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In situ monitoring of crystallographic changes in Pd induced by diffusion of D

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Crystallographic changes in a palladium wire cathode were monitored *in situ*, as deuterium was electrochemically deposited on the surface and diffused radially into the wire. Initially, the wire was pure Pd. A constant electrolysis current density of 1 mA/cm^2 was maintained and D slowly diffused into the wire. As the D concentration increased, the wire transformed from pure Pd, to the α phase, and finally into the β phase. This reversible phase transformation begins on the surface and progresses radially inward. During the experiment, x-ray-diffraction data were collected from a volume element of about 180 pl. This volume element was systematically moved in 50-μm steps from the edge to the center of a 1.0 mm diameter Pd wire. Throughout the course of the experiment, the bulk value of x in PdD$_x$, as determined from simultaneous measurements of the electrical resistivity, increased from 0 to ~0.72. For each setting of the volume element, a monotonic increase in the volume of the α phase was observed, until the material entered the two-phase region. Once the β phase appeared, the volumes of both phases decreased slightly with continued loading. The integrated intensities of diffraction peaks from each phase were used in conjunction with the known phase diagram to estimate the rate of compositional change within the volume element. The diffusion rate for the solute atoms was estimated to be 57 ± 8 nm/s, based on the temporal and spatial dependence of the integrated intensities of the diffraction peaks from each phase. These data also were used to evaluate the time dependence of the concentration of the solute atoms $\partial c/\partial t$ and their diffusivity D. The value of $\partial c/\partial t$ increased linearly from 6.2×10^{-5} s^{-1} at the surface, to 7.6×10^{-5} s^{-1} midway into the wire. D was computed to be $(3.1\pm1.0)\times10^{-11}$ m^2/s when the transition began at $r=250$ μm; 2 ks later it had decreased to $(2.1\pm0.3)\times10^{-11}$ m^2/s. This may be due to the fact that the volume of the β lattice also decreased during this period. [S0163-1829(98)01846-3]

INTRODUCTION

The mechanism whereby hydrogen or deuterium is incorporated into a metallic lattice is both interesting and complex. Even the palladium-hydride or -deuteride system, which has been extensively investigated, is not completely understood—especially at high solute concentrations.[1,2] The work reported here was initiated to ascertain information about the diffusion of D into Pd and to provide *in situ* crystallographic information from regions inaccessible with routine diagnostic tools.

Also detailed in this paper is a method of measuring diffusion rates. The high penetrating power and extreme brightness of synchrotron-wiggler radiation are used to systematically monitor the crystallography of a very small volume element as a function of position and time. The measured structural changes, combined with the known phase diagram, allow determination of the concentration as a function of position and time, and hence the diffusivity of the solute atoms.

The results in this paper represent a summary of several experiments in which D was electrochemically deposited onto the surface of a Pd wire. During deposition, the crystallographic structure of the wire was monitored, as a function of position and time, using energy-dispersive x-ray-diffraction methods. In order to obtain diffraction data from the interior of the wire, these experiments were performed using the x rays generated on the superconducting-wiggler
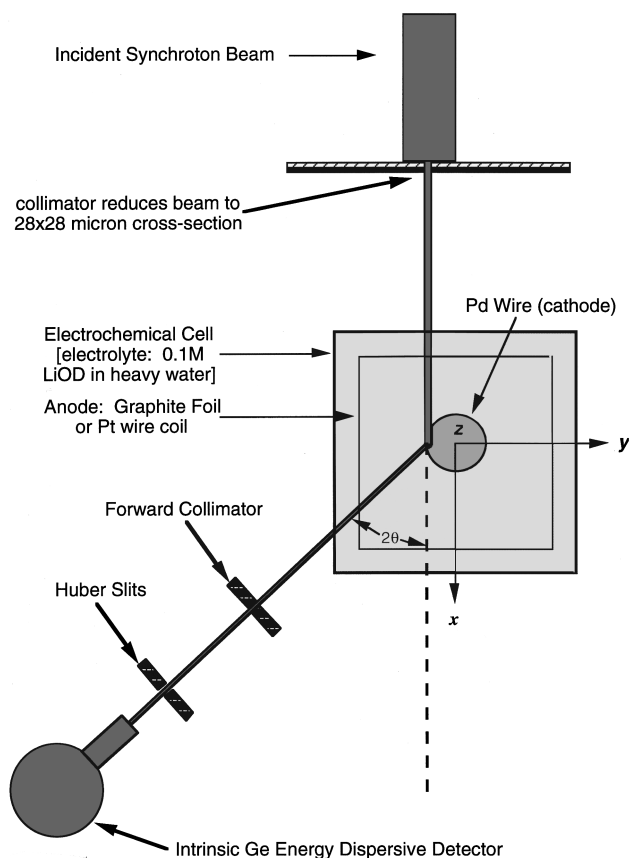
FIG. 1. Schematic drawing of the experimental setup, top view, and not drawn to scale.

