Kinetics of hydrogen absorption by Pd(110)

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A coupled high-pressure—ultrahigh-vacuum technique is employed to make the first kinetic measurements of high-pressure hydrogen absorption through an atomically clean palladium surface, Pd(110). The hydrogen uptake kinetics in the α-phase region are found to be rate limited by diffusion of atomic H into the bulk rather than by dissociative chemisorption of H_2 at the surface as previously reported. Our findings strongly suggest that previous high-pressure measurements of hydrogen absorption by palladium may be suspect due to uncharacterized surface contamination. The bulk diffusivity of hydrogen in palladium determined in this study has an activation barrier of 5.39 ± 0.30 kcal/mol with a preexponential factor of $(2.83\pm0.05)\times10^{-3}$ cm^2/s.

INTRODUCTION

The interaction of hydrogen with metals is both fundamentally and technologically important. From a fundamental viewpoint the dissociative chemisorption of molecular hydrogen on transition-metal surfaces is one of the simplest heterogeneous chemical reactions. This reaction also plays a key role in many industrially important catalytic processes such as olefin hydrogenation, the Fisher-Tropsch process, and ammonia synthesis. The subsequent permeation of atomic hydrogen into the bulk gives rise to such deleterious effects as hydrogen-induced embrittlement and cracking. Penetration of hydrogen into the bulk is also important in first-wall interactions in fusion reactors and metal hydride solid-state hydrogen storage materials.

The hydrogen palladium system is the classic metalhydride system and extensive literature[1,2] concerning its bulk properties exists dating back to the early work of Graham.[3] However, there have only been a few studies which address the kinetics of bulk hydrogen uptake.[4-8] The results of these studies indicate that the rate of hydrogen uptake is limited by the dissociative chemisorption of molecular hydrogen rather than by the diffusion of atomic hydrogen into the bulk.

Recently, there has been a large number of surface-science experiments reported[9-14] which study the interaction of hydrogen with well-characterized single-crystal Pd surfaces. These experiments have proven useful in elucidating both the energetics and bonding of dissociatively adsorbed hydrogen on the surface. A key result of these studies is that the dissociation probability of a hydrogen molecule impinging on an atomically clean Pd surface is near unity.

The previous high-pressure absorption kinetic measurements[4-8] which indicate that hydrogen uptake is surface limited are in conflict with ultrahigh-vacuum thermal desorption studies[9,12-14] which show the hydrogen surface dissociation probability to be large. In order to resolve this conflict, we have undertaken a high-pressure kinetic study of hydrogen absorption by a well-characterized single-crystal Pd sample. Herein, we report the first high-pressure kinetic measurements of bulk hydrogen uptake through an atomically clean palladium surface, Pd(110). Our findings show that the uptake rate is limited by bulk atomic diffusion rather than by dissociative chemisorption and strongly suggest that previous absorption rate data[4-8] may be suspect due to uncharacterized surface contamination.

EXPERIMENTAL

The high-pressure kinetic measurements reported here were conducted in a specialized apparatus shown schematically in Fig. 1. The apparatus consists of two ultrahigh-vacuum chambers separated by a metal-seal in-line valve. Both chambers have base pressures below 2×10^{-10} torr. The sample, a 1-cm-diameter by 0.88-mm-thick Pd single-crystal disk (Metal Crystals Ltd., Cambridge, United Kingdom) is cut and polished to within $\pm\frac{1}{2}$° of the (110) orientation. The crystal is spot welded to two 0.5-mm-diameter W wires through which it is connected to a long-throw bellow manipulator enabling translation between the two chambers. The sample is heated resistively and its temperature monitored with a Chromel-Alumel thermocouple.

The lower chamber houses an ion gun, quadrupole mass spectrometer, and a cylindrical-mirror Auger electron energy analyzer. These instruments are utilized to clean and characterize the Pd(110) crystal both before and after hydrogen absorption. The Pd(110) single crystal was initially cleaned by heating to 800 K in 2×10^{-7} torr of O_2 for 5 min followed by a 5-min exposure to H_2 at the same temperature and pressure. A 1-min anneal to 1100 K in vacuum completed the cleaning procedure, yielding an Auger spectrum free of O, S, and C contamination.

