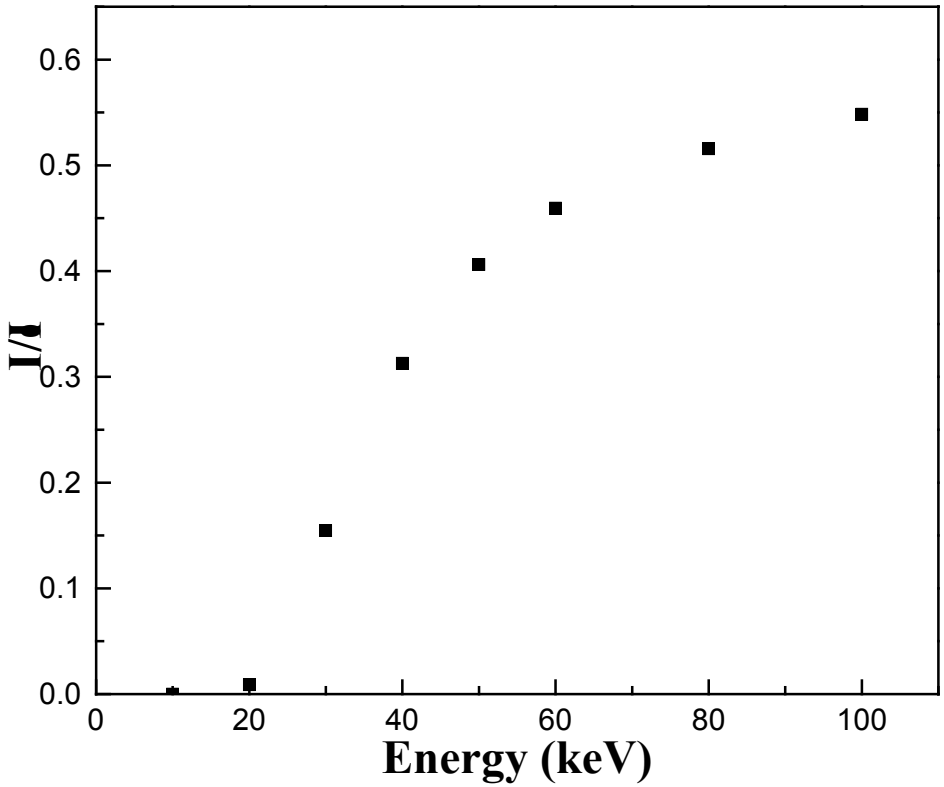
No Calorimetry!

