Potential Dependent Surface Relaxation of the Pt(001)/Electrolyte Interface

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X-ray reflectivity measurements were used to determine the structure of the Pt(001)/solution interface as a function of the applied potential in alkaline and acid electrolytes. Unlike the Pt(001)/vacuum interface, the electrolyte interface was found to be unreconstructed at all potentials. The lattice spacing between the first and second layer was found to be a function of potential in the region where approximately a monolayer of H was adsorbed. The expansion was up to 2.5% of a lattice spacing (0.05 Å) in alkaline electrolyte, and up to 1% of a lattice spacing in acid electrolytes.

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The nature of the metal/solution interface has in the past few years become a topic of much investigation after the development of scanning tunneling microscopy and synchrotron x-ray scattering techniques. In particular, several recent studies have investigated both the potential dependent adsorption of metals onto single crystal surfaces [1] and potential dependent reconstructions of surfaces [2–4]. In the latter case, anion adsorption and desorption (controlled by potential) appear to play a critical role in the removal and formation of the reconstruction. These studies have concentrated on chemically quite inactive surfaces (such as silver and gold) where contamination problems are relatively insignificant and the energy associated with adsorption is quite small. In contrast, platinum surfaces have generally much higher interaction energies with most adsorbates than is the case for gold, and thus adsorption may have a more profound effect on the surface structure and issues of cleanliness are of crucial importance. X-ray scattering studies have shown that the vacuum interface of the Pt(001) surface at room temperature is reconstructed, with the top layer well represented by an incommensurate-distorted-hexagonal overlayer which is rotated approximately ±0.8° from the [110] direction [5]. The vacuum interface reconstruction is removed, however, on exposure to hydrogen [6], water vapor, and several other adsorbates [7]. *Ex situ* low-energy electron diffraction (LEED) studies of the electrolyte interface [8] strongly suggest that the reconstruction is unstable in electrolyte at any potential, although this has not previously been conclusively demonstrated *in situ*. The interaction of H with Pt is very different from the interaction of H with Au. In electrolyte, from voltammetric studies and thermodynamic calculations an adsorbed state of H is known to exist on Pt at potentials positive of H_2 evolution [9]. No such state exists at the Au/electrolyte interface. Even though the H/metal interaction is one of the most fundamental to physical chemistry, it is very difficult to study (especially *in situ*), and the details of the bonding are still a subject of controversy [10].

In this Letter we describe our x-ray scattering experiments to probe the Pt(001) interface with aqueous alkaline and acid electrolytes. In all cases the Pt was found to be unreconstructed at all potentials within the region of thermodynamic stability of water. However, a previously unobserved and unexpected expansion of the top Pt layer was found in the potential region in which close to a monolayer (ML) or more of H was adsorbed on the surface. The expansion occurred continuously with potential in alkaline and acid electrolytes until saturating at approximately 2.5% of the layer spacing in $0.1N$ KOH electrolyte, and approximately 1% in $0.1N$ $HClO_4$ and H_2SO_4 electrolytes.

The experimental procedures and equipment used have been described previously [4] and only the major points will be mentioned. The Pt(001) single crystal used consisted of a disk oriented within 0.5° of the [001] direction. The crystal was prepared by flame annealing in a hydrogen flame for a few minutes (approximate temperature 1000 °C) and cooling in flowing hydrogen [11,12]. The surface was then protected from airborne contamination by placing a drop of water onto the crystal immediately after removal from the hydrogen stream. This procedure ensures a very quick and clean transfer of the sample, which was checked using electrochemical diagnostic measurements (i.e., cyclic voltammetry), prior to the x-ray studies to ensure that the cell was free from detectable contaminants [4]. Although a palladium/hydrogen reference electrode was used, all potentials quoted in this paper are referenced to the reversible hydrogen electrode (rhe).

X-ray data were taken on beamline 7-2 at the Stanford Synchrotron Radiation Laboratory (SSRL), where a wavelength of 1.377 Å was used, and on beamline X10A at the National Synchrotron Light Source (NSLS) where a wavelength of 1.365 Å was used. The scattering vector **Q** is given in terms of (Ha^*, Kb^*, Lc^*) where $a^* = b^* = c^* = 2\pi/a$, $a = 3.991$ Å, and L is along the surface normal direction. In both cases the four-circle goniometer used was configured with slits such that the in-plane resolution at $L = 2$ was approximately 0.010 Å^{-1} half width at half maximum (HWHM) and the lon-

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gitudinal resolution along the surface normal direction was $\Delta Q_z \approx 0.014$ Å^{-1}.

