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ELECTROCHEMICAL AND NEUTRON DIFFRACTION MEASUREMENTS OF PdD_x CATHODES

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ABSTRACT

Potentiometric and in-situ neutron diffraction measurements have been carried out on PdD_x cathodes in LiOD-saturated D₂O solution. Open-circuit potentials of the PdD_x electrode after interruption of high-intensity cathodic currents (300-500 mA/cm²) showed a more negative potential ($\epsilon = -1010$ mV, measured against a Hg/HgO reference electrode) than that expected from the literature. The anomalous potentials were observed for about 10-20 min after current interruption at $x > 0.7$ concentrations of deuterium. This phenomenon may indicate a metastable phase of the Pd-D system, which may be detected by neutron diffraction. In-situ neutron diffraction measurements, so far, have indicated only the evolution of the known α and β phases of PdD_x. Successful neutron diffraction measurements in electrochemical cells suggest the viability of this technique for in-situ investigations of metal-hydride battery electrodes in experiments when heavy-water electrolyte is used to model the MH_x/H₂O electrode.

INTRODUCTION

Recent years have seen a renewal of interest in metal hydride/deuteride systems, partly due to the great importance of the new MH_x battery electrodes used in Ni/MH_x cells and partly due to the involvement of deuterides of Pd and Ti in the "cold fusion" experiments. In this paper, we describe a combination of electrochemical and neutron diffraction measuring techniques that we have found to be useful in studying the PdD_x electrode. The present experiments have evolved from previous work [1,2].

Palladium metal has long been known as an excellent absorber of hydrogen. Historically, the Pd/H₂ system has been the most extensively investigated of the binary metal hydrides, primarily owing to the high solubility and mobility of hydrogen atoms in the face-centered cubic (fcc) Pd

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lattice (space group $Fm\bar{3}m$). 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 $x \geq 0.607$ (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, with 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/H₂ system has been written by Wicke and Brodowsky [3].

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 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 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 populations 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 [4].

MEASURING TECHNIQUES AND RESULTS

The experiments combine three techniques: (1) cathodic synthesis of PdD_x phases, (2) potentiometry, and (3) neutron diffractometry. Two types of Pd-D/LiOD-saturated D_2O /Pt cells were used in these experiments. One of the cells was used to conduct the potentiometric studies and to prepare the PdD_x phases for *ex-situ* neutron diffractometry. The other cell -- in which the quantity of materials other than the PdD_x phases was minimized -- was used for *in-situ* neutron diffractometry. This latter method allowed us to monitor the evolution of the deuteride phases, while the *ex-situ* measurement has the advantage of shorter diffractometer time and absence of foreign materials (except electrolyte trapped in the pores) in the neutron diffractometer sample. For the *ex-situ* measurements, the PdD_x cathode was removed from the electrochemical cell and, after weighing, was placed in the diffractometer.

Figure 1 shows the cell used to conduct potentiometric studies and to prepare the PdD_x phases for the *ex-situ* neutron diffraction measurements. The wrought Pd cathode (99.96% pure, 0.63-cm diameter, and 5.0-cm long) was supplied by Johnson Matthey (AESAR #12557) and was degassed before each experiment at 650°C for an hour in air and at 600°C in vacuum for about 18 hours. The Pt wire anode (99.95% pure, 0.1-cm diameter, and 100-cm long) was supplied by

Johnson Matthey (AESAR #10258), and was wound into a 3.2-cm diameter coil to snugly fit into the cell container tube. The Pd cathode was supported by a stainless-steel-tube current lead, which was covered by a Nalgene tube to preclude any involvement in the electrochemical reaction.

The electrolyte was 40 cm³ of LiOD-saturated D₂O (about 12 wt% LiOD). The electrolyte was prepared from 99.9% pure Li metal supplied by Johnson Matthey (AESAR #10767) and 99.8% pure D₂O supplied by Aldrich (15,188-2). The cell was covered, leaving only a small gap to allow the gases to escape and to minimize the back diffusion of H₂O vapor from the ambient atmosphere. Nonetheless, some H₂O entered the electrolyte, as was shown by the post-experiment analysis of the electrolyte. After 460-h operation of the cell, a H/D atom ratio of 0.02 was found by chemical analysis of the electrolyte.