Brightness of NSLS Beam Lines

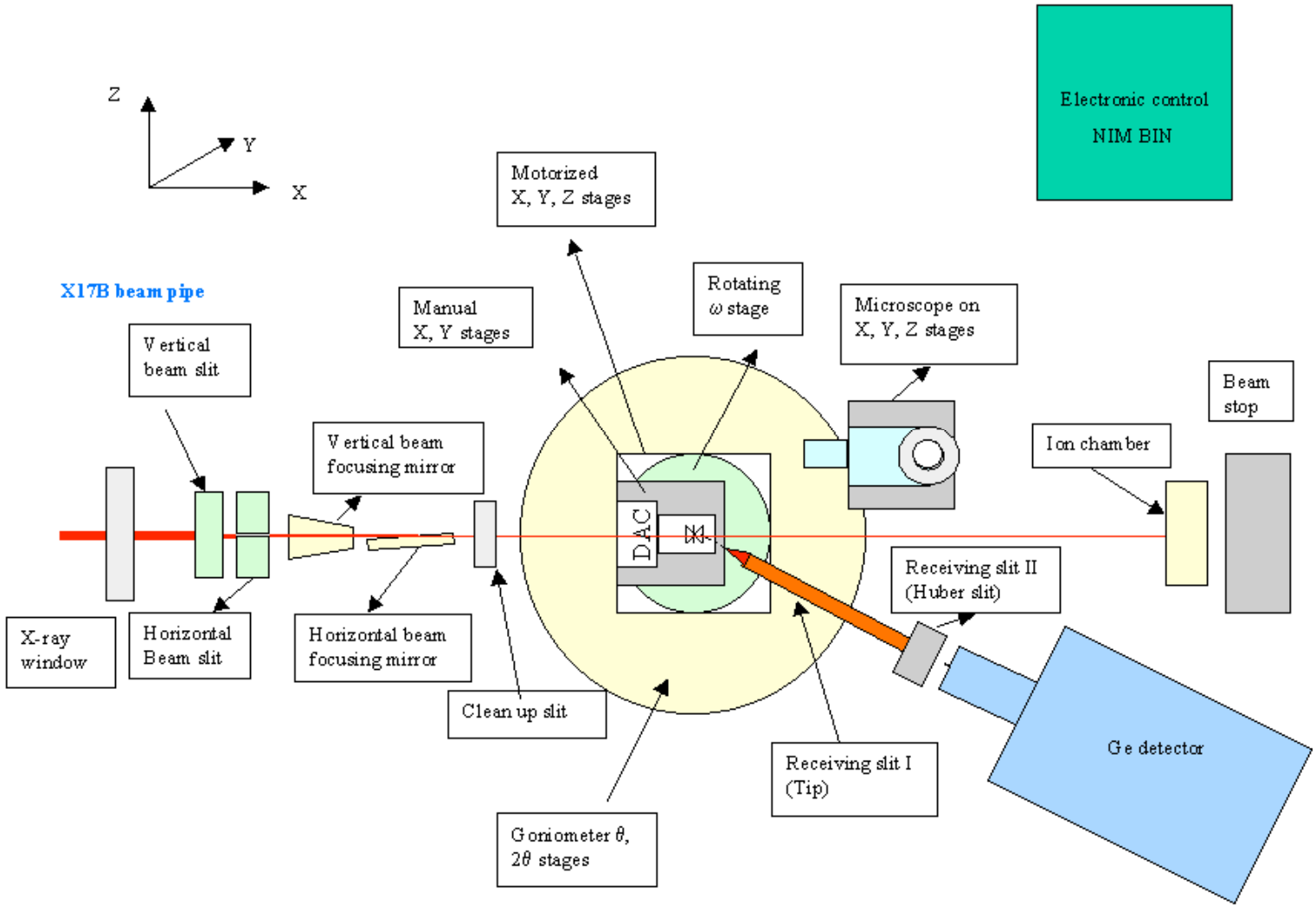


X-Ray Transmission through Electrochemical Cell

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

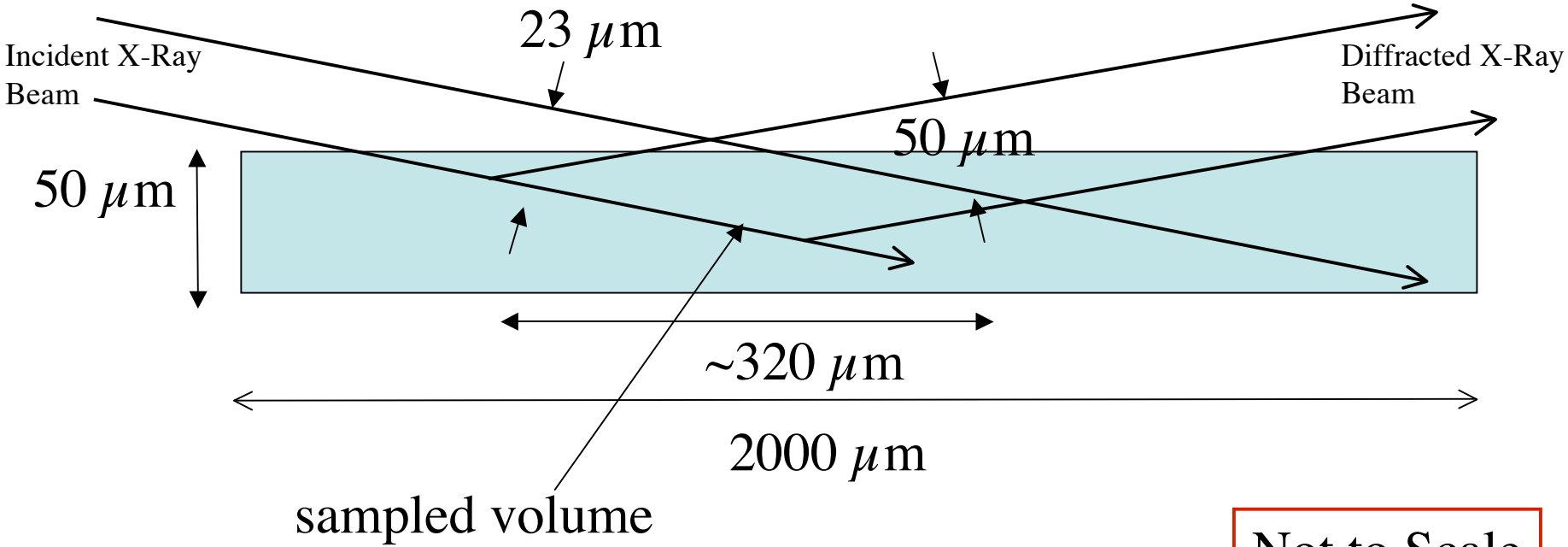
$$Ed \sin\theta = 6.1992n$$

Continuous energy picks out d for properly oriented planes

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

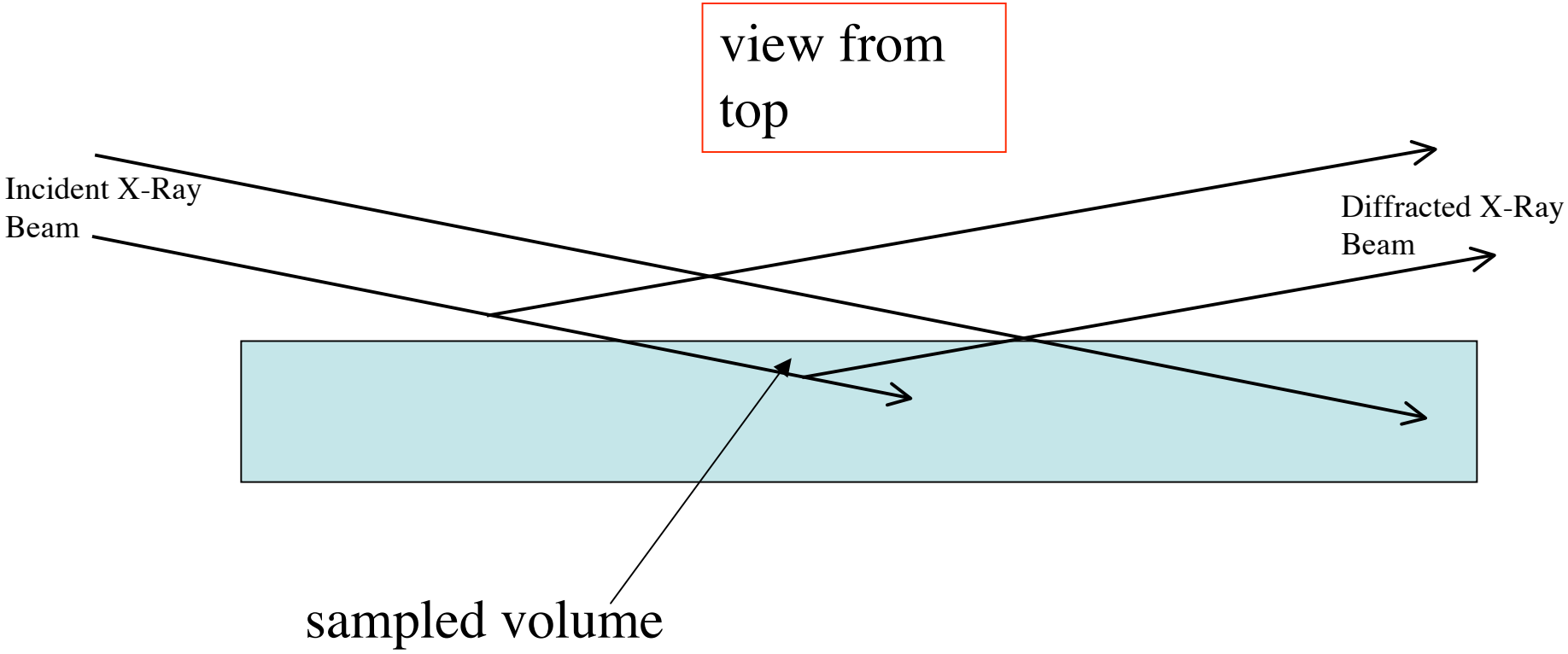
collimated X-ray beam is 23 μm wide x 14 μm tall
collimated diffracted beam is 50 μm wide x 500 μm tall
2θ = 13 degrees

view from top



Not to Scale

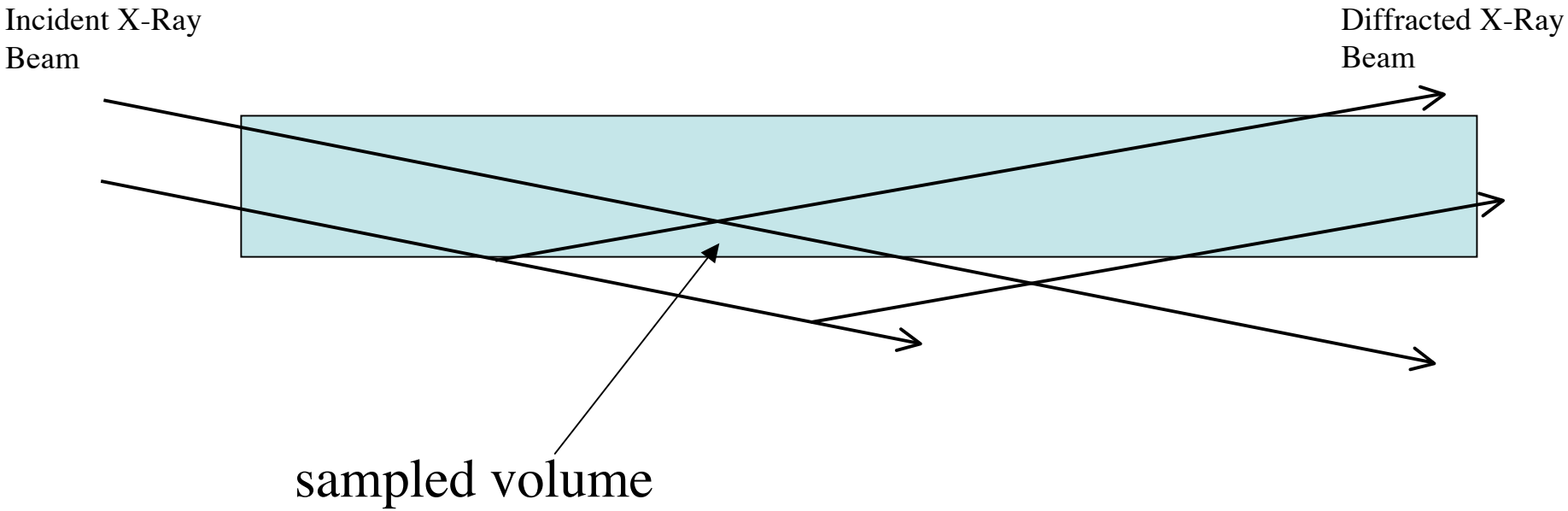
Detection Volume



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.

