PALLADIUM DEUTERIDE FORMATION IN THE CATHODE OF AN ELECTROCHEMICAL CELL: AN IN SITU NEUTRON DIFFRACTION STUDY

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Introduction

Palladium metal has long been known as an excellent absorber of hydrogen. Historically, the Pd/H_2 system has been the most extensively investigated of the binary metal hydrides owing primarily to the high solubility and mobility of hydrogen atoms in the fcc (space group *Fm3m*) Pd lattice. The phase diagram for the formation of PdH_x is relatively simple: two phase pure regions exist when $x \leq 0.008$ (α-hydride) and when $x \geq 0.607$ (β-hydride), with both phases coexisting at intermediate values of x. Structurally, hydrogen has been found to occupy octahedral sites in the fcc palladium lattice in both the α- and β-hydride phases, with a concomitant expansion of the cubic lattice constant. The crystal structure of both hydride phases is fcc and has the appearance of two interpenetrating fcc lattices - Pd centered at (0,0,0) and H, at (1/2,1/2,1/2). When all octahedral sites are occupied, x = 1.0. An excellent review of the Pd/H_2 system has been written by Wicke and Brodowsky.[1]

During the past two years, a great deal of interest has been piqued by the discovery of abnormal heat generation as some electrochemical cells, containing a palladium cathode in the presence of deuterated electrolyte, were charged

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galvanostatically under otherwise ambient conditions. Some researchers have theorized that the excess heat is the product of a nuclear fusion of deuterium atoms in the palladium lattice.[2]

Diffraction is an extremely powerful tool for determining the structure of materials exhibiting periodicity in one or more dimensions. Neutron or x-ray diffraction measurements from powders and single crystals can provide information about the relative arrangement of atoms within the crystalline structure. The presence and relative positions of the diffraction maxima in plane or d spacing (d) yield information on the size of and symmetry within the crystal lattice, while the relative intensities of the maxima indicate the sites of the atoms in the lattice and the population of those sites.

We realized that neutron diffraction measurements of the palladium cathode in a working electrochemical cell might allow us to measure the maximum amount of deuterium taken up by the Pd lattice during charging (i.e., can x be greater than 1.0?). Also, such an in situ experiment should be capable of determining the sites in the Pd lattice that deuterium atoms occupy during charging (i.e., are any sites other than the octahedral sites occupied, and if so, what are the diffusion pathways?). Neutron diffraction is a particularly useful technique for this case, and for metal hydrides in general, because neutrons scatter much more strongly from hydrogen (and its deuterium isotope) than do x-rays. In the case of neutron powder diffraction, metal deuteride samples are preferred over the analogous hydrides because neutrons scattered from deuterium contribute almost exclusively to the diffraction maxima, whereas a significant number of those scattered from hydrogen contribute to background, which may obscure weak diffraction maxima and make structural determinations difficult.[3]

Experimental

An electrochemical cell, with a wrought Pd rod [Johnson Matthey (AESAR #12557), 99.96% pure, 5.0-cm long, 0.63-cm diameter] as cathode, Pt anode, and circulating LiOD-saturated D_2O electrolyte [about 12 wt% LiOD], all contained in a quartz tube, was constructed for this purpose and is shown in Fig. 1. The cell was designed to minimize the contribution of amorphous scattering from the liquid electrolyte and quartz tube and to eliminate crystalline scattering from elements of the cell other than the palladium cathode. The cell was situated in the sample

chamber of the General Purpose Powder Diffractometer (GPPD) at Argonne's IPNS facility;[4] a schematic representation of the GPPD and its sister instrument, the Special Environment Powder Diffractometer, is shown in Fig. 2. The GPPD utilizes the time-of-flight technique in which detectors are placed at fixed scattering angles (2θs) relative to the incident neutron beam and all wavelengths from the pulsed source neutron spectrum are detected, providing the d spacing variation. Diffraction data as a function of charging time (to approximately 62.6 h) were collected on the GPPD while the cell was being galvanostatically charged and cell voltage was monitored. A 1.14-A current was applied for the first 41.5 h of charging and a 3.42-A current thereafter.