For the *in-situ* neutron diffractometry, an electrochemical cell (Fig. 2) was constructed with a wrought Pd rod (the same as in the cell shown in Fig. 1) as cathode, Pt anode, and circulating LiOD-saturated D₂O electrolyte, all contained in a quartz tube. 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. Two anode rings, one above and the other under the quartz tube window, were used to decrease the inevitable nonuniform current distribution of this configuration and leave the cathode unobstructed in the neutron pathway. The neutron beam was confined to a 5.0 cm by 0.5 cm cross section. The electrolyte layer between the cathode and the quartz tube was minimized to 0.1 cm. This narrow gap, however, left little room for volume and shape change (bending) of the PdD_x cathode. The electrolyte was circulated through the cell to remove the heat that evolved during electrolysis and help the gases leave the cell quickly.

Electrosynthesis and Potentiometry of PdD_x

The cell shown in Fig. 1 was operated galvanostatically at current densities between 12 and 500 mA/cm². The concentration of deuterium in the Pd cathode was measured gravimetrically at regular intervals. The buildup of the deuteride phases and the concentration variation during a long (460 h) experiment are shown in Fig. 3. The cell current was interrupted periodically during the experiment for a short time, and the open-circuit potential of the PdD_x electrode was measured against a Hg/HgO reference electrode filled with the same electrolyte as that of the cell. A double electrolyte bridge, filled with the cell electrolyte, was used to avoid mercury contamination of the electrolytic cell. At $x < 0.6$ concentrations, the measured open-circuit potentials (Fig. 4) were in agreement with previously reported data [5,6], i.e., we found a potential of about 30 mV relative to a Pd/D₂ reference (assuming a 920 mV difference between the Pd/D₂ and the Hg/HgO electrodes). However at $x > 0.7$ concentrations, after prolonged electrolysis at high current densities (300-500 mA/cm²), however, the open-circuit potential was measured as low as -90 mV. This low potential was not stable, lasting for only about 10-20 min after current interruption and shifting later to less negative values.

Neutron Diffraction Measurements

For the *in-situ* measurements, the cell shown in Fig. 2 was placed in the sample chamber of the General Purpose Powder Diffractometer (GPPD) at Argonne's IPNS facility [7]; a schematic

representation of the GPPD and its sister instrument, the Special Environment Powder Diffractometer, is shown in Fig. 5. The GPPD utilizes the time-of-flight technique in which detectors are placed at fixed scattering angles (2θ) 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 (Fig. 5) while the cell (Fig. 2) was 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.

Subsequent diffraction measurements with the same Pd rod after degassing at high temperature and charging in an electrochemical cell (Fig. 1) outside of the GPPD were carried out in an attempt to verify the presence of an unknown structural phase suggested from the anomaly in the open-circuit potential measurements. The rod was charged initially to a deuterium concentration of approximately $x = 0.8$, measured for approximately 1 h with the GPPD, and returned to the cell for subsequent charging and further diffraction measurements. Three such measurements were performed over a period of approximately one week.

The *in-situ* neutron diffraction data indicate that 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 [8], assuming [1 0 0] and [1 1 0] texture directions using the March function [9], of $2\theta = -90^\circ$ data from the virgin Pd rod was unsuccessful, indicating the possibility of multidirectional texture. These data also indicate that the observed Bragg intensities from Pd, α -PdD_x, and β -PdD_x are all consistent with fcc (Fm3m) unit cells (see Fig. 6), and the observed Bragg intensities from β -PdD_x are fully consistent with deuterium occupation of octahedral lattice sites. Figure 7 shows the changes occurring 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 the sample 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. 8. The β -deuteride phase is broadened by about a factor of 2-1/2 relative to the GPPD resolution at $2\theta = \pm 90^\circ$, 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.