After cleaning, the sample is raised into the upper chamber and the valve separating the two chambers is closed. The upper chamber constitutes the high-pressure absorption cell and has a measured volume of 650 cm^3. To initiate the absorption, the valve on the upper ion pump is closed and the valve leading to the gas manifold is opened allowing a known quality of ultrapure H_2 gas (Matheson, 99.9995%, used without further purification)
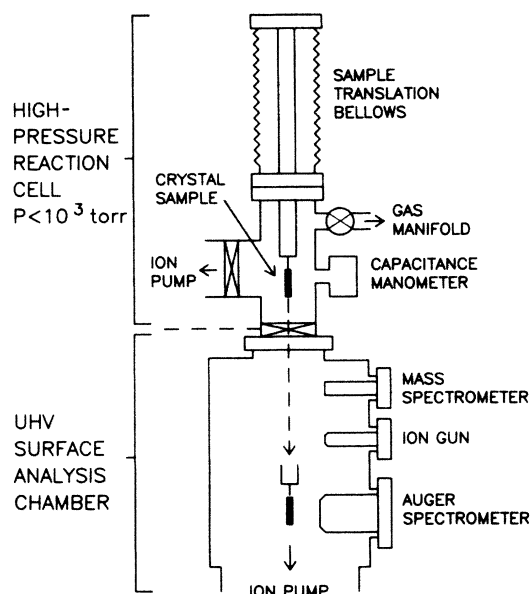

HIGH-PRESSURE SURFACE REACTOR

FIG. 1. Schematic diagram of the experimental apparatus.

to enter the absorption cell. Absorption rates were determined by monitoring the pressure in the absorption cell with a capacitance manometer as a function of time. A control experiment performed in the absence of the Pd sample indicated that the pressure drop due to H_2 adsorption on the reactor walls is negligible.

During an actual run, pressure readings are recorded every three seconds until the pressure decays to an equilibrium asymptotic value. Typical data of this type are displayed in Fig. 2. The equilibrium hydrogen-to-metal stoichiometry is easily calculated if the reactor volume, crystal mass, and measured pressure drop are known. The initial H_2 gas pressure was kept below 5 torr to prohibit formation of the β hydride phase[1,2] which is known to undergo a lattice expansion over the α solid solution phase. Upon completion of an absorption run the high-pressure

cell was evacuated and the sample was heated to ~800 K to remove the absorbed hydrogen. Five minutes of heating and pumping was sufficient to remove all hydrogen from the sample. Subsequent Auger analysis of the sample in the lower chamber showed the sample surface to be free of impurities.

RESULTS AND DISCUSSION

Hydrogen absorption measurements were carried out over the pressure range of 1—5 torr for temperatures between 60 and 140 °C. These conditions correspond to hydrogen-to-metal (H-M) atomic ratios[15] in the range 0.001 to 0.005. Figure 2 displays the time dependence of the gaseous hydrogen pressure in the absorption cell for an initial pressure of 4.7 torr at a temperature of 100 °C. As clearly seen in the figure, the pressure decays from its initial value of 4.70 torr to a steady asymptotic limit of 4.43 torr, yielding a net pressure drop of 0.27 torr. As previously mentioned, the measured pressure drop is directly proportional to the hydrogen stoichiometry in the metal, i.e., the H-M ratio. Figure 3 shows a plot of the measured pressure drop versus the square root of the final absorption-cell pressure, for a temperature of 100 °C. The observed square-root dependence of the measured pressure drop upon final pressure indicates that for the experimental conditions examined the hydrogen dissolved in palladium exhibits ideal solid solution behavior (i.e., Sievert's law is obeyed) (Refs. 1 and 2) and is in the α phase. The H-M ratios calculated from the measured pressure drops are in good agreement with the pressure-composition-temperature relationships reported by Wicke and Nernst,[15] indicating the system attains thermodynamic equilibrium during the experiment. Another point to note is that the observed pressure drops are a relatively small fraction ($\leq 10\%$) of the initial absorption-cell pressure for all experimental conditions examined. Thus, the mea-
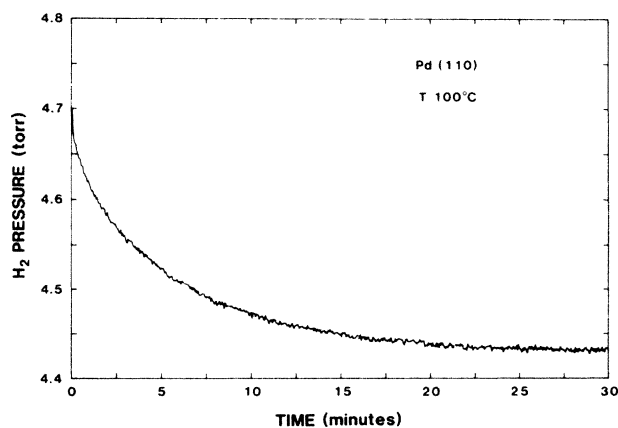