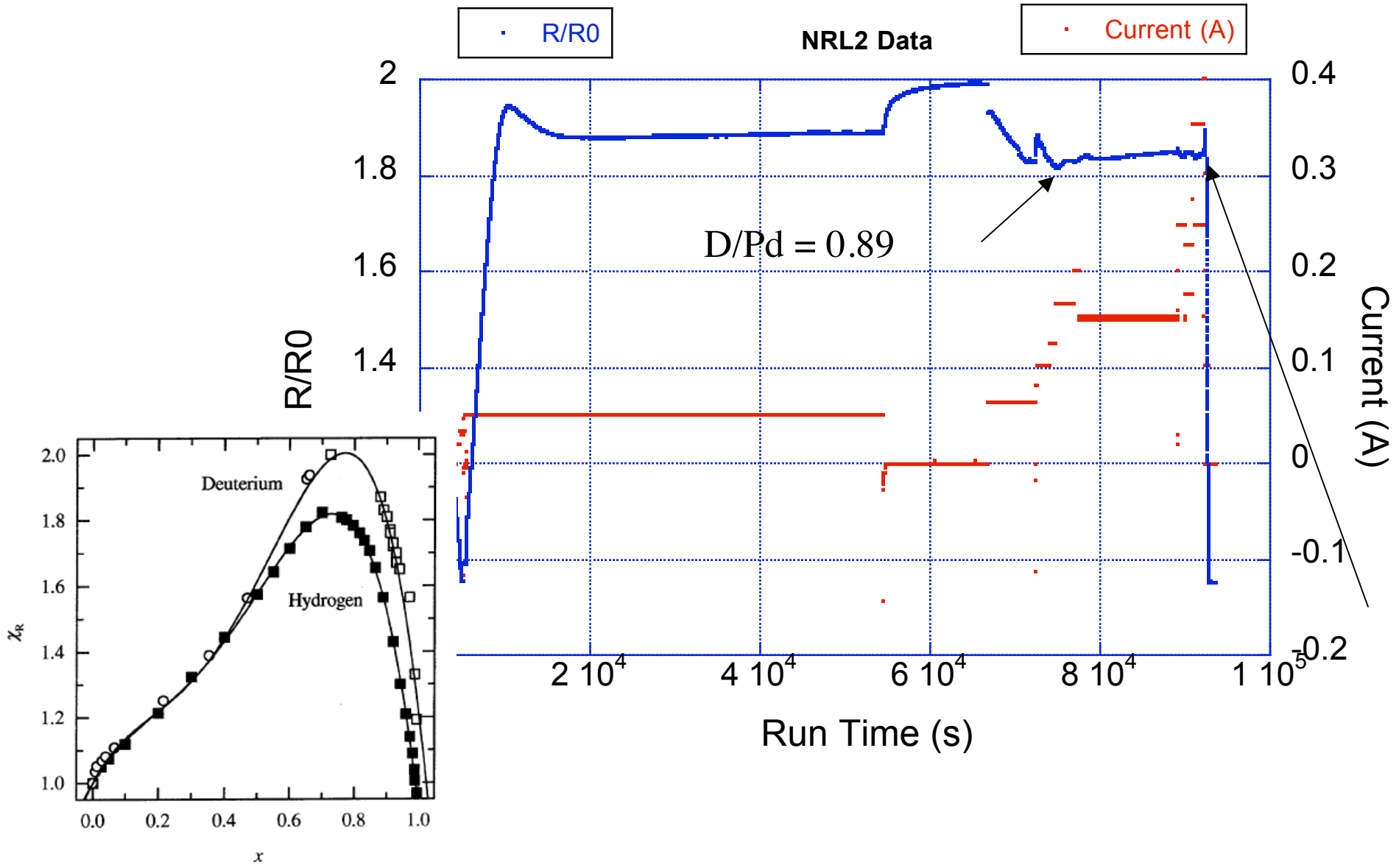
Cathode Loading Descriptions

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

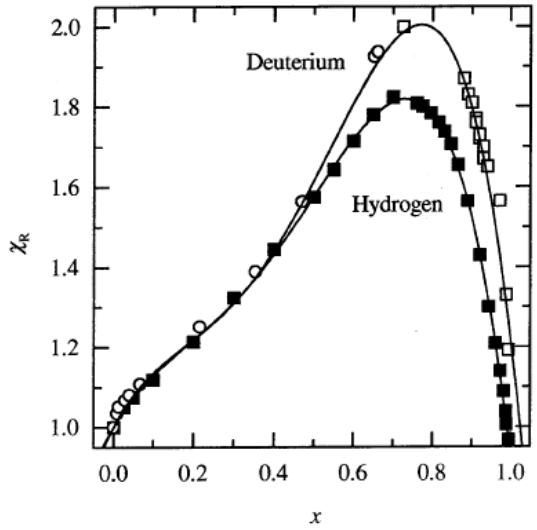
Tentative observations:

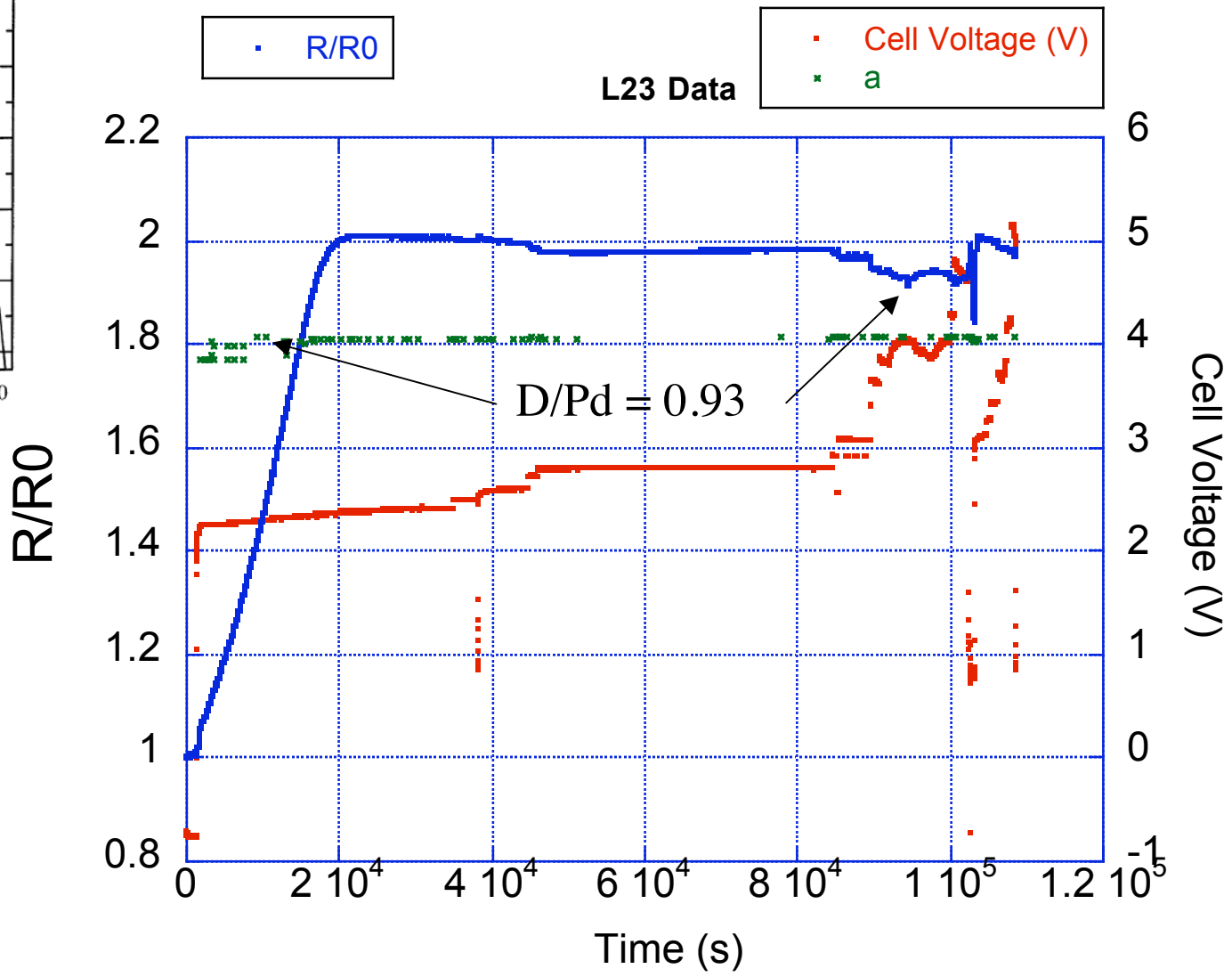
- R/R0 four point probe underestimates loading ratio
- R/R0 is a good in situ qualitative guide for loading ratio
- Thinner foils loaded to higher ratio