The results from the *ex-situ* measurements are similar. The neutron powder data from the Pd rod charged in the cell outside the GPPD exhibit diffraction maxima consistent with an fcc lattice; no additional reflections were observed. Preliminary Rietveld analysis of the *ex-situ* data yielded a deuterium concentration of $x = 0.88(1)$ after four days of charging at 50 mA/cm² current density, $x = 0.91(1)$ after one additional day of charging (100 mA/cm²), and $x = 0.93(1)$ after 6 more days of charging (100 mA/cm²). These data were also affected by, but not corrected for, preferred

orientation, but to a much lesser extent than the in-situ experiment due to strain in the Pd rod induced by three previous deuterium charge/discharge cycles. The deuterium concentrations determined from the ex-situ neutron diffraction data are in agreement with those determined from gravimetric measurements of the Pd rod after each charging period. These results do not rule out the possible presence of a metastable deuteride phase with an Fm $\bar{3}$ m structure different from either the α - or β -deuteride phases in the rod at these deuterium concentrations.

What quantitative information may be gleaned from the in-situ experiment despite the existence of significant preferred orientation in the sample, which cannot be modeled with the current 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 9 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 experiments described above demonstrate 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. Neutron diffraction from the Pd cathode in an operating cell, in which the volume of electrolyte is such to minimize background signals, allows us to (1) measure the amount of deuterium taken up by the Pd lattice during charging and (2) monitor the evolution of the Pd-D phases. The ex-situ neutron diffraction measurements produced, in essence, the same results as the in-situ measurements concerning the presence and the characteristic scattering of the two deuteride phases. The ex-situ measurements allowed us to compare the results of the gravimetric and diffraction measurement of deuterium concentration in the palladium. The agreement of the x values (for PdD_x) obtained for the two methods shows the viability of concentration measurements with neutron diffraction in addition to the structural information.

The results of the in-situ experiment are in agreement with those from a similar experiment carried out by Ross and coworkers [10] using the POLARIS diffractometer in the ISIS facility at the Rutherford-Appleton Laboratory, U.K. A higher charge was applied in this experiment to produce an inferred maximum deuterium concentration in the Pd electrode of x = 0.78. And, as with our measurements, preferred orientation in the electrode impacted the ability to extract quantitative structural information from the diffraction data.

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 [11]. We are hopeful that the incorporation of this formalism into the IPNS Rietveld analysis software package [12] 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 add yet another variable in the experiment.

With neutron diffractometry, we have not been able to demonstrate the presence of other structural configurations in the palladium cathode than the well-known α and β phases of PdD_x . The meaning of the measured -90 mV (vs. Pt/D_2 electrode) transient potential value of the PdD_x electrode is uncertain at this time. Absence of unusual neutron scattering peaks does not exclude the possibility for the existence of a metastable Pd-D phase. A metastable Pd-D phase may exist on the surface of the cathode in a very thin Pd layer in a quantity that is not enough to detect with neutron scattering, which refers to the average bulk properties of the electrode. The same low quantity on the surface of the PdD_x electrode, however, can be enough to be detected by the extremely sensitive electrode potential measurement. The observed -90 mV potential of the PdD_x electrode at $x > 0.7$ compositions may indicate the presence of electrochemically deposited impurities on the surface of the electrode, which slowly dissolve in the electrolyte after current interruption. This latter explanation, however, is less probable because we used high-purity materials in our experiment.

Further in-situ diffraction measurements have to be carried out to much longer charging times to investigate the structural behavior of the PdD_x cathode for x values of 1.0 and beyond.

The measurements reported here show the viability of neutron diffractometry for in-situ monitoring of the electrochemically induced phase formations in operating cells. Results also suggest that this technique could be applied to investigate in-situ metal-hydride battery electrodes in experiments when heavy-water electrolyte is used to model the $\text{MH}_2/\text{H}_2\text{O}$ electrode.