A precise description of the structure of a crystal surface can be obtained by measuring crystal truncation rods (CTR's), both specular and nonspecular [2,4,5,13]. Two CTR's for a Pt(001)/0.1N KOH solution interface at 0.02 V and 0.42 V are shown in Fig. 1 for the (00L) and (11L) rods [Figs. 1(a) and 1(b), respectively]. At 0.02 V the surface is believed to be covered by approximately a ML of adsorbed H [14], while at 0.42 V adsorbed H is absent. Each point shown in Figs. 1(a) and 1(b) was measured by first rocking the crystal about the (HKL) position and calculating the (background subtracted) integrated area. The detector was then positioned at the peak and the scattering intensity recorded as the potential was cycled using small steps for an average scan rate of 5 mV/sec. The above scheme was found to significantly reduce long term drifts and problems associated with contamination. In KOH electrolyte the system was stable for over 12 h, whereas in acid electrolytes the system was stable for only a few hours, probably due to x-ray induced decomposition of the electrolyte [4].

For all points shown in Figs. 1(a) and 1(b) the measured scattering lies below the scattering expected for an ideal interface. This indicates that the Pt(001) is rougher than the ideal interface. Furthermore, at no potentials between H_2 evolution and oxide formation does the specular CTR exhibit the characteristic shape associated with the reconstruction [2,4,5] and no in-plane peaks associated with the reconstruction were observed, conclusive evidence that the Pt surface is in the (1 × 1) state. The fits to the data shown were obtained using a model similar to the one described in Ref. [4], which allowed variations in the top-layer density, rms displacement term, and spacing between the first and second layers. In addition, the presence of an incommensurate adsorbed water layer was included, and the existence of Pt islands or steps within the x-ray correlation length was permitted. The (00L) and (11L) rods were modeled simultaneously using the same parameters. The fit shown for the data at 0.42 V includes a top Pt layer with an 85% occupancy, a top-layer rms displacement of 0.09 Å (bulk thermal rms displacement of 0.015 Å), and an expansion of the top-layer spacing, d_{12}, relative to the bulk lattice spacing, d_b, of $\Delta d = (d_{12} - d_b)/d_b = 0.010 \pm 0.005$, which is equivalent to a shift of 0.02 Å away from the unrelaxed bulk site. The inclusion of a second layer spacing change did not significantly improve the fit. The model also includes a water layer with parameters similar to those used by Wang *et al.* [15], except for an increased rms displacement term. The effect of the water layer on the scattering intensity is negligible above $L = 1.5$ on the (00L) CTR and for the entire (11L) rod [15].

The scattering intensity changes when the potential was changed from 0.42 V to 0.02 V are easily seen in Figs. 1(c) and 1(d), which show the normalized intensity changes on changing the potential from 0.42 V to 0.02 V [explicitly, $\Delta I_1/I_0 = (I_1 - I_0)/I_0$ where I_0 and I_1 are the integrated intensities at 0.42 V and 0.02 V, respectively]. The solid lines were obtained by using the model for the interface at 0.42 V [Figs. 1(a) and 1(b), dashed line] and allowing only d_{12} to vary. Only the (11L) CTR was modeled since the scattering intensity for this rod is not sensitive to changes occurring on the electrolyte side of the interface which are incommensurate with the Pt lattice. Note that there are *no* changes to the scattering near the Bragg or anti-Bragg positions, a clear signature that the changes are due to top-layer lattice changes and are not artifacts due to contamination. The fit shown corresponds to a potential dependent increase in the top-layer spacing ($\delta\Delta d$) of 0.015 ± 0.003 or 0.03 ± 0.006 Å from the top-layer spacing at 0.42 V (i.e., $\Delta d = 0.025 \pm 0.005$). Figure 1(d) shows that the agreement to the (11L) rod is excellent, while for the (00L) rod the discrepancies between the model and data between $L = 0.5$ and 1.5 are similar to changes in the double-layer structure observed previously [15,16]. The fit was improved slightly if the second layer spacing (d_{23}) was allowed to expand by $\Delta d_{23} = 0.003 \pm 0.003$, with a somewhat smaller discrepancy for the (00L) rod between $L = 2.5$ and 3.5. The equivalent fits to the full CTR are shown as solid curves in Figs. 1(a) and 1(b).