Results

The in situ neutron diffraction data indicate that: (1) the orientation of the crystallites in the Pd rod is not random nor is it amenable to a simple preferred orientation model, which limits the ability to extract quantitative structural information from the data - Rietveld analysis,[5] assuming [1 0 0] and [1 1 0] texture directions using the March function,[6] of 2θ = -90° data from the virgin Pd rod was unsuccessful, indicating the possibility of multidirectional texture; (2) the observed Bragg intensities from Pd, α-PdD_x and β-PdD_x are all consistent with fcc (*Fm3m*) unit cells (see Fig. 3); and (3) the observed Bragg intensities from β-PdD_x are fully consistent with deuterium occupation of octahedral lattice sites. Figure 4 shows the changes occuring in the 2 2 0 Bragg reflection as a function of charging time. The β-deuteride phase begins to form after about 2.5 h of charging, while the formation of α-deuteride appears to begin upon charging. However, the resolution of the data is limited by the sample, making it impossible to distinguish between the Pd and α-PdD_x phases - the full width at half-maximum (FWHM) of the 2 2 0 reflection shows virtually no variation with charging time. The FWHM for the 2 2 0 reflection of β-PdD_x shows some variation with charging time, and it is about twice as large as that for the Pd/α-deuteride.

In general, diffraction peaks will broaden relative to instrumental resolution if strains are introduced into or particle size distributions change in the sample. In strain broadening, the FWHM of the peaks varies in proportion to d, while particle size broadening is evident if the variation of the FWHM is proportional to d^2. The situation for the Pd cathode of the electrochemical cell after 62.6 h of charging is

depicted in Fig. 5. The β-deuteride phase is broadened by about a factor of 2-1/2 relative to the GPPD resolution at $2\theta = \pm 90°$, while Pd/α-deuteride peaks are marginally broader than GPPD resolution. The variation of the FWHM with d for β-PdD_x is best fit with a straight line, indicating that deuterium absorption introduces a significant strain in the Pd cathode.

What quantitative information may be gleaned from this experiment despite the existence of significant preferred orientation in the sample which currently cannot be modeled in the data? If we assume that the absorption of deuterium will not substantially change the preferred orientation present in the palladium rod, the ratio of the integrated intensity for the 2 2 0 Bragg reflection of the β-deuteride, normalized by the squared structure factor (F^2) for 2 2 0 of $PdD_{1.0}$, to that for the Pd/α-deuteride, normalized by F^2 for 2 2 0 of Pd, should provide an approximate measure of the deuterium absorbed by the Pd cathode. Figure 6 shows this ratio and the approximate concentration of deuterium in the Pd cathode as a function of charging time. After 62.6 h of charging, x in PdD_x is approximately 0.2, still well within the mixed phase region of the phase diagram.

Discussion

The experiment described above demonstrates the efficacy of neutron powder diffraction as a tool for structural studies of metal deuterides/hydrides and the feasibility of in situ diffraction measurements from a working electrochemical cell. The results agree with those from a similar experiment carried out by Ross and co-workers using the POLARIS diffractometer at the ISIS facility at the Rutherford-Appleton Laboratory, U.K.[7] A higher charge was applied in this experiment to produce an inferred maximum deuterium concentration in the Pd electrode of 0.78. And, as with our measurements, preferred orientation in the electrode impacted the ability to extract quantitative structural information from the diffraction data.

During calorimetry experiments, open-circuit potentials of the PdD_x electrode after interruption of high-intensity cathodic currents were observed to be more negative than expected.[8] The anomalous potentials persisted for about 10-20 minutes after current interruption at cathodic deuterium concentrations greater than 0.7. This phenomenon may be an indication of a heretofore unknown metastable phase in the Pd-D system, formed in the cathode under these

conditions. To investigate this possibility, a series of ex situ diffraction measurements were carried out using the GPPD: a palladium rod was charged initially to a deuterium concentration of approximately 0.8, measured for approximately one hour with the GPPD, and returned to the cell for subsequent charging. Three such measurements were performed over a period of approximately one week. The results from these ex situ measurements are inconclusive, but they do not rule out the possible presence in the rod at these deuterium concentrations of a metastable deuteride phase with an *Fm3m* structure different from either the α- or β-palladium deuteride phases.[9]

Recently, we have become aware of an approach to model preferred orientation in samples by means of an orientational distribution function based on spherical harmonics.[10] We are hopeful that the incorporation of this formalism into the IPNS Rietveld analysis software package[11] will allow the present and any future experiments on this system to yield quantitative structural information. Another possibility to circumvent the preferred orientation problem would be to produce texture-free cathode material for future experiments. However, the electrochemical behavior of such a material would provide another variable in the experiment.