ACKNOWLEDGMENT

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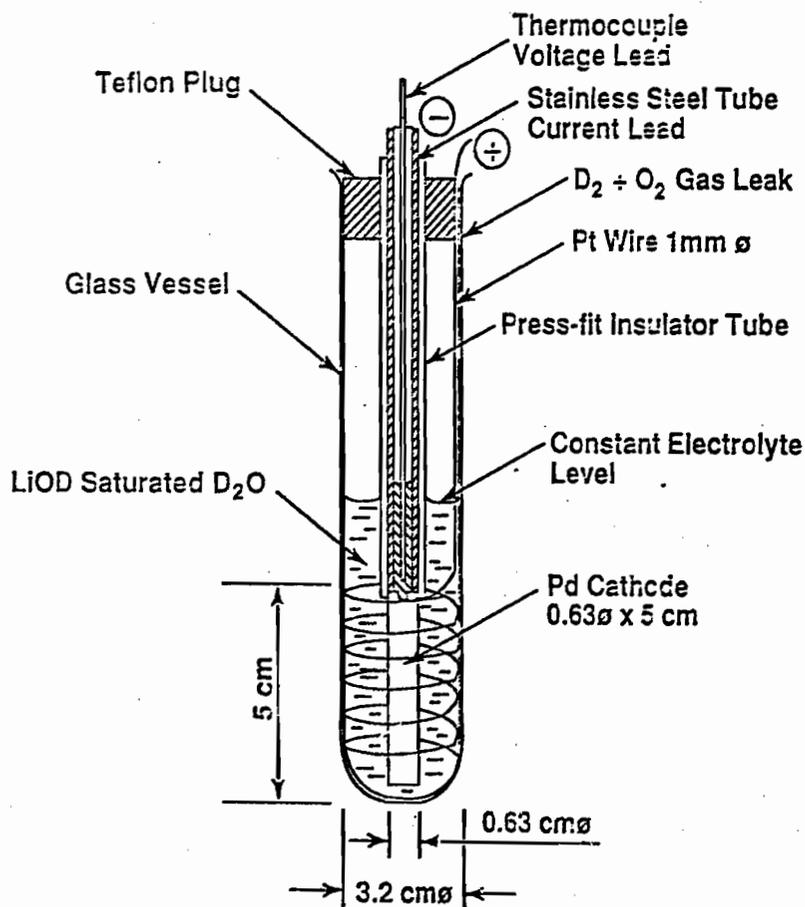


Figure 1. Electrochemical cell used in electrosynthesis and potentiometry of PdD_x phases.

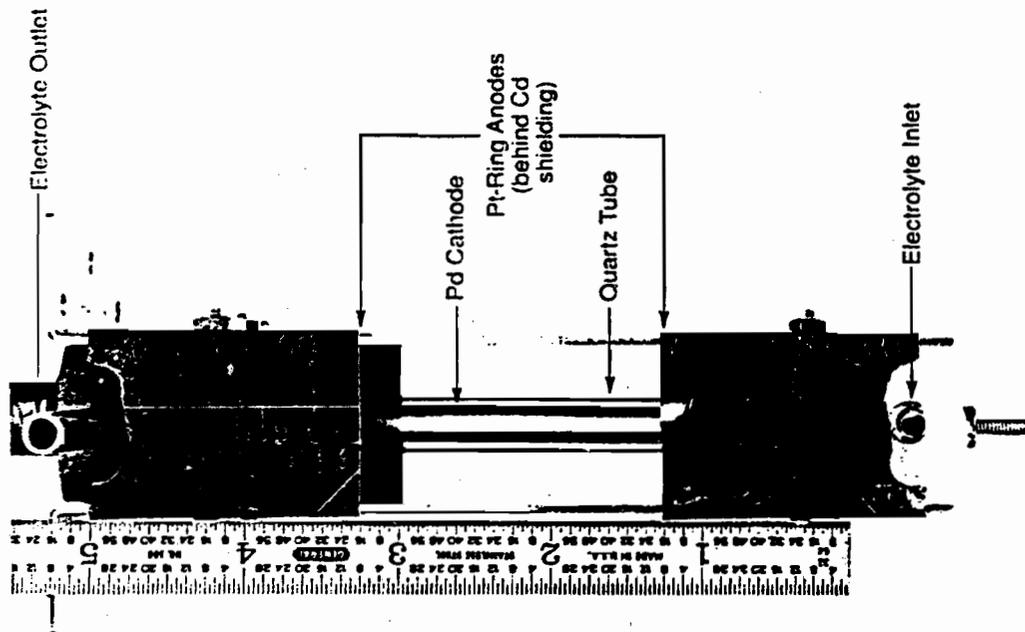


Figure 2. The electrochemical cell used in the in-situ neutron measurements. The electrical connections are made on the back side of the cell.