Observation of Spontaneous Deloading

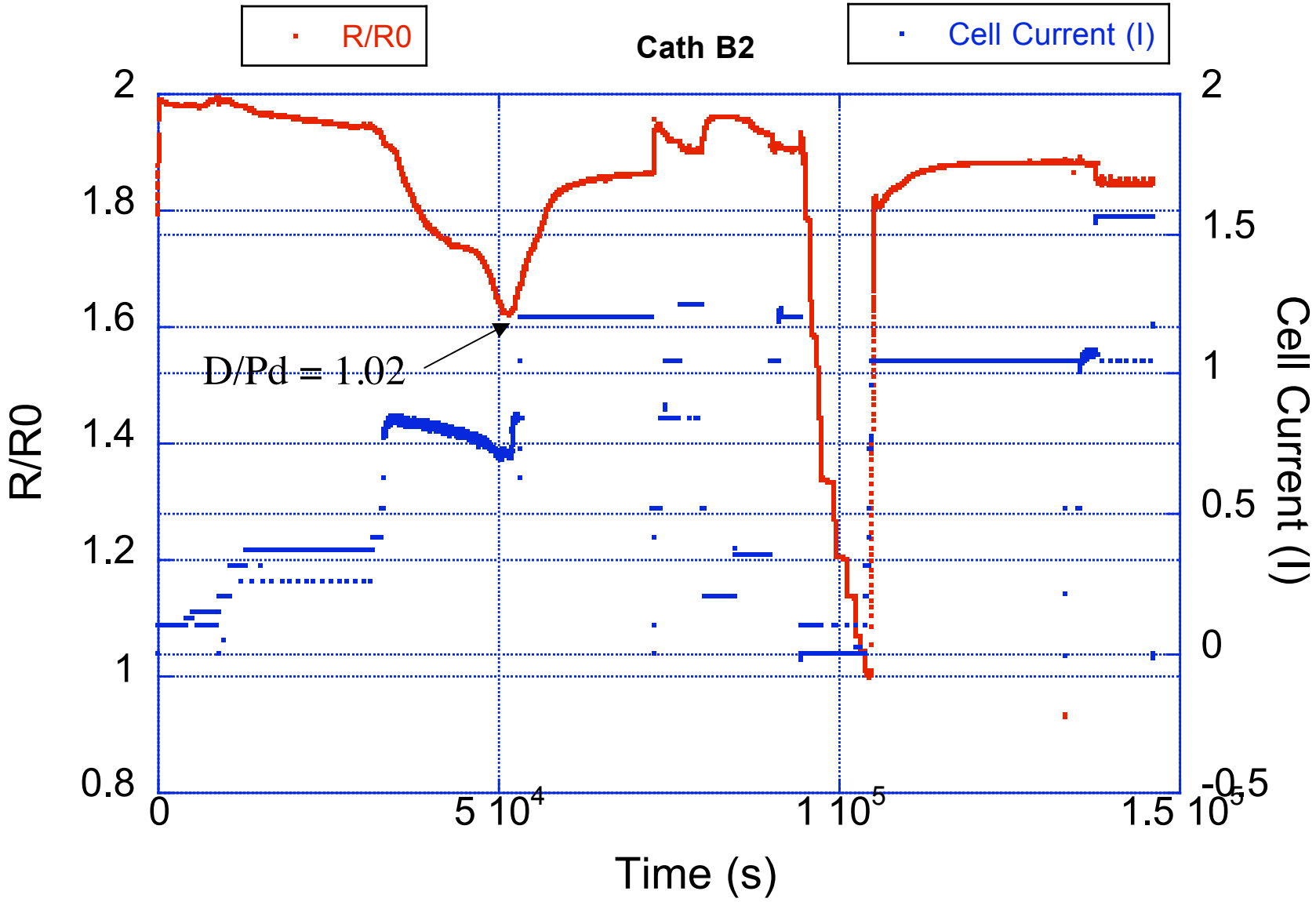


Electrochemical History

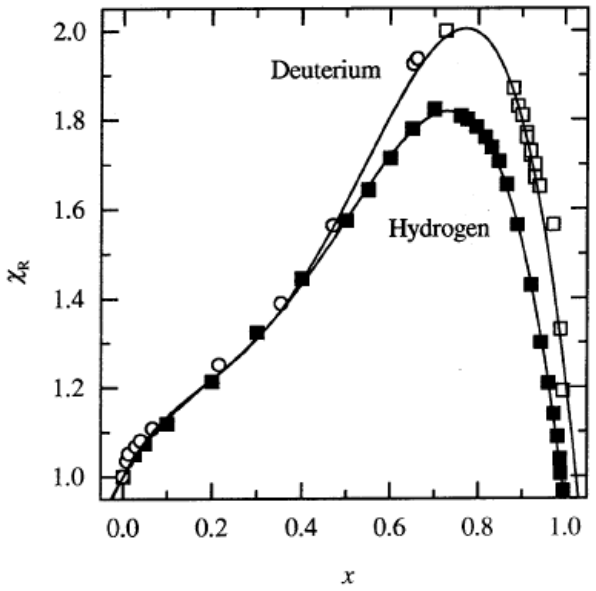


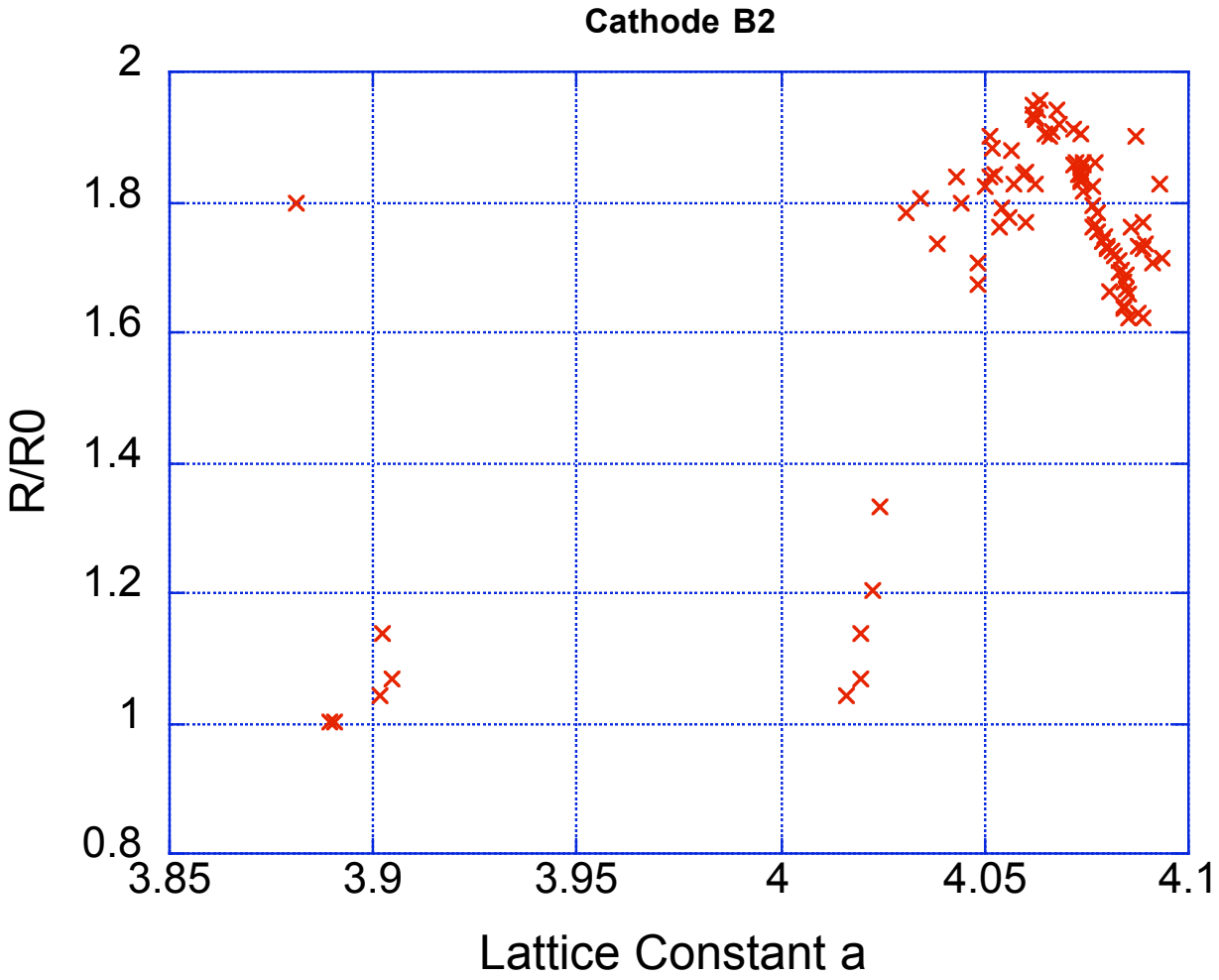


Electrochemical History



Systemmatics of Loading