Further in situ diffraction measurements are being planned to much longer charging times to explore the possibility of metastable phase formation at deuterium concentrations greater than 0.7 in the palladium cathode and to observe the structural behavior of PdD_x for x values of 1.0 and beyond. In an initial attempt, after approximately 128 h of charging, macroscopic strain in the Pd cathode caused the quartz tube to break and the cell to fail.

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Figure Captions

Fig. 1. The electrochemical cell used in the in situ neutron measurements. The electrical connections are made on the back side of the cell.

Fig. 2. Schematic diagram showing the overall layout of the GPPD at IPNS. In the standard configuration, detectors are grouped in arrays along the detector mounting track, centered at 2θ values of ±148°, ±90°, ±60°, +30°, and -20°.

Fig. 3. Comparison of neutron diffraction data from the Pd cathode of the electrochemical cell collected on the GPPD in the 2θ = -90° detectors before charging (bottom curve) and after charging for 62.6 h (upper curve). 2×10^4 counts have been added to the upper curve to displace it from the lower curve. Both spectra are normalized by the incident neutron flux. The three lowest order Bragg reflections are identified in each pattern. "α" indicates a reflection from the Pd/α-deuteride phase, and "β", from the β-deuteride phase.

Fig. 4. The variation of the 2 2 0 Bragg reflection with charging time. The labeling is the same as that in Fig. C. Each spectrum is normalized by the incident neutron flux and normalized to the spectrum at 0 h. Data were not collected between 15 and 40 h and between 53 and 56 h.

Fig. 5. The variation of FWHM with d spacing for the Pd/α-deuteride (circles) and β-deuteride (squares) phases after 62.6 h of charging. Error bars have been plotted for all points; some are smaller than the plotting symbol. Dashed lines through the points indicate the best linear fit to the points. The instrumental resolution for the GPPD 2θ = ±90° detectors is also shown.

Fig. 6. The variation of the ratio of the normalized (see text) integrated intensity of the 2 2 0 reflection from the β-deuteride phase to that from the Pd/α-deuteride phase with charging time. The secondary axis is the approximate concentration of deuterium in the Pd cathode (x in PdD_x). Error bars are smaller than the plotting symbols.

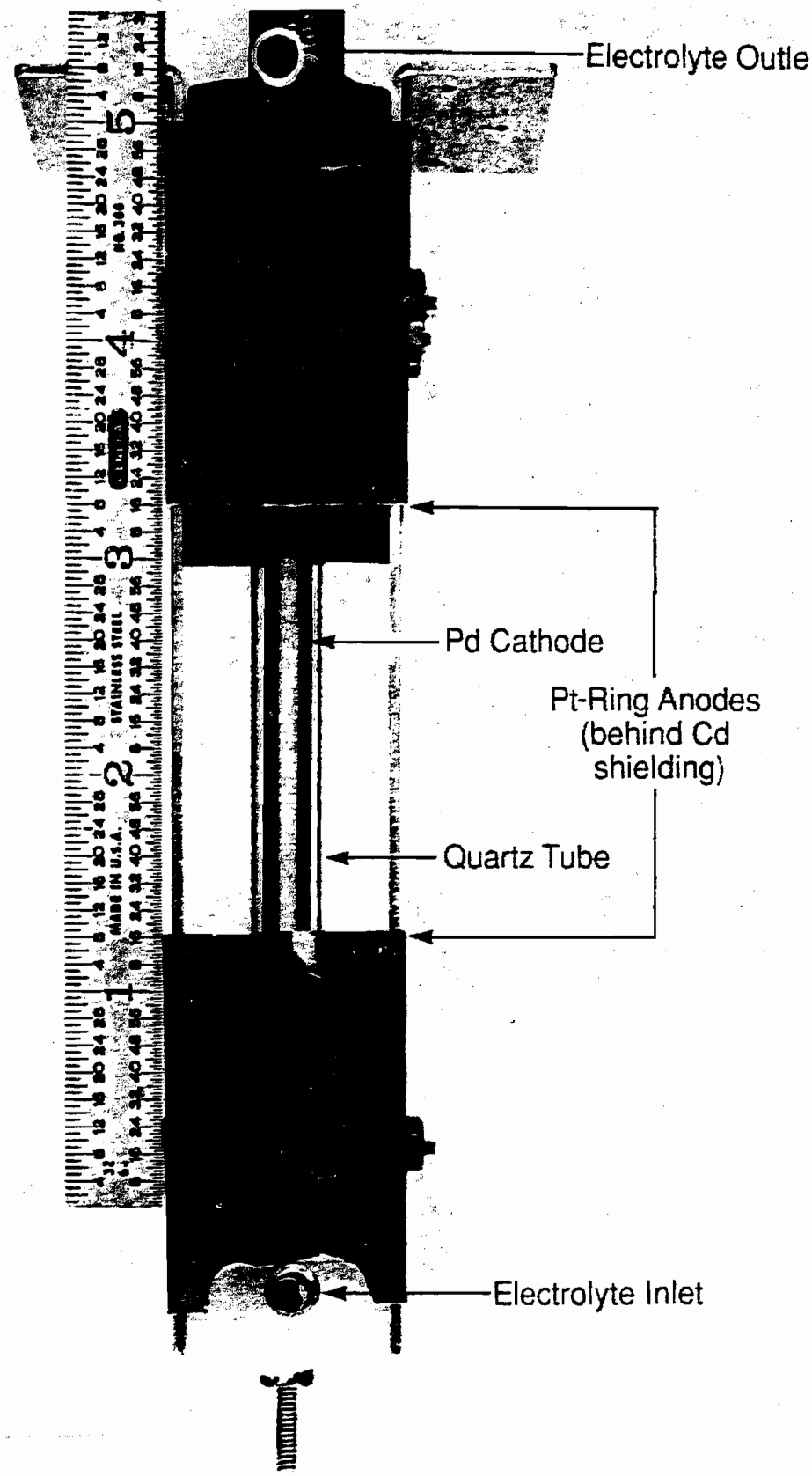
Electrolyte Outle
Pd Cathode
Pt-Ring Anodes
(behind Cd
shielding)
Quartz Tube
Electrolyte Inlet