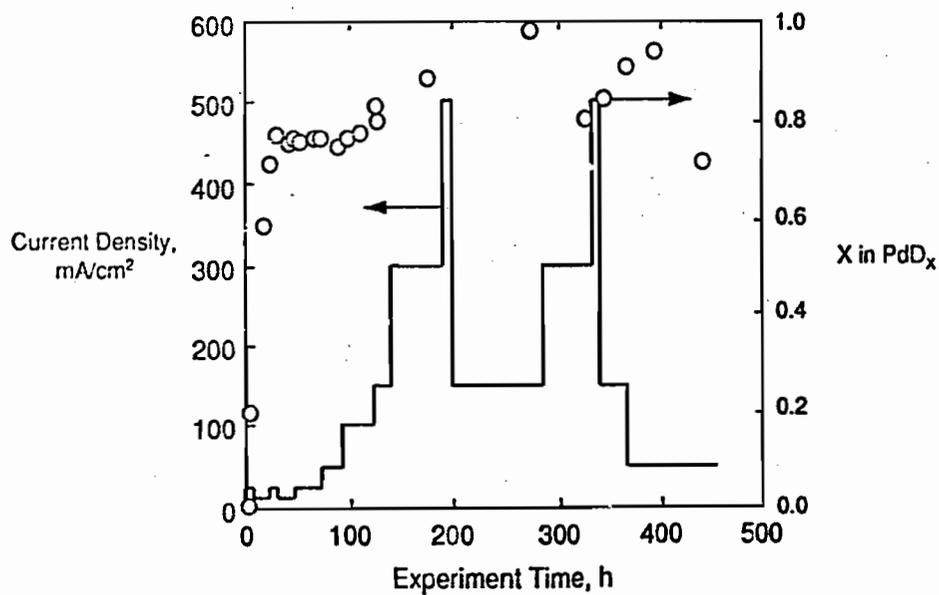


Figure 3. Concentration variation of deuterium in the PdD_x cathode during a 460-h experiment.

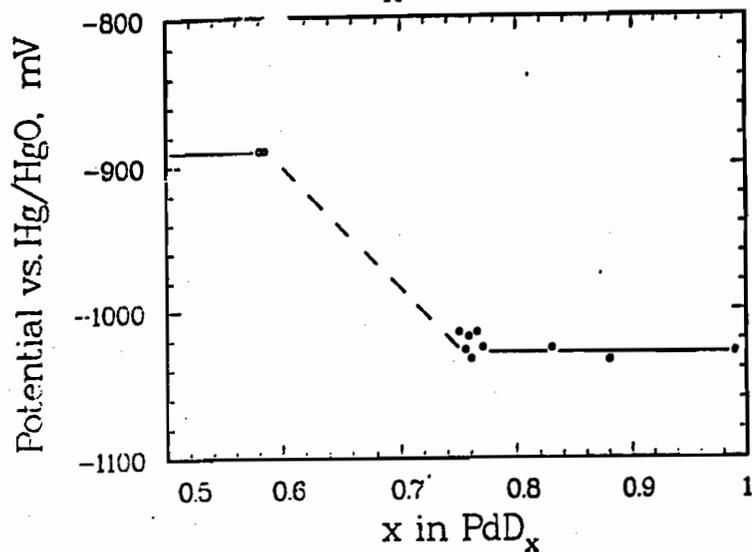


Figure 4. Open-circuit potentials of a PdD_x electrode in LiOD-saturated D₂O electrolyte vs. Hg/HgO reference electrode as function of deuterium concentration in Pd.