Careful attention was paid to the question of whether the observed changes could be due to scattering from a

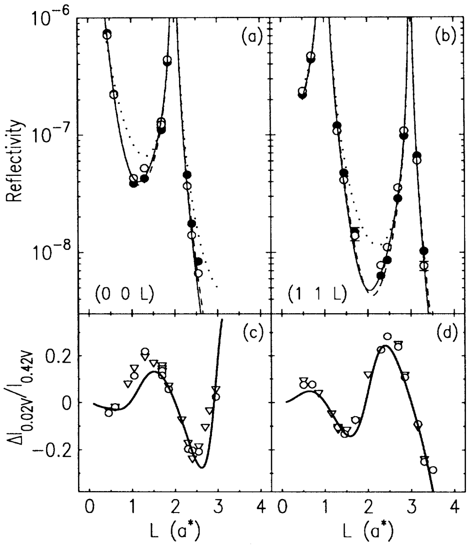

FIG. 1. (a) and (b) show the absolute x-ray reflectivities of the Pt(001) crystal in 0.1N KOH electrolyte for the (00L) and (11L) rods, respectively. The open (closed) circles show the reflectivity at 0.02 V (0.42 V). The dotted lines are the theoretical reflectivity from an ideal Pt(001) surface. The dashed (solid) lines show fits described in the text to the 0.42 V (0.02 V) data. (c) and (d) show the normalized deviations of the scattering intensity at 0.02 V as referenced to the scattering at 0.42 V (see text). These changes are shown with two symbols for two different samples.

potentially dependent water adlayer or other adsorbed ML film. For the data at 0.0 V, however, no reasonable set of parameters for an adsorbed water layer could be found which adequately described the data *without the inclusion of a top-layer spacing expansion.* An adsorbed ionic layer could also be ruled out as responsible for the changes since specifically adsorbed hydroxyl ions are essentially indistinguishable (with x rays) from water, and potassium ions are strongly hydrated in solution and therefore do not adsorb. Possible contamination effects (e.g., anions other than hydroxyl or organics) were also examined. The multiple current peaks associated with H adsorption are a particularly sensitive measure of the cleanliness of the system [10]. Figure 2(a) shows the current passed on cycling the potential as measured in the hanging meniscus geometry (i.e., ideal) and in the x-ray cell just prior to an x-ray measurement. Note that although the data taken with the x-ray cell show a pronounced tilt to negative currents at the most negative potential (due to the cathodic current from the reduction of residual oxygen in the electrolyte), the features associated with H adsorption (between 0.1 and 0.6 V) are all clearly visible. After a few hours the tilt associated with oxygen is eliminated, although the "background" current increases due to electrolyte leaking around the crystal. The features associated with H adsorption were, however, still clearly visible even after several hours. Finally, we note that the expansion was observed repeatedly in four different electrolytes, and was even found on somewhat contaminated surfaces.

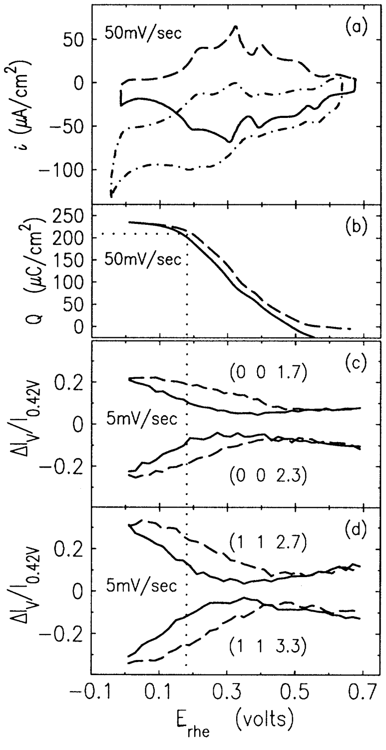

FIG. 2. (a) Potential/current sweep of the Pt(001) crystal in 0.1N KOH electrolyte measured in the hanging-meniscus cell (dashed and solid lines) and in the x-ray cell (dot-dashed line). (b) Integrated charge calculated from the hanging-meniscus data shown in (a). The dotted line indicates the potential for approximately ML H coverage. (c) X-ray scattering intensity changes ($\Delta I_V/I_{0.42\text{ V}}$) at the (0 0 1.7) and (0 0 2.3) positions. The data were normalized by the intensity at 0.42 V ($I_{0.42\text{ V}}$) and are displaced by ±0.05 for clarity. (d) Similar data as shown in (b) for the (1 1 2.7) and (1 1 3.3) CTR positions.