Figure 1

IPNS Special Environment and General Purpose Powder Diffractometers

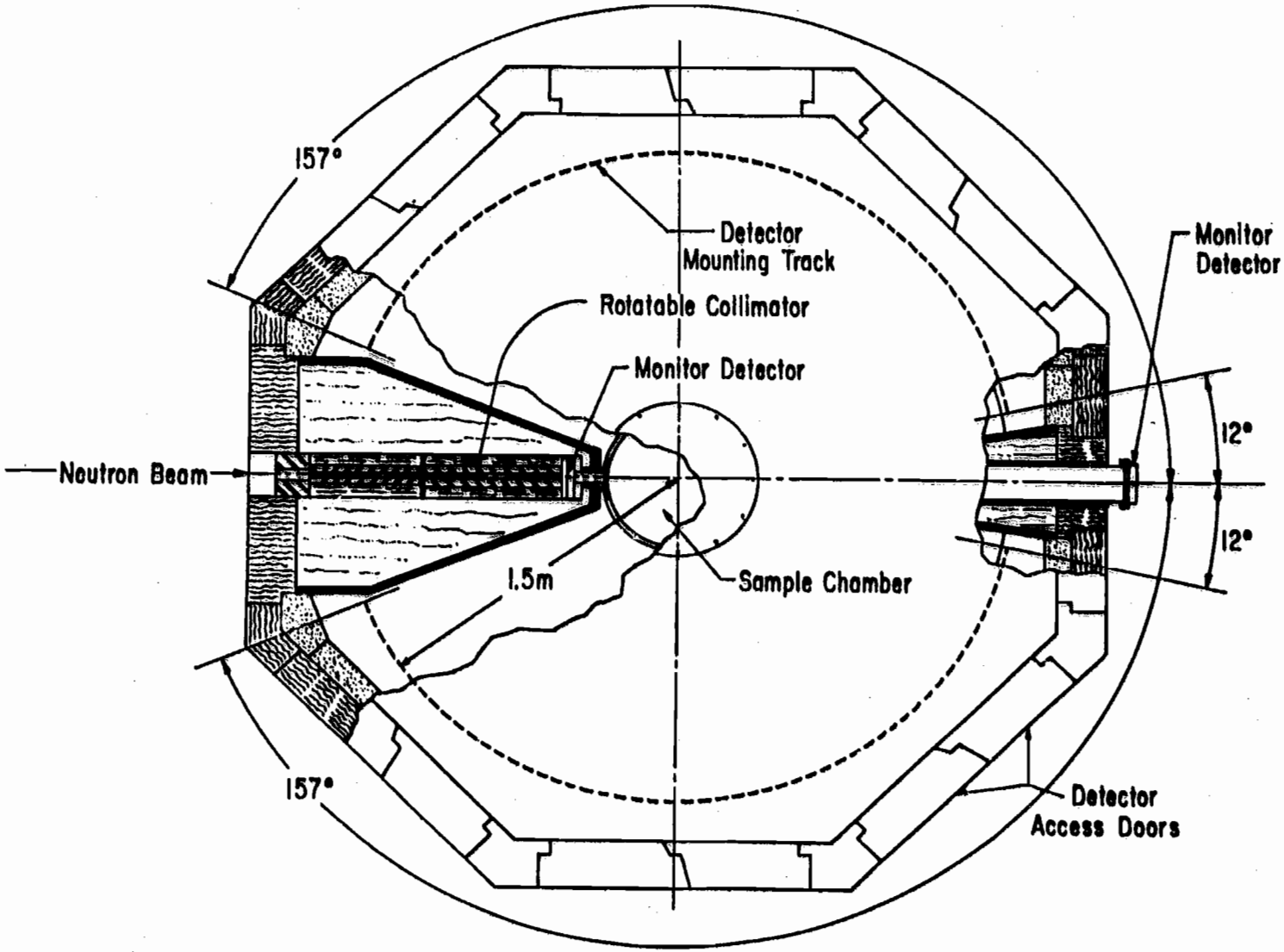

Figure 2

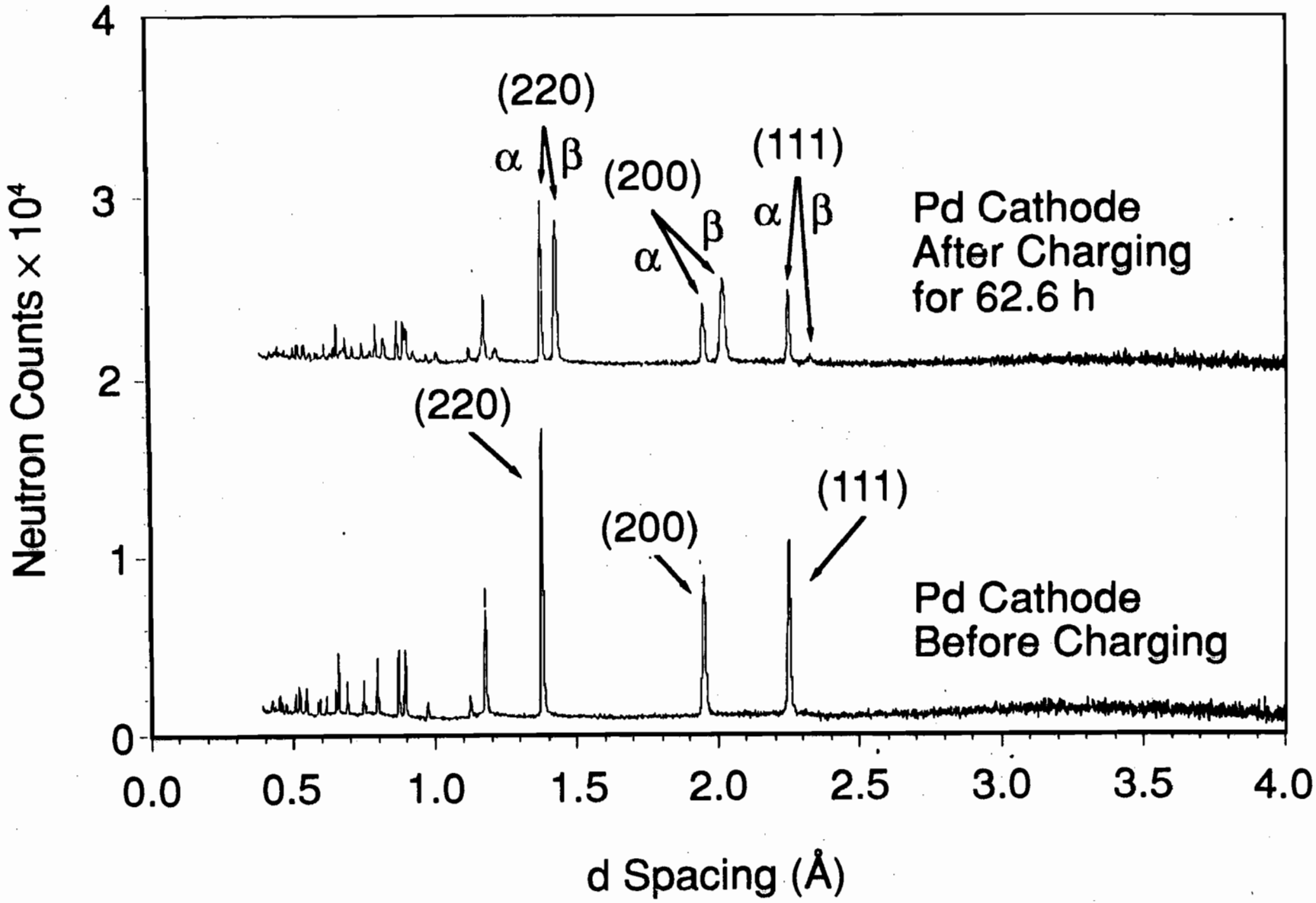
Neutron Counts × 10⁴
4
3
2
1
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
d Spacing (Å)
(220)
α
β
(200)
α
β
(111)
α
β
Pd Cathode
After Charging
for 62.6 h
(220)
(200)
(111)
Pd Cathode
Before Charging