IPNS Special Environment and General Purpose Powder Diffractometers

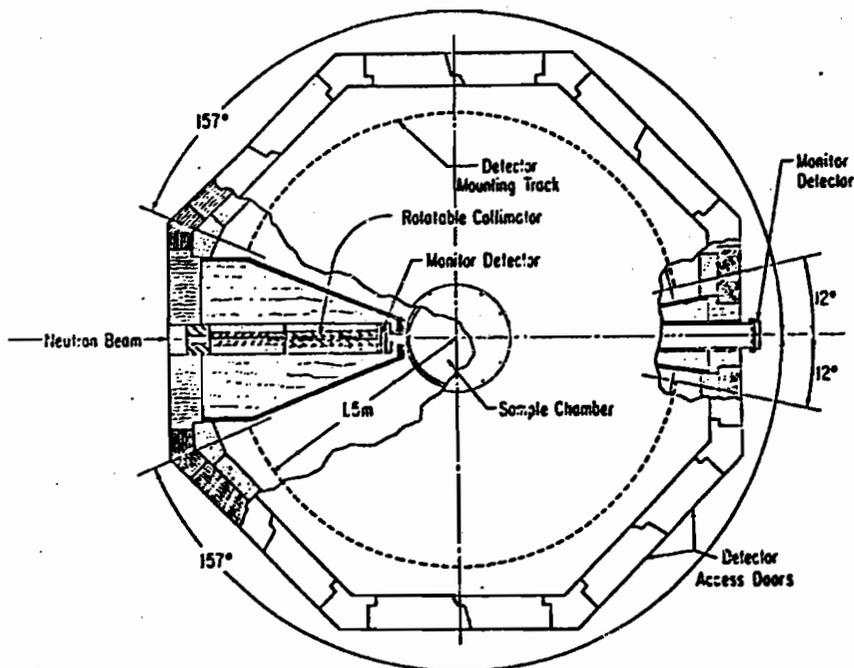


Figure 5. Schematic diagram showing the overall layout of the GPPD at IPNS. In the standard configuration, detectors are grouped in arrays along the detector mounting track, centered at 2θ values of $\pm 148^\circ$, $\pm 90^\circ$, $\pm 60^\circ$, $+30^\circ$, and -20° .

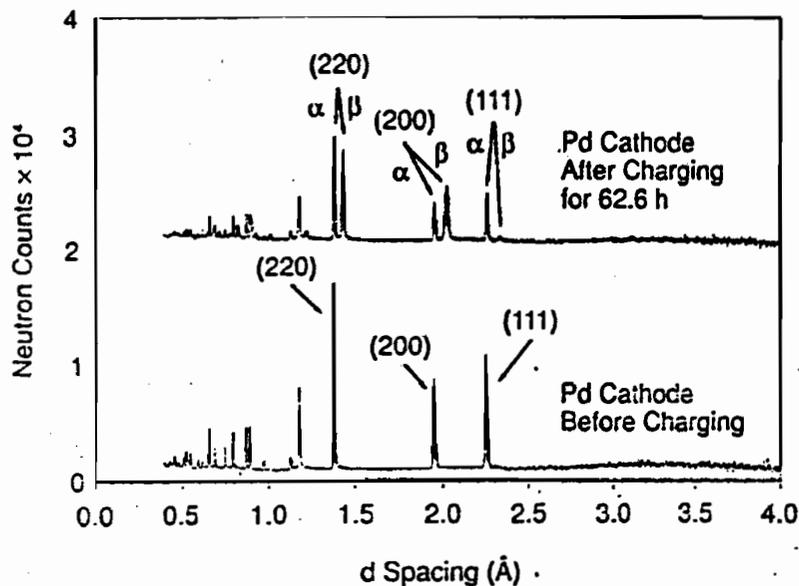


Figure 6. Comparison of neutron diffraction data from the Pd cathode of the electrochemical cell collected on the GPPD in the $2\theta = -90^\circ$ detectors before charging (bottom curve) and after charging for 62.6 h (upper curve). 2×10^4 counts have been added to the upper curve to displace it from 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.

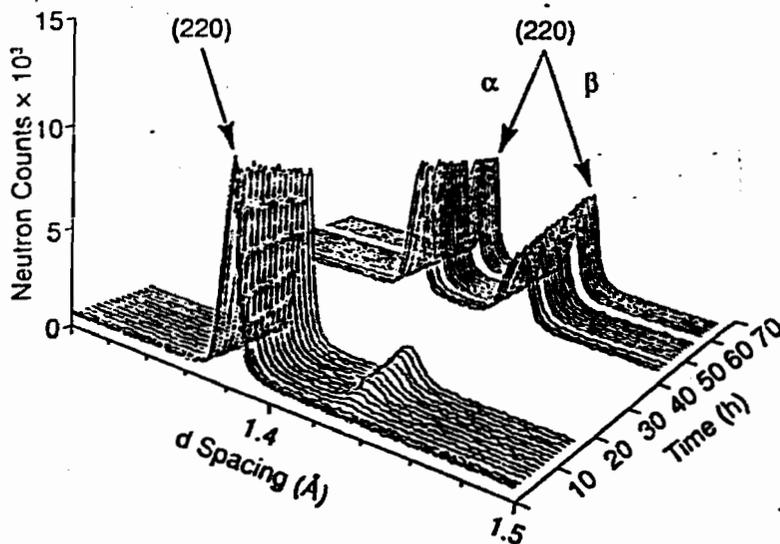


Figure 7. The variation of the 2 2 0 Bragg reflection with charging time. The labeling is the same as that in Fig. 6. Each spectrum is normalized by the incident neutron flux and normalized to the spectrum at 0 h. Data were not collected between 15 and 40 h and between 53 and 56 h.