beam line (X17C) at the National Synchrotron Light Source, Brookhaven National Laboratory. X rays available on X17C have energies in excess of 80 keV and intensities many orders of magnitude brighter than those of either a conventional x-ray tube or a rotating anode especially in the region of high photon energies.

As D diffuses into Pd at room temperature, i.e., as x in PdD$_x$ increases, based on the known phase diagram,[3] the solvent lattice passes through three different crystallographic regions: for $x=0$, pure Pd, for $0<x\lesssim0.03$, the material is in the α phase; for $0.03\lesssim x\lesssim0.58$, a mixture of α and β phases exists; and for $x\gtrsim0.58$, the sample is in the β phase.[4] Each of the phases appears first on the surface and then progresses radially inward, toward the center of the wire. All three phases, pure Pd, α, and β, are face-centered cubic. Neutron-diffraction studies have shown that the absorbed D atoms are located in the Pd octahedral, interstitial sites.[5] There are four octahedral sites per unit cell. Therefore, at the stoichiometric composition, PdD is in the $B1$ (or rocksalt) structure.

EXPERIMENTAL PROCEDURE

A 1 mm diameter Pd wire, 3 mm in length, and of 99.9% purity was rigidly mounted and centered in a polyethylene or glass electrochemical cell (both were used). The wire served as the cathode in the electrochemical circuit and was surrounded by an anode of either graphite foil or a Pt wire coil (both were used). A schematic drawing of the experimental setup is given in Fig. 1. The deuterium was electrochemically deposited onto the surface of the wire using 0.1 M

LiOD in D$_2$O as the electrolyte. (Complete experimental details are reported elsewhere.[6]) The axial electrical resistance of the Pd cathode was continuously monitored *in situ* using a four-point technique. These resistance data were used to estimate the value of x, using published resistance ratio-loading variations.[7] These concentration estimates are nominal, and do not take into account any concentration gradient which may exist.

The entire cell was mounted on a platform which could be translated in either of three orthogonal directions. Polychromatic x rays from the superconducting wiggler on X17C were reduced to a narrow pencil of radiation, 28×28 μm^2 in cross section, by polished tungsten blocks. The scattered radiation was measured at a fixed, but adjustable angle (2θ) with an intrinsic Ge, energy sensitive detector. The microspot in the Pd wire from which diffraction data were collected is defined by the intersection between the incident x-ray beam and the beam path defined by the apertures in front of the Ge detector. This spot contained a volume of 180 pl ($=1.8\times10^{-13}$ m^3). During the experiment, the scattering geometry remained fixed and the cell (and hence the wire) was systematically translated in 50 μm steps normal to the beam and in the plane of diffraction (y direction in Fig. 1). At each position, the diffraction pattern from the volume element was measured. The intensity of the diffraction peaks from each phase is proportional to the volume of diffracting material of each phase in the volume element. Using these intensity data, and the known phase diagram for the Pd-D system, the radial and temporal dependence of the concentration of D was determined.

The energy scale of the detector electronics and multichannel analyzer was calibrated using a set of known fluorescence peaks excited with an Am^{241} radioactive source. The 2θ angle of the diffractometer was calibrated to within $\pm0.001°$ using a gold foil standard. It was held fixed at $13.000°$ throughout the duration of the experiments. Additional details of the energy-dispersive setup on X17C and the experimental procedures are reported elsewhere.[8,9]

RESULTS AND DISCUSSION

Determination of the diffusivity (D)

An energy-dispersive diffraction spectrum of the wire recorded before the start of the experiment is shown in Fig. 2. The unit-cell parameter determined from the diffraction peaks in the figure is 3.8874 ± 0.0006 Å. This is about 0.05% less than the accepted value for Pd (3.8898 Å).[10] The small difference in unit-cell parameters may be due to the fact that the Pd wire used was only 99.9% pure.