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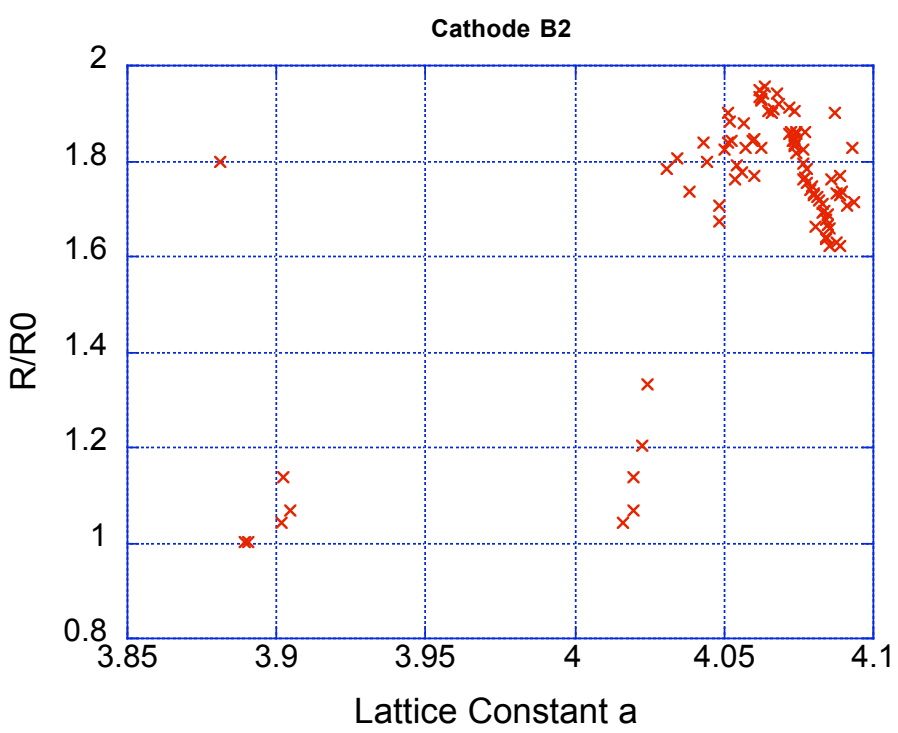
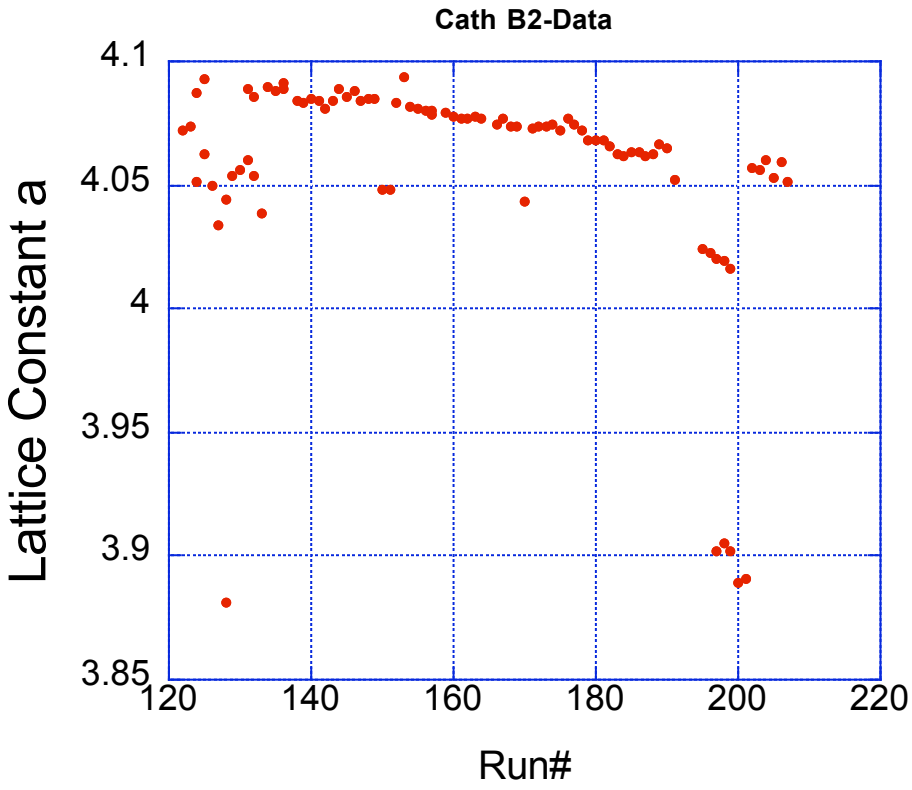
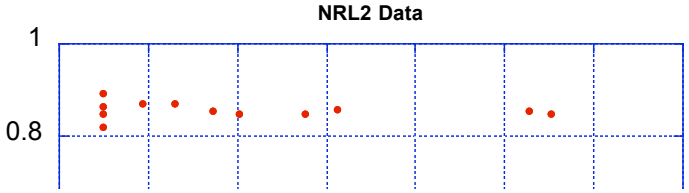
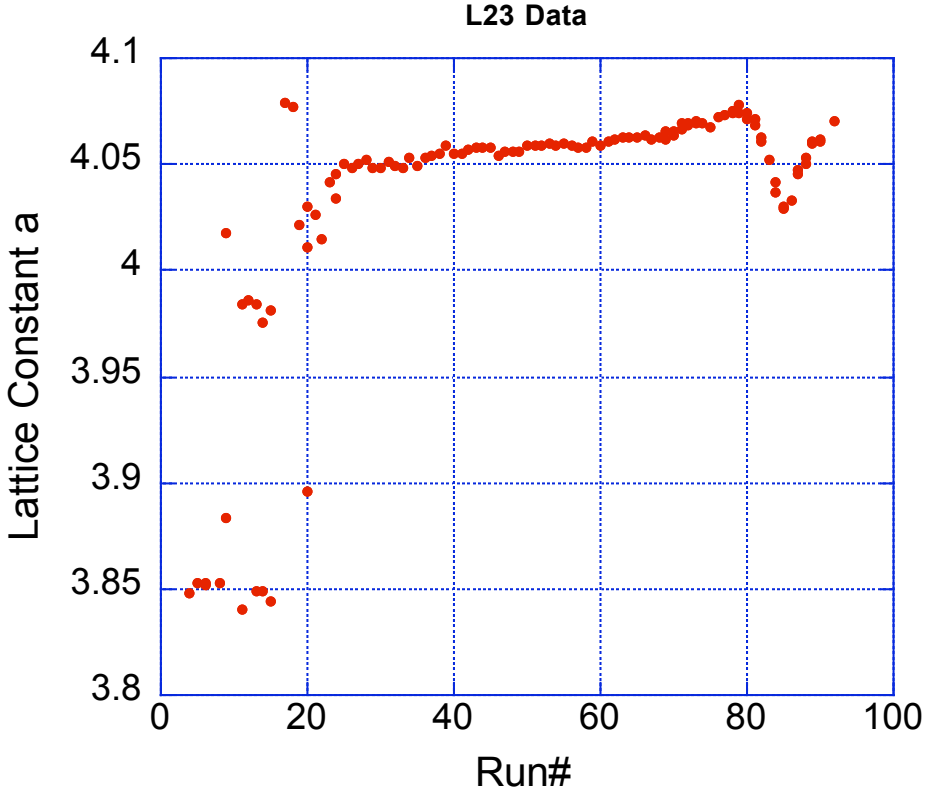
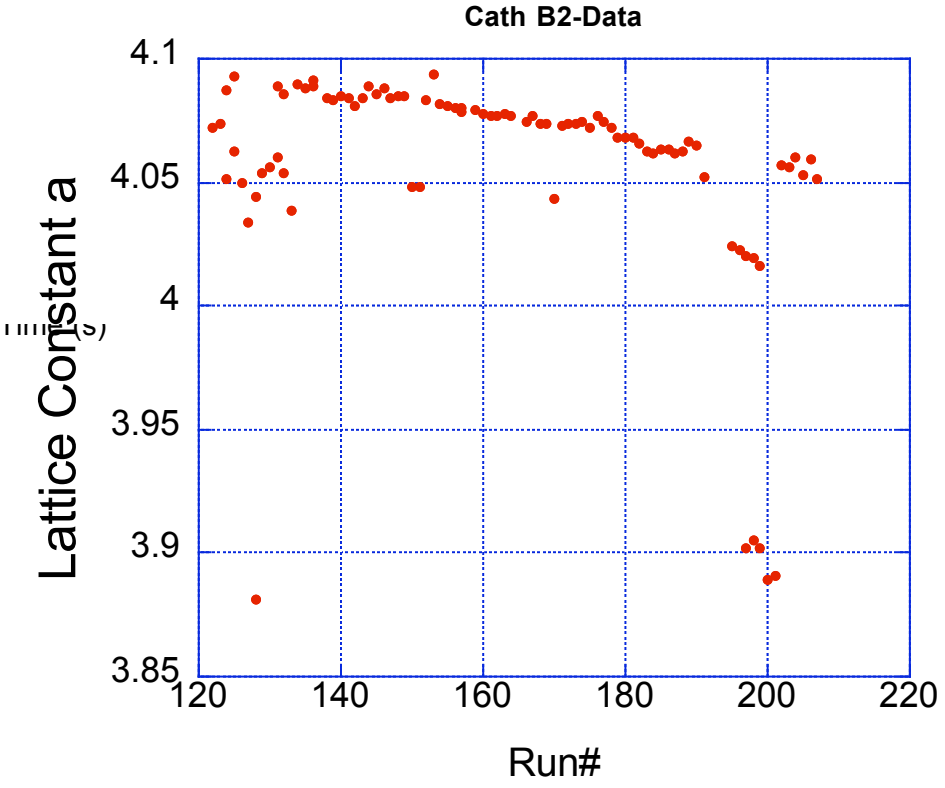