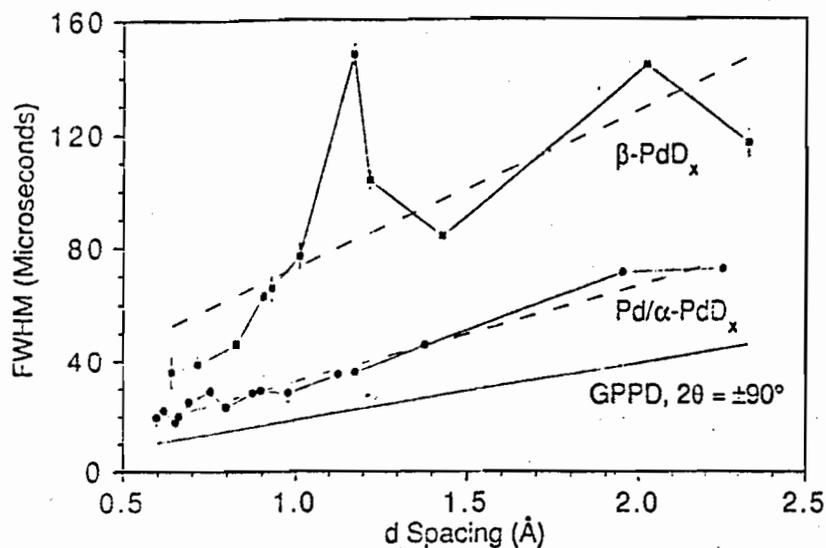


Figure 8. The variation of FWHM with d spacing for the Pd/ α -deuteride (circles) and β -deuteride (squares) phases after 62.6 h of charging. Error bars have been plotted for all points; some are smaller than the plotting symbol. Dashed lines through the points indicate the best linear fit to the points. The instrumental resolution for the GPPD $2\theta = \pm 90^\circ$ detectors is also shown.

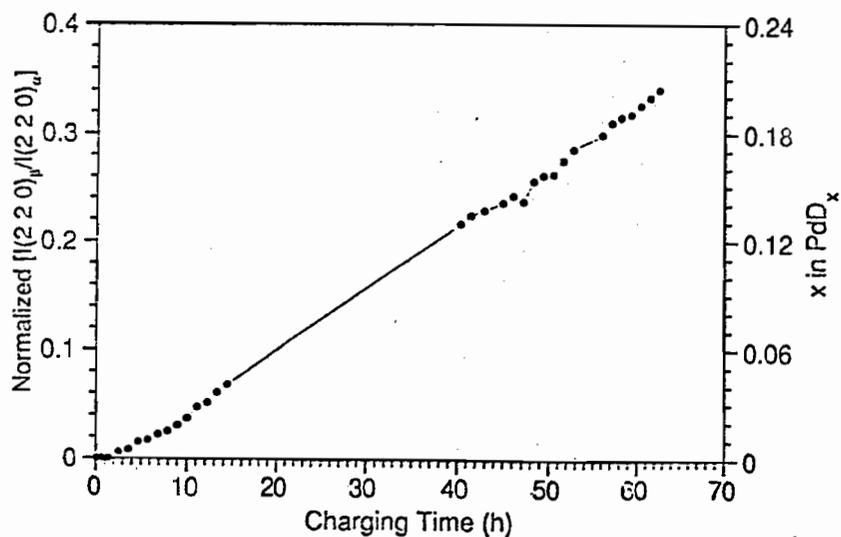


Figure 9. The variation of the ratio of the normalized (see text) integrated intensity of the 2 2 0 reflection from the β -deuteride phase to that from the Pd/ α -deuteride phase with charging time. The secondary axis is the approximate concentration of deuterium in the Pd cathode (x in PdD_x). Error bars are smaller than the plotting symbols.