When recorded from a region near the center of the wire, the spectrum contains only the higher energy diffraction peaks; the lower energy peaks are lost due to absorption. Because each of the phases involved in this study is cubic, any one of the diffraction peaks can be used to monitor the crystallographic changes. The (422) peak was selected for two reasons: (1) It occurs at a sufficiently high energy to be seen from all positions within the wire and (2) there is no overlap between it and other peaks in either phase. However, the full diffraction spectrum was monitored in all cases and no crystallographic changes were observed, other than those already discussed.
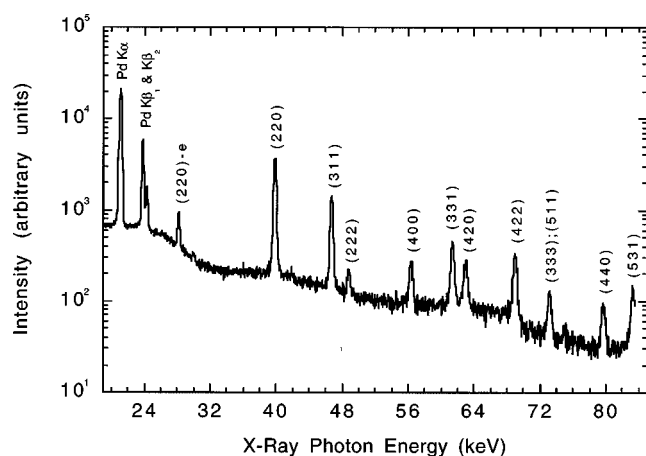
FIG. 2. Energy-dispersive diffraction pattern from a 180 pl volume of a Pd wire taken from a region near the surface. (Data collection time was 2.00 min.)

FIG. 3. Temporal dependence of the intensity of the (422)-diffraction peaks of the α and β phases recorded near the surface of the wire as the phase change progressed. (A shift to lower energy corresponds to an increase in the interatomic spacing and hence to an increase in the volume.)

If axial movement of the solute atoms can be ignored, then diffusion occurs only in the radial plane and the local concentration of the solute atom c is a function of only two variables, the radial position r and time t.   (The variable x is used in this paper to represent the bulk concentration of the solute; the variable c is used to represent the nominal, local concentration, i.e., that within the 180 pl diffracting volume element.)   The cylindrical symmetry of the experiment allows Fick's second law of diffusion to be written in the following form:[11]

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r}\right), \qquad (1)$$

where D is the diffusivity of the solute atom in Pd. Evaluation of the partial derivatives in Eq. (1) allows determination of D.

To our knowledge, the detailed manner in which the deuterium moves from the surface into the interior of the Pd has not been determined experimentally. Based on our experiment, we cannot comment on the nature of the α-β interaction, nor whether there is, or is not, any intermingling between the two phases. Our observations are that within the 180-pl volume element from which our data are collected, initially all the diffraction is from either Pd or α-phase crystallites (we cannot distinguish between the two), then from both α- and β-phase crystallites, and then from only β-phase crystallites. This scenario was repeated as the volume element was moved from the surface to the core.

This effect is represented in Fig. 3. The integrated intensities of the (422)-diffraction peaks are plotted as a function of time from the same fixed volume element. As the α-to-β transition progresses, the intensity of the (422) peak of the α phase decays, accompanied by the concomitant growth of the intensity of the (422) peak of the β phase. While diffraction from both phases is present, the intensities of the diffraction peaks for each phase can be correlated to the relative amount of diffracting material in each phase. This, in turn, can be correlated to the concentration of the solute atoms within the volume element, using the known phase diagram, as discussed below.