FIG. 2. Time dependence of the gaseous hydrogen pressure in the absorption cell for an initial pressure of 4.7 torr and a temperature of 100 °C.
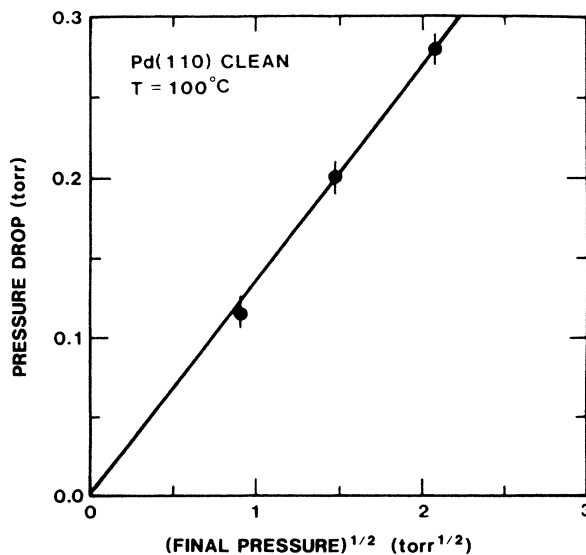

FIG. 3. Measured pressure drop versus the square root of the final absorption-cell pressure. The linearity of this plot indicates Sievert's-law behavior.

surements are carried out under quasi-isobaric conditions.

As first proposed by Wagner in 1932,[4] the transfer of hydrogen from the gas phase into the Pd lattice is composed of at least two steps. First, the dissociative chemisorption of H_2 molecules impinging on the surface, followed by the subsequent atomic diffusion of atomic hydrogen into and through the bulk. These steps are schematically represented by the following equations:

$$H_2(gas) \rightleftharpoons 2H(adsorbed) , \tag{1}$$

$$H(adsorbed) \rightleftharpoons H(bulk) . \tag{2}$$

The pressure dependence of the initial hydrogen uptake rate depends upon which of these processes is rate limiting. If the dissociative chemisorption of impinging H_2 is rate limiting, the initial absorption rate is linearly dependent upon the gaseous H_2 impingement rate which is directly proportional to the gaseous H_2 pressure. If atomic diffusion into the bulk is the rate-limiting step in hydrogen uptake, the initial rate will depend linearly upon the concentration of H in the near-surface region since this drives the diffusion. For cases where Sievert's law is applicable (such as in α-Pd) this concentration is proportional to the square root of the gaseous H_2 pressure.

The initial hydrogen uptake rate is determined from the initial slope of the reactor pressure versus time curve (see Fig. 2). The absolute value of this slope (having units of torr/s) is easily converted to a flux of hydrogen being absorbed by the Pd if the reactor volume (650 cm^3) and the crystal surface area (1.57 cm^2) are known. Figure 4 displays a plot of the experimentally measured initial H_2 absorption rate expressed as a flux of hydrogen molecules

moving through the Pd surface [$H_2/(cm^2 s)$] as a function of pressure for a sample temperature of 100 °C. The square-root pressure dependence of the initial absorption rate is indicative of a diffusion limited process. Similar results are obtained at the other temperatures (60, 80, 120, and 140 °C) studied.

Our observation that hydrogen uptake is limited by diffusion into the bulk is in conflict with previous high-pressure measurements[4-8] which reported initial absorption rates exhibiting a linear pressure dependence indicative of a surface limited process. Since the rates in these studies have different pressure dependences, a comparison of the results must be made at a fixed pressure. This comparison is shown graphically in Fig. 5, which is an Arrhenius plot of our results and those of Auer and Grabke[5] (calculated from Eq. 17 of their paper[5]) for a gaseous H_2 pressure of 4.7 torr. As clearly seen in this figure, our measured initial rates are between 50 and 100 times faster than those found by Auer and Grabke[5] even though our sample is 350 times thicker. The slope of the Arrhenius plot of our initial rate data yield an activation energy of 5.5±0.5 kcal/mol in excellent agreement with the accepted barrier[16] for bulk diffusion of H in Pd (5.30 kcal/mol).