Figure 3

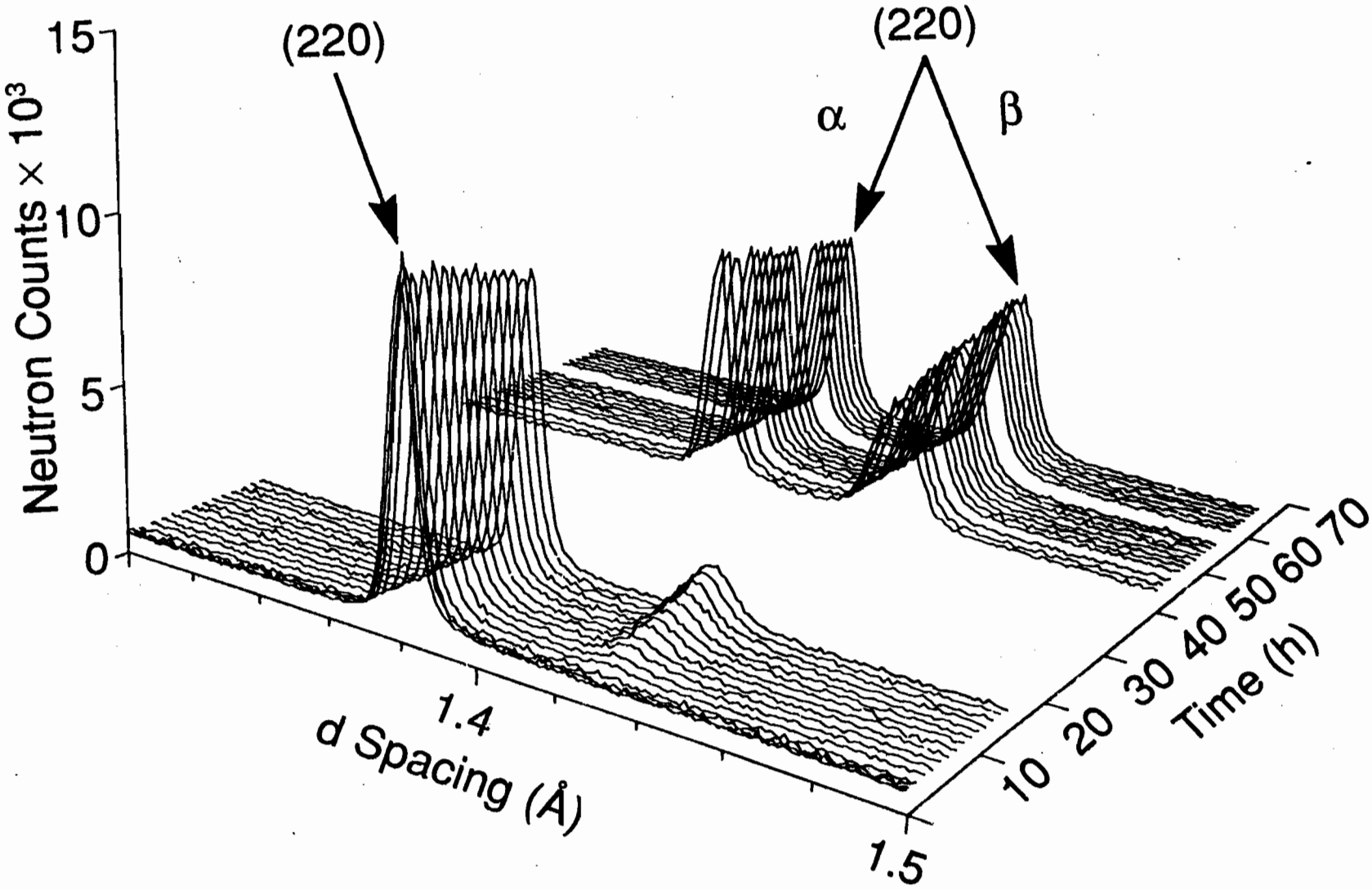
(220)
(220)
α
β
15
10
5
0
Neutron Counts × 10³
1.4
1.5
d Spacing (Å)
10
20
30
40
50
60
70
Time (h)