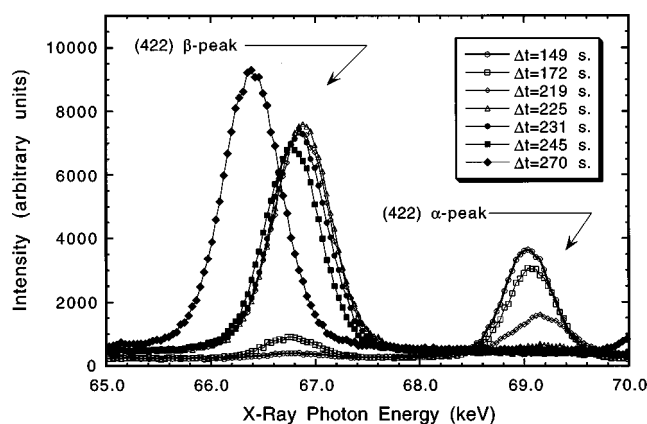At each radial position, the measured, integrated intensity of the (422) diffraction peak of each phase was corrected for background contributions and the decay of the synchrotron beam current. These values were then normalized to the intensity values in the single phase regions. As an example, the results plotted in Fig. 4 were measured at the point $r = 450\ \mu$m, where r is the radial distance measured from the center of the Pd wire. The decay of the α phase and the concomitant growth of the β phase appear to be linear in time. The magnitudes of the two slopes are equal, to within the experimental uncertainty, as they should be, since this is a binary system. For all the measurements, the decay rate of the α phase was linear. However, in some cases, the growth rate of the β phase was erratic. It is presumed that this is because of insufficient randomness in the orientation of the β-phase crystallites. Therefore, only the decay rates of the α phase were considered in the analysis to follow.

In this analysis, values of r were restricted to the outer half of the wire, i.e., $250 \leqslant r \leqslant 500\ \mu$m. Because of the length of the diffracting volume element parallel to the incident beam direction (x direction in Fig. 1), volume elements with mean radii $<250\ \mu$m spanned too large a range of radii. A least-squares fitting routine was used to determine the lin-
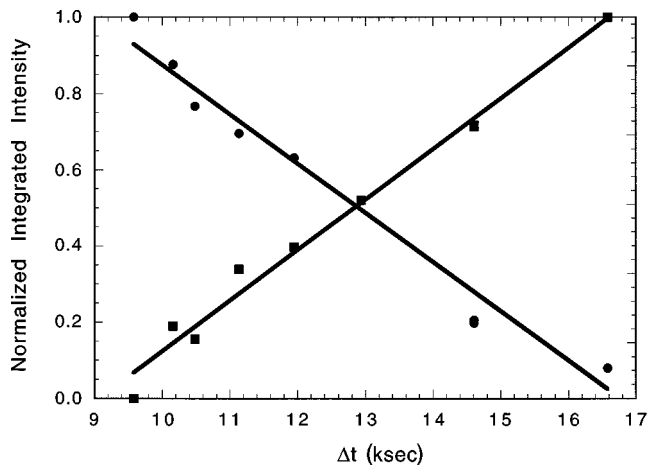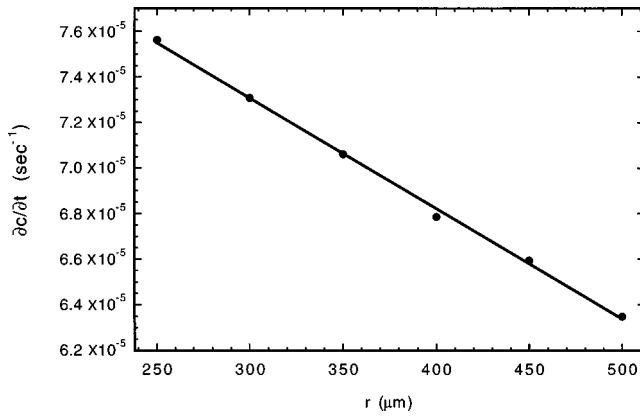

FIG. 4. Temporal dependence of the normalized, integrated intensities of the (422) diffraction peaks of the α phase (circles) and β phase (squares) recorded at $r = 450\ \mu$m. (All measurements were made at a constant electrolysis current density of 1 mA/cm^2.)

FIG. 5. Spatial variance of $\partial c/\partial t$.

ear curve representing the time dependence of the normalized integrated intensities of the (422) peaks of the α phase in the two-phase region. The slopes of these lines were used to estimate the diffusion rate of the solute atom through the wire.