High Loading Fractions at Early Time

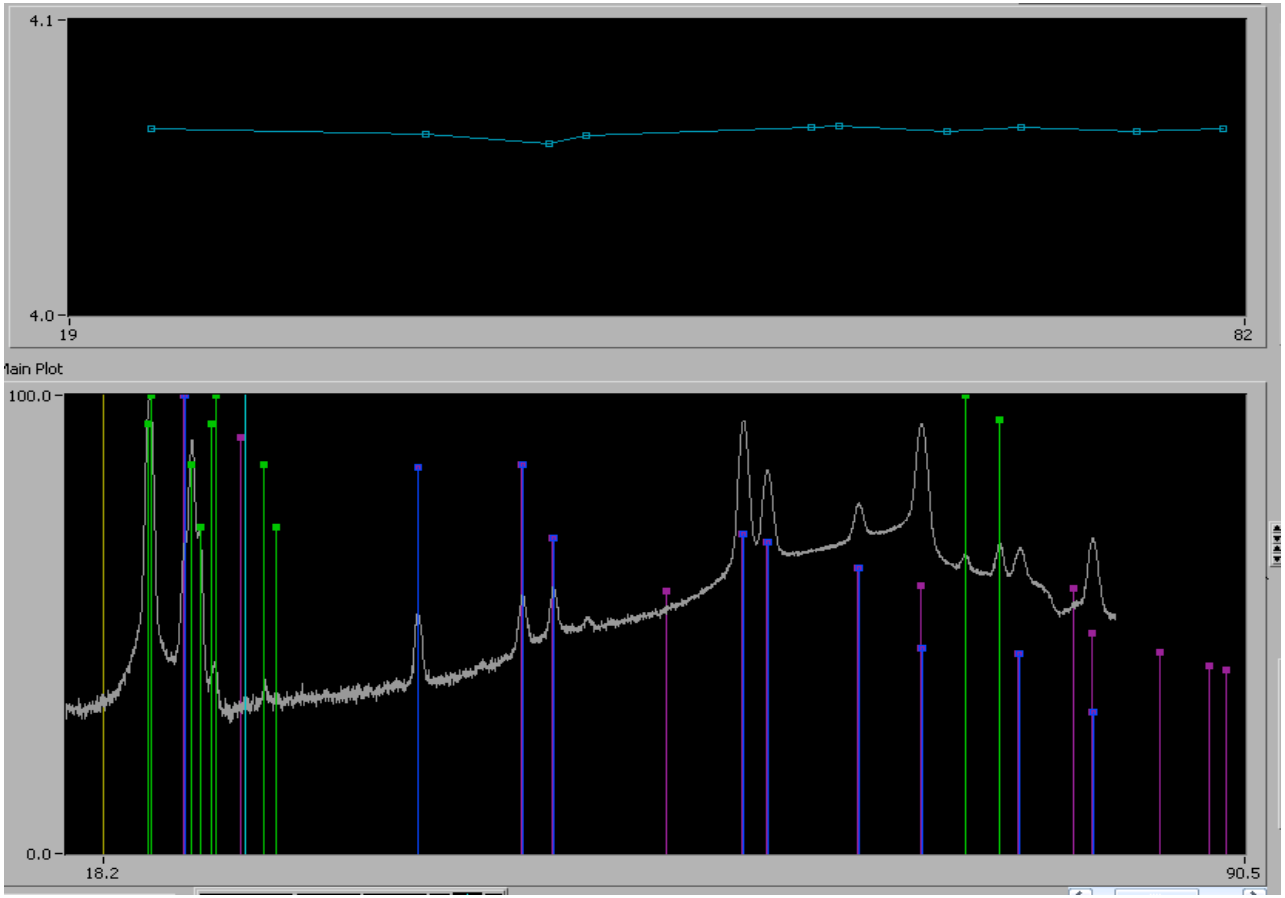






Typical X-Ray Spectrum

Semi-Log Plot

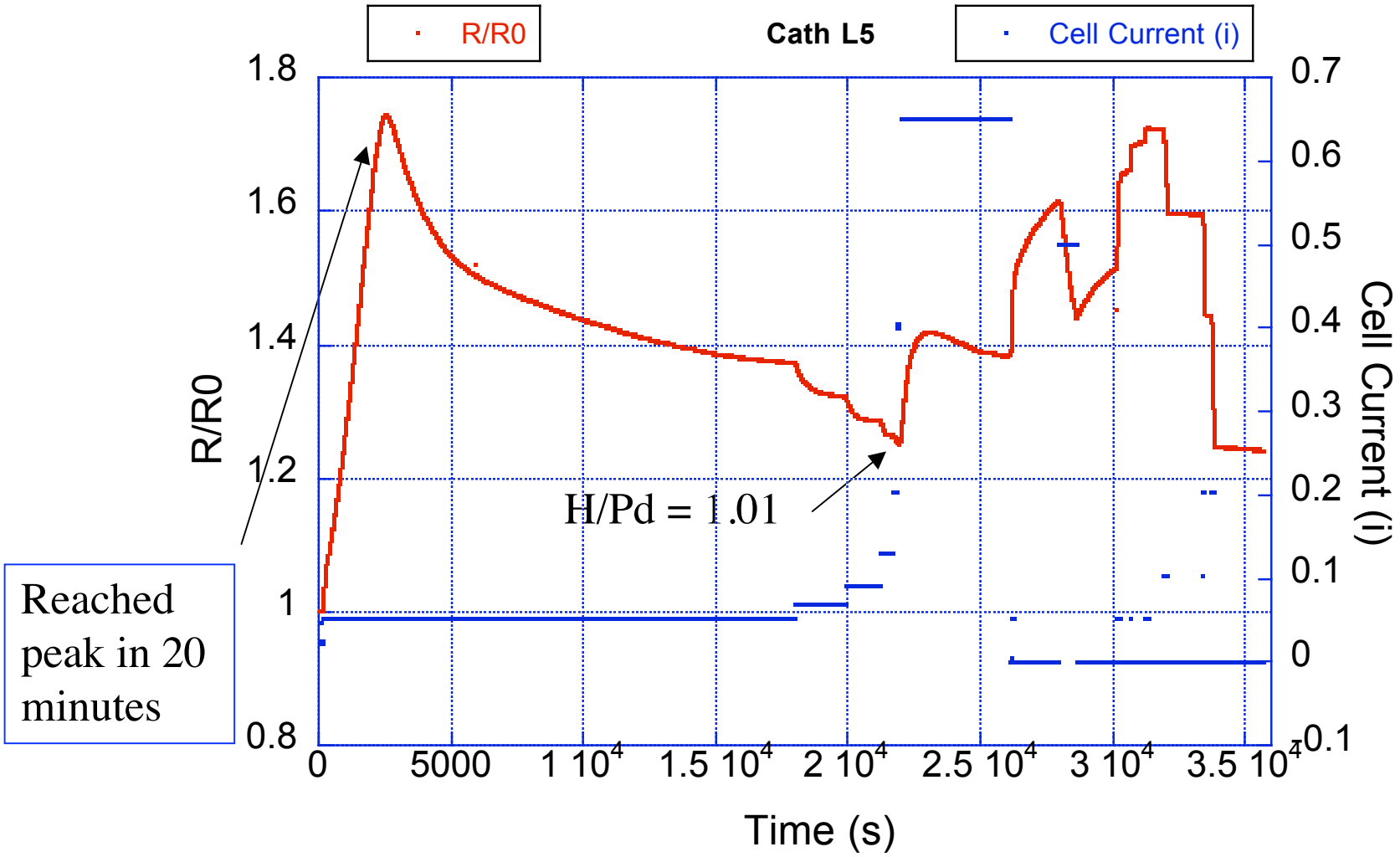


- Intensity falls off at low E due to absorption in electrolyte
- Pd K-edge absorption below 23 keV
- Intensity falls off at high E due to x-ray beam intensity fall-off
- In this spectrum, 10 x-ray diffraction peaks fit well

- 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.