The results of Auer and Grabke[5] indicate a surface limited process with an activation energy of 6.8 kcal/mol. The dissociative chemisorption on atomically clean Pd is known to be nonactivated from both temperature-programmed thermal desorption[9,12-14] as well as molecular-beam scattering experiments.[10,11] Furthermore, the initial dissociatve sticking probabilities (sticking coefficients) are large (≥ 0.1) for impinging H_2 molecules. An
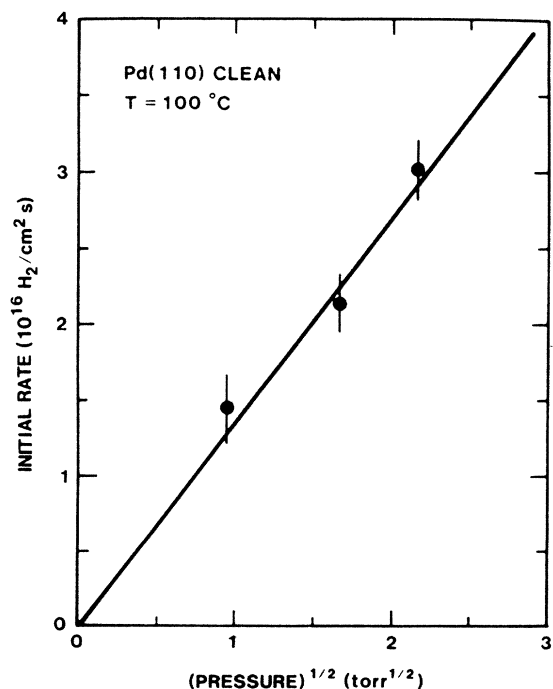

FIG. 4. Plot of the initial hydrogen absorption rate as a function of the square root of the H_2 gas pressure at a temperature of 100 °C.
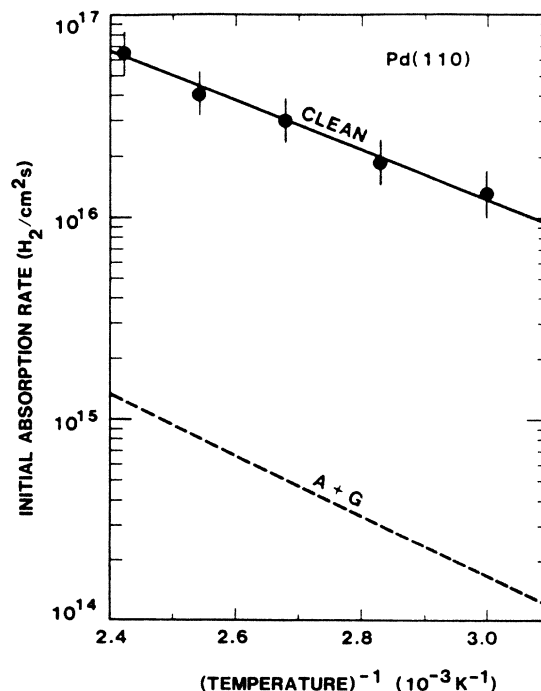
FIG. 5. Arrhenius plot of the measured initial hydrogen absorption rate at 4.7 torr. The dashed line is the result of Auer and Grabke (Ref. 5) at the same pressure for comparison.

effective dissociative sticking coefficient is rapidly calculated for the Auer and Grabke measurement[5] by simply dividing their measured initial absorption flux by the gas kinetic impingement flux $[J = P(2\pi m kT)^{-1/2}]$,[17] assuming a Maxwellian velocity distribution of the gaseous H_2. The result of this simple calculation yields an apparent dissociation probability of 8×10^{-8} at a temperature of 100 °C.