Based on the phase diagram, at room temperature, the concentration of the solute atom at the onset and completion of the α-to-β transition is 0.03 and 0.58, respectively. The bulk volume change in the two-phase region varies as a linear combination of the volumes of the two phases, V_α and V_β. Therefore, it can be assumed that the concentration within the diffracting volume element also varies linearly throughout the two-phase region. Values of $\partial c/\partial t$ were determined from the $c(t)$ plots for each radial position. These values increased linearly from the surface inward, as shown in Fig. 5. This behavior is probably related to the radial nature of the diffusion.

In Fig. 6, the spatial and temporal variations of the local concentration are plotted for eight different concentrations. The points in Fig. 6 were determined from the linear decay curves for the α phase at each radial position, such as the one shown in Fig. 4. The solid curves in Fig. 6 represent linear fits to the $(r,\Delta t)$ values, using a least-squares procedure. The temporal intercepts with the curves in Fig. 6 then were used to generate $c(r)$ plots. These are shown in Fig. 7 for two values of Δt.

A third-order polynomial was fitted to the points in Fig. 7 for each of the two values of Δt. The equations of these fitted functions then were used to evaluate the two terms on
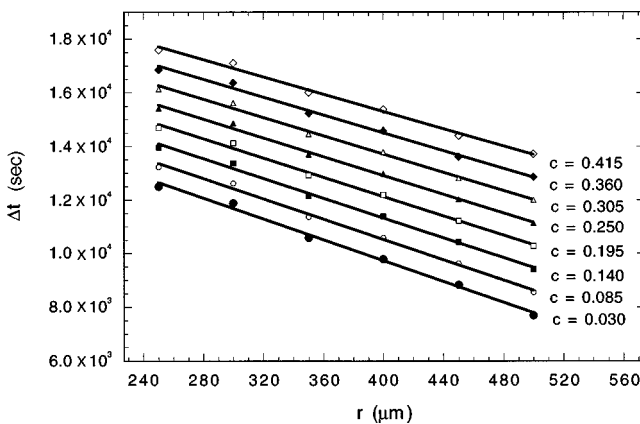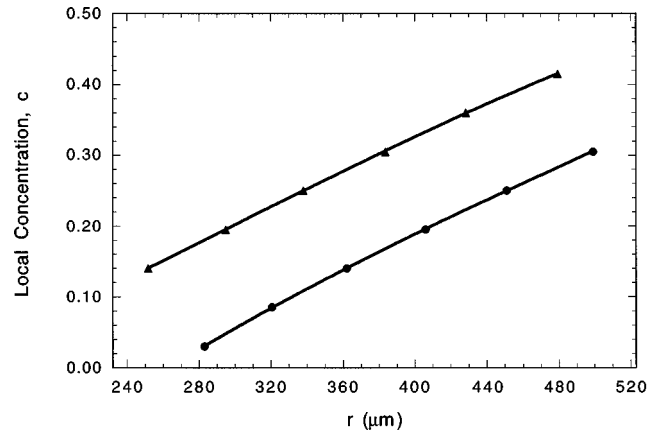

FIG. 6. Temporal and spatial dependence of the local concentration.

FIG. 7. Spatial dependence of the concentration c, as determined from the $r(t)$ curves at $\Delta t = 12$ ks (circles) and at 14 ks (triangles).

the right side of Eq. (1) and hence the diffusivity. The computed values for D are $(3.1\pm1.0)\times10^{-11}$ m²/s for $\Delta t = 12$ ks and $(2.1\pm0.3)\times10^{-11}$ m²/s for $\Delta t = 14$ ks. The small decrease that we observe in D over this 2 ks period may be due to the fact that we also observe a small decrease in the volume of the β lattice over this same period, as discussed below.

These values are slightly less than values determined by other methods. Powell and Kirkpatrick report D to be 4.7 $\times10^{-11}$ m²/s for diffusion of deuterium into Pd at room temperature, based on P-V-T gas up-take experiments.[12] However, it is noted that the concentration range of their study was very dilute, $0.00\lesssim c\lesssim0.01$. Flanagan and Oates report a value of 5.5×10^{-11} m²/s, based on several different types of diffusion experiments.[13]

Volume changes

The volume of the unit cells of each phase are related to the energies of the diffraction peak centers (E) through Bragg's Law:

$$E d_{hkl}\sin\theta = \frac{1}{2} h'c',   (2)$$

where d_{hkl} is the interplanar spacing which is related to the unit-cell parameter through the Miller indices (hkl); θ is the Bragg angle; h' is Planck's constant; and c' is the speed of light.