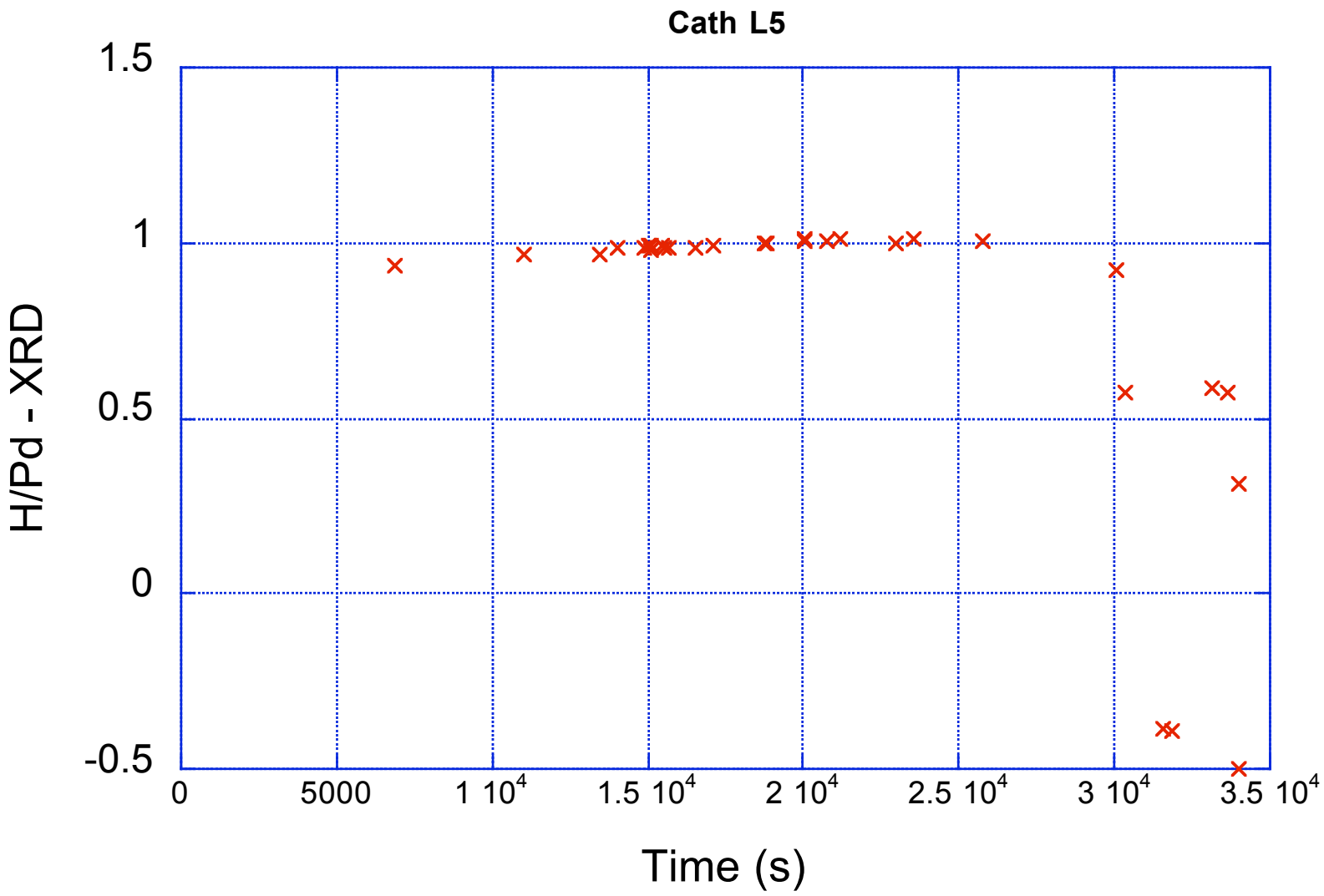
- Concentrations of H and D up to 1:1 in 0.1 M LiOH/LiOD in H_2O/D_2O electrolytes were obtained.

- 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

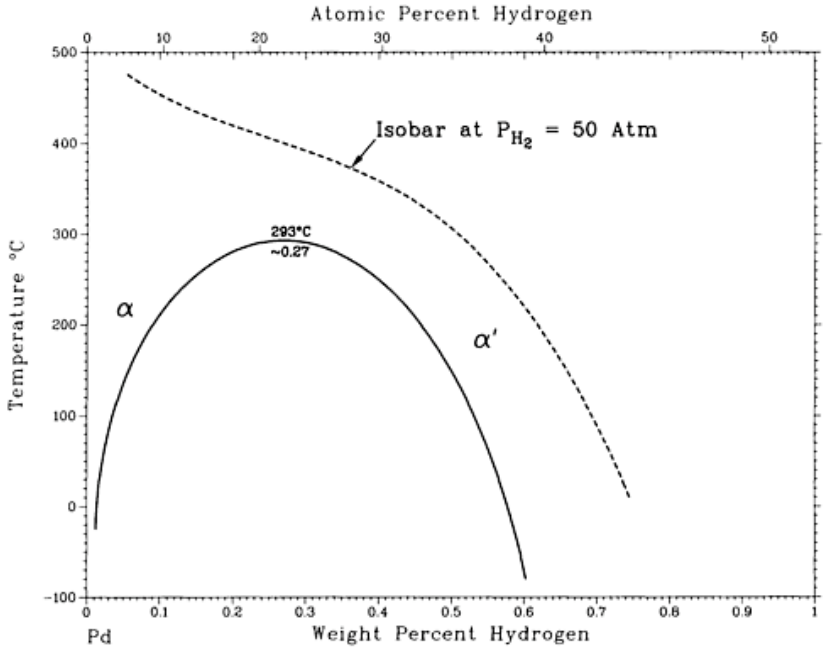


Figure 1: The phase diagram of Pd-H system.

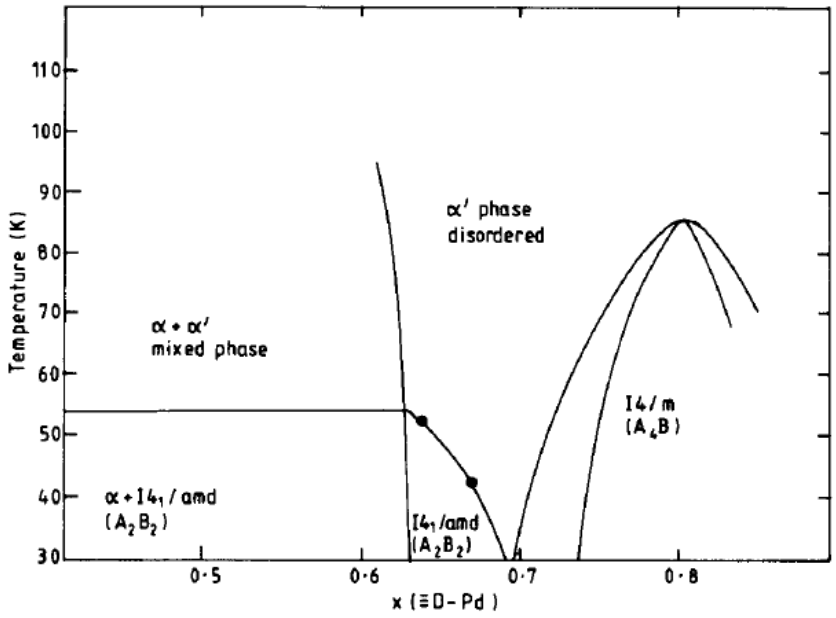


Figure 2: The phase diagram of Pd-D system (Here, α' phase means β) at low temperatures.