The low apparent H_2 dissociation probability observed by Auer and Grabke[5] may arise from uncharacterized surface contamination on their sample. Previous studies measuring permeation rates of hydrogen through Pd membranes have found marked decreases in permeation rates when the membrane is exposed to mercury vapor or compounds containing S, As, I, or Br.[18,19] Recently, Comsa and co-workers[20,21] have reported angle-resolved time-of-flight velocity distribution measurements of D_2 desorbing from clean and sulfur-contaminated Pd(100) following permeation through the bulk. Their findings indicate a strong dependence of both the angular and velocity distributions of the desorbing D_2 flux with sulfur coverage. These results strongly suggest that H_2 adsorption can become activated on "poisoned" surfaces. We have performed high-pressure absorption measurements on sulfur poisoned Pd(110) and observe an appreciable reduction in the H_2 uptake rate at submonolayer surface sulfur coverages.[22] Another indication of the dominant role surface contamination can play in the rate of H_2 uptake by Pd is exhibited by attempts to absorb hydrogen on our Pd(110) sample prior to cleaning. Under conditions identical to those used in the studies on atomically clean Pd(110), no measurable H_2 uptake was observed. Subsequent Auger analysis revealed the sample surface to be heavily contaminated with carbon.

In the present study the rate of hydrogen uptake into atomically clean Pd(110) is found to be diffusion limited, thus it is possible to extract a value for the bulk diffusivity from the experimental data. Since the Pd(110) crystal width is over 10 times greater than its thickness, the diffusion is to a good approximation one dimensional. Thus, the hydrogen uptake can be considered as absorption by a plane sheet of thickness l whose boundaries are immersed in a constant concentration of hydrogen (gaseous H_2 pressure). The one-dimensional diffusion equation for these boundary conditions has been previously solved.[23] The solution is

$$\frac{M(t)}{M(\infty)} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left[\frac{-D(2m+1)^2\pi^2 t}{l^2}\right],$$

(3)

where $M(t)$ is the total amount of hydrogen absorbed at any time t, $M(\infty)$ is the total amount of hydrogen absorbed at equilibrium, D is the diffusion coefficient (cm^2/s), and l is the sample thickness $(l = 0.088$ cm). The quotient $M(t)/M(\infty)$ is readily calculated from data of the type shown in Fig. 2:

$$\frac{M(t)}{M(\infty)} = \frac{P(0) - P(t)}{\Delta P},$$

(4)

where $P(0)$ is the initial H_2 pressure in the absorption cell,

$P(t)$ is the absorption-cell pressure at a time t after the H_2 is admitted to the absorption cell, and ΔP is the pressure difference between the initial $[P(0)]$ and asymptotic absorption-cell pressures.

To analyze the measured pressure decay curves (Fig. 2) it is useful to define a time to half absorption $(t_{1/2})$ such that $M(t_{1/2})/M(\infty) = \frac{1}{2}$. This time is simply the time for the measured pressure drop to reach half of its final value and is easily determined from the experimental data. The relation between $t_{1/2}$ and the diffusion coefficient can be determined from Eq. (3) (Ref. 24) and is

$$t_{1/2} = \frac{-l^2}{\pi^2 D} \ln\left[\frac{\pi^2}{16} - \frac{1}{9}\left[\frac{\pi^2}{16}\right]^9\right].$$

(5)

As seen from Eq. (5), $t_{1/2}$ explicitly depends only upon the sample thickness l and the diffusion coefficient D. Thus, for a diffusion limited process, $t_{1/2}$ should be independent of the H_2 pressure in the absorption cell. Figure 6 displays a plot of various experimentally determined $t_{1/2}$ values as a function of H_2 pressure in the absorption cell. The observed pressure independence of $t_{1/2}$ is indicative of a process limited by bulk diffusion.