Figure 4

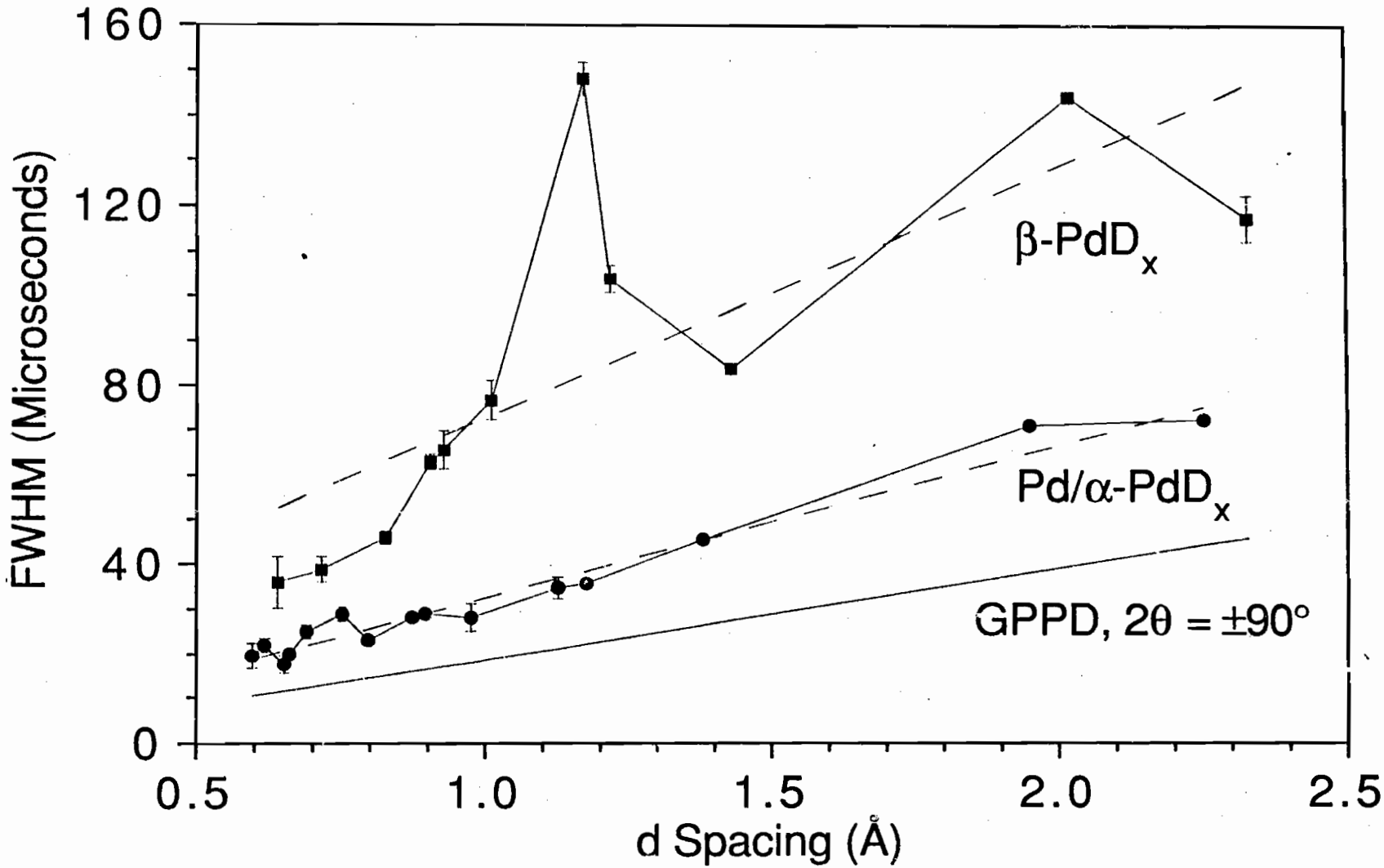
160
120
80
40
0
FWHM (Microseconds)
0.5
1.0
1.5
2.0
2.5
d Spacing (Å)
β-PdD$_x$
Pd/α-PdD$_x$
GPPD, 2θ = ±90°