Shifts in XRD peaks with time

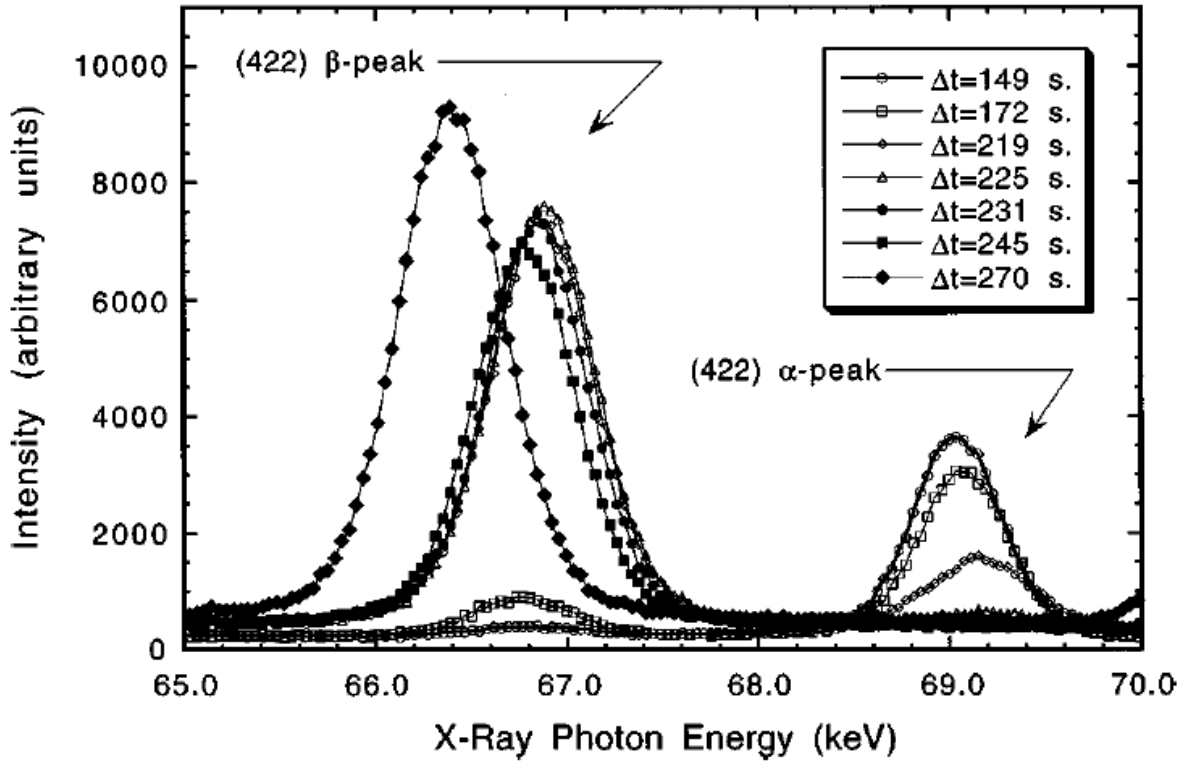
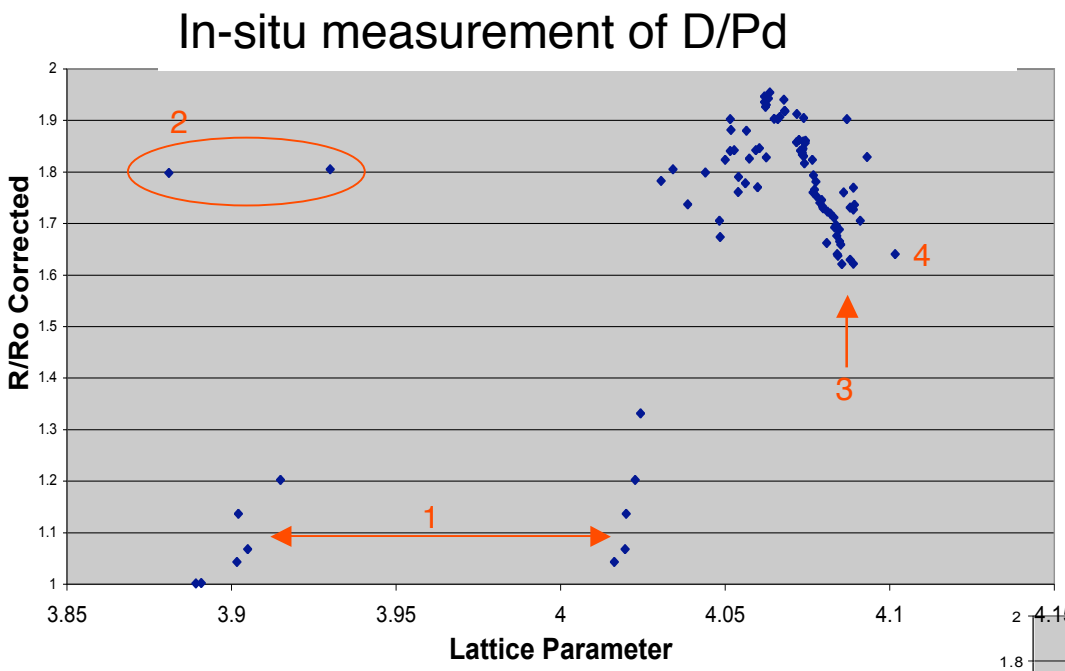
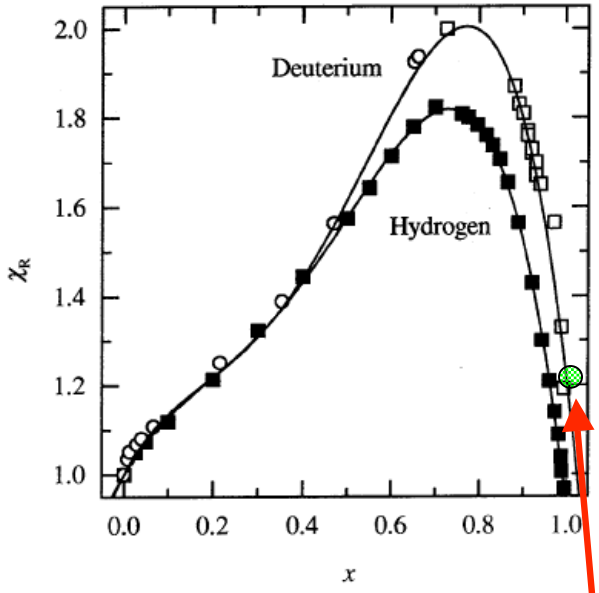
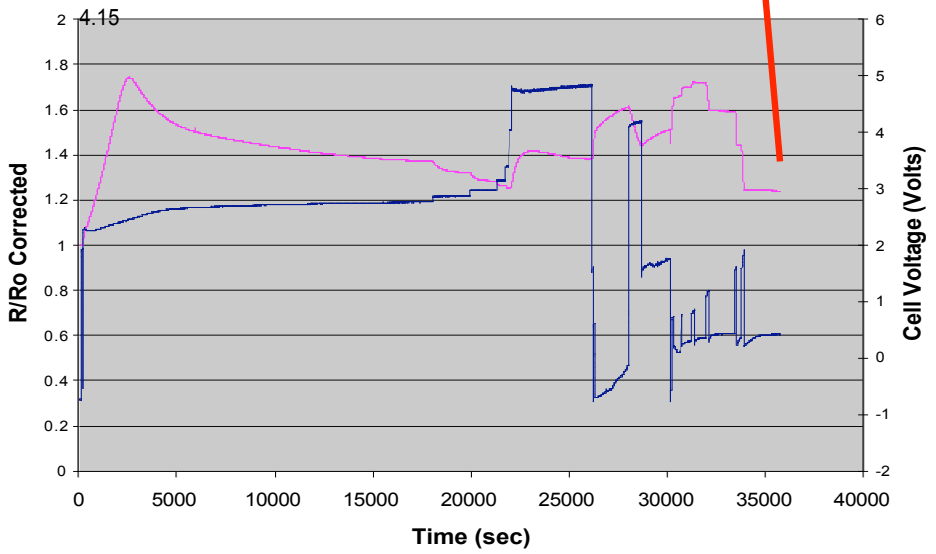


Figure 5: Temporal dependence of the intensity of (422) diffraction peaks of α and β phases.

D/Pd > 1







1 alpha-beta phase change

2 rapid surface deloading

3 high D content

4 suggestion of phase change