The fractional volume change of each phase and the temporal dependence of the bulk concentration are plotted in Fig. 8. The volume changes can be summarized as follows: As x increases from 0 to about 0.04, V_α increases monotonically by about 0.3%; for $0.04\lesssim x\lesssim0.11$, the material is in the two-phase region and both V_α and V_β decrease slightly with increasing x. The composition at the onset of the phase transition is consistent with the accepted phase diagram. However, the composition at the completion of the transition is well below that associated with the phase diagram. This is reasonable because the data presented in Fig. 8 were recorded near the surface of the wire, where the local concentration of solute atoms was greatest and hence larger than the bulk values.

The time of initiation of the β phase is approximately coincident with the discontinuity in the $V_\alpha(t)$ shown in the
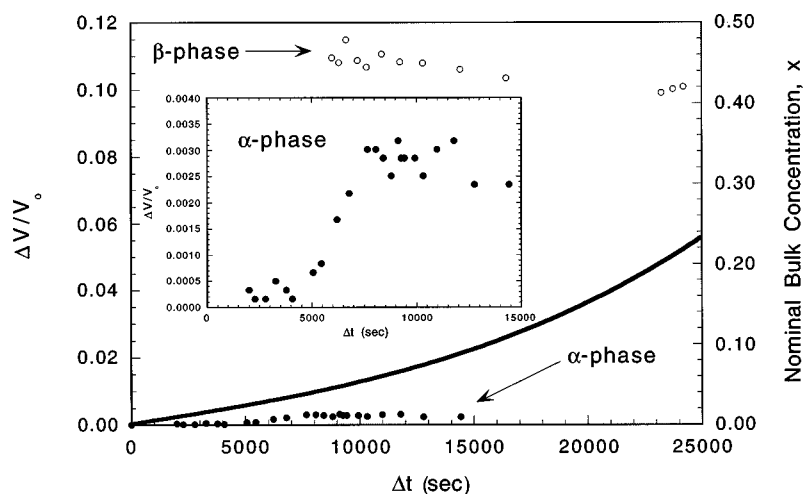
FIG. 8. Fractional volume change of the α phase (filled circles) and β phase (open symbols) measured from a 180 pl volume element near the surface of the wire. [The discontinuity in $\Delta V/V_0(x)$ for the α phase that accompanies the onset of the β phase is seen more clearly in the inset.] The solid curve is referenced to the right ordinate axis and represents the measured bulk composition.

inset in Fig. 8. The small volumetric decrease in both $V_\alpha(t)$ and $V_\beta(t)$ is probably related to the relatively large (~11%) volume change associated with the α-β transition and the accompanying internal pressure that may result. These observed volume changes agree with the previously reported linear volume increase of 2.8 ± 0.2 Å^3 per atom over the range $0.1 \lesssim c \lesssim 0.7$.[14]

Our measured volume dependences also are in agreement with an earlier x-ray study of Batalla, Zwartz, and Judd.[15] They did not measure the composition, but monitored the crystallographic structure of a Pd foil during electrolysis. They reported an overall volume change of 12.7% and an erratic and highly nonlinear behavior of the cell volume. In another x-ray study, Yamamoto *et al.*[16] monitored the (220) peak of the β phase as a function of applied electric potential in their electrolysis cell. They found a monotonic increase in the lattice size with increasing negative electrode potential, i.e., with increasing charging current. These earlier measurements were made only at the surface and, in both cases, it was the surface opposite to that to which the electrodes were attached.

CONCLUSIONS

In summary, we report in this paper results on *in situ*, simultaneous x-ray-diffraction and electrical resistance measurements of Pd as D is deposited on the surface of a Pd wire and diffuses radially inward. These data represent to our knowledge the first time that the Pd lattice expansion has been measured in an electrochemical cell during water electrolysis as a function of distance across the cathode and during electrolysis time. The results provide information about the effect of x on the structure of PdD$_x$, the rate and the spatial dynamics of composition change ($\partial c/\partial t$), the diffusivity of the solute atom through the Pd lattice, and associated volume changes.

ACKNOWLEDGMENTS

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