Figure 5

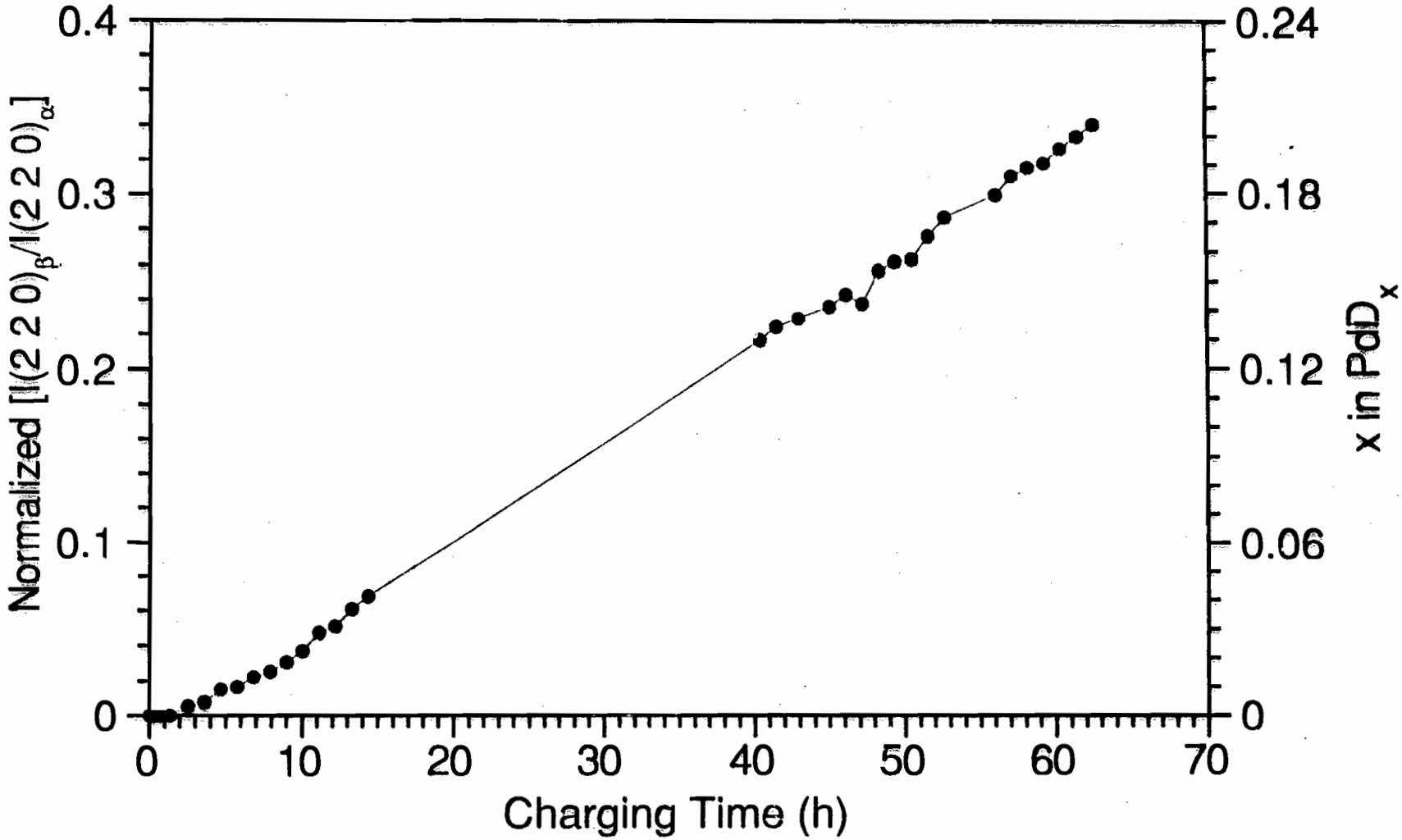
0.4
0.3
0.2
0.1
0
Normalized [I(2 2 0)β/I(2 2 0)α]
0.24
0.18
0.12
0.06
0
x in PdDx
0
10
20
30
40
50
60
70
Charging Time (h)

Figure 6