Hydrogen diffusion in bulk Pd is known to be activated and to exhibit Arrhenius behavior,[16] thus an Arrhenius plot of $t_{1/2}$ should be linear with a positive slope due to the reciprocal relation between $t_{1/2}$ and the diffusion coefficient, D [see Eq. (5)]. Figure 7 displays an Arrhenius plot of the experimentally determined $t_{1/2}$'s and confirms this expectation. Both the preexponential factor and activation energy can be determined from Fig. 7 using Eq. (5). Table I shows a comparison of the experimentally determined diffusivity with the tabulated value;[16] the agreement is excellent.
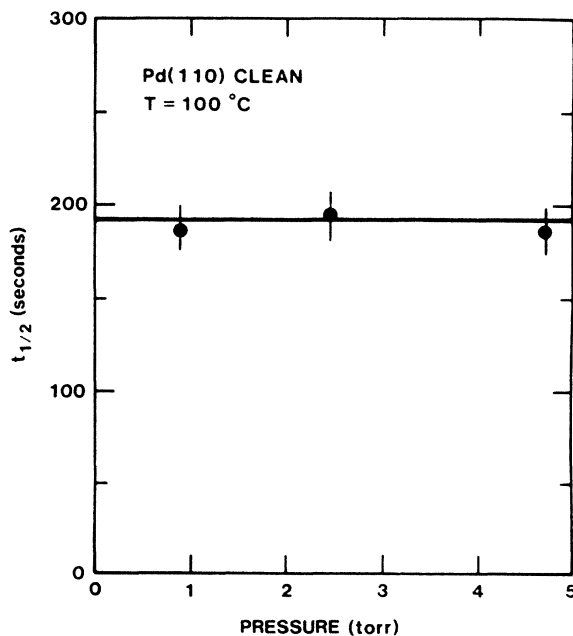

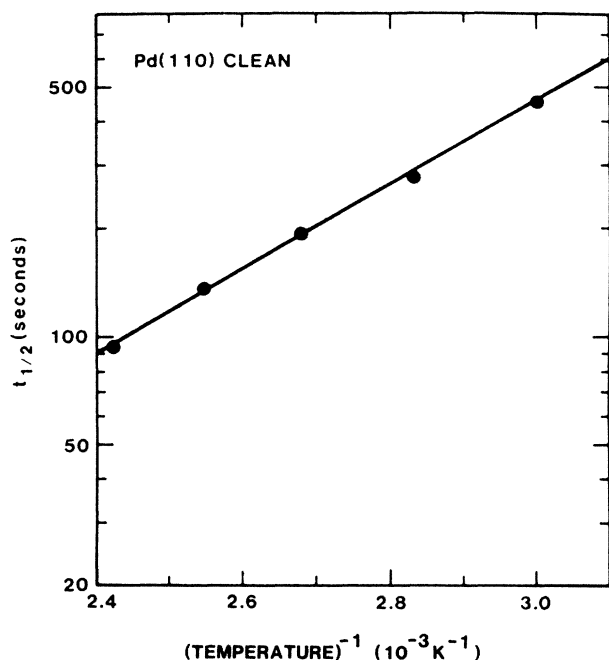FIG. 6. Pressure dependence of the experimentally determined half absorption times for a temperature of 100 °C.

FIG. 7. Arrhenius plot of the experimentally determined half absorption times.

TABLE I. Comparison of measured and tabulated hydrogen diffusivity in palladium.

	This work	Accepted value[a]
D_0 $(10^{-3}$ cm^2/s)	2.83±0.05	2.9
E_D (kcal/mol)	5.39±0.30	5.3

[a]Reference 16.

SUMMARY AND CONCLUSIONS

Herein we have reported the first kinetic measurements of high-pressure hydrogen absorption through an atomically clean well-characterized single-crystal palladium surface, Pd(110). Our findings show the initial hydrogen uptake rate to be controlled by atomic diffusion of H into the bulk rather than by dissociation of H_2 at the surface as previously reported.[4-8] This result is in good agreement with expectations based upon the known large dissociative sticking probabilities for H_2 on clean single-crystal Pd surfaces[9-14] and further supported by the enhanced hydrogen uptake rates recently observed on niobium single crystals covered with a palladium overlayer.[25-28] The diffusion coefficients determined in the present study are in excellent agreement with the accepted values[16] for bulk diffusion of hydrogen through palladium.

The results of this study strongly suggest that previous kinetic measurements on the hydrogen-palladium system may be severely influenced by uncharacterized surface contamination. We have recently undertaken a detailed study of the effect submonolayer surface sulfur coverages have on the hydrogen absorption kinetics in Pd(110); the results are published elsewhere.[22] Pd(110) has recently been shown to exhibit a hydrogen-induced surface reconstruction[12-14] giving rise to a subsurface hydrogen chemisorption site. The role of such a subsurface site in hydrogen uptake is currently under active study.[29-31] Current efforts in our laboratory focus on studying the kinetics of high-pressure hydrogen absorption by other clean and chemically modified low-index planes of palladium.

ACKNOWLEDGMENTS

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