Figure 2 also shows the integrated charge (b) and the changes of x-ray scattering intensity at four points [(c) and (d)] as a function of the applied potential. The charge was obtained by measuring the current passed on a potential sweep at 50 mV/sec [Fig. 2(a)] and integrating from 0.55 V [17]. Figures 2(c) and 2(d) show the scattering intensity measured at CTR positions 0.3c^* above and below the (002) and (113) Bragg peaks. At these positions the x-ray scattering intensity is quite sensitive to changes in the Pt layer spacings near the surface (see Fig. 1). Note in particular that the scattering intensity at *both* positions below the Bragg peaks increases continuously as the potential decreases below approximately 0.25 V, while the scattering intensity at points above the Bragg peaks shows the opposite effect. These intensity changes are characteristic of a lattice expansion of the top Pt layer away from the second layer. The theoretical charge for an adsorbed ML of H (assuming one H atom per Pt surface atom) is shown with a dotted line in Fig. 2. This clearly shows that the expansion of the top-layer spacing occurs primarily in the potential region where *close to a ML of H* is adsorbed on the surface (assuming all the charge passed below approximately 0.45 V is associated with H adsorption).

The data discussed so far were measured in a dynamical system while cycling the potential at 5 mV/sec. Using much slower sweep rates, a maximum change in the top-layer spacing of $\delta\Delta d = 0.022 \pm 0.03$ was inferred. In addition, excursions into the potential region in which H_2 evolution occurs resulted in similar maximum expansions, with no further expansion of the top layer at potentials below −0.1 V. Potential stepping studies showed that the expansion occurred approximately exponentially with time on stepping near 0.0 V, with a time constant of 16 ± 5 sec. A small expansion of d_{12} at potentials positive of 0.42 V can also be inferred from the changes to the scattering shown in Figs. 2(b) and 2(c). At 0.69 V the modeling indicates an increase in the top-layer spacing of $\delta\Delta d = 0.002 \pm 0.001$.

Similar measurements were made using 0.1N sulfuric acid and 0.1N perchloric acid solutions. The expansion of the top Pt layer at potentials just above H_2 evolution was again observed, although the expansion was significantly smaller than measured in alkaline electrolyte. Again, the expansion was observed mainly in the potential region where a ML or more of H was adsorbed on the surface [18]. Detailed fits to the truncation rods and the changes in the scattering with changes in potential indicate that at 0.32 V the interface was well described for $\Delta d = 0.030 \pm 0.005$. At -0.05 V the increase in the top-layer spacing is $\delta\Delta d = 0.006 \pm 0.002$, equivalent to a potential dependent expansion of approximately 0.012 Å. In perchloric acid, at 0.32 V $\Delta d = 0.010 \pm 0.005$ and at 0.05 V $\delta\Delta d = 0.006 \pm 0.002$. The larger expansion found in alkaline as compared to acid electrolyte may be related with the different H coverage, which is larger in alkaline electrolyte [14], or perhaps to the coadsorption of acid anions with H [19]. A definitive explanation awaits further study.

We are aware of only one other published study which reports on the expansion of the Pt(001) surface with H adsorption, a study of the vacuum interface which used Rutherford backscattering [6]. In that study it was found that an "almost clean" surface [covered by (5–10)% of a ML of H] was almost unrelaxed ($\Delta d = 0.005 \pm 0.005$), while a surface which was covered with approximately 1 ML of H had a top-layer expansion of $\Delta d = 0.013 \pm 0.005$, or an increase of $\delta\Delta d = 0.008 \pm 0.005$, markedly less than found here in alkaline electrolyte.

That the Pt(001) does not have the vacuum reconstruction in aqueous solution is almost certainly due to the high adsorption energies associated with the (1×1) structure. In this study, the expansion of the top-layer spacing at potentials just positive of the thermodynamic potential for H_2 evolution appears to be caused by the adsorption of a ML or more of H. Unfortunately, H atoms are almost impossible to observe using x-ray scattering and therefore their location is uncertain. Molecular dynamical or other calculations will be necessary to determine whether the adsorbed H occupies surface sites, or perhaps subsurface sites, as has been found for Pd(111) [20]. However, the nature of H species on Pt (and metals in general) in both vacuum and aqueous environments is still relatively poorly understood despite its fundamental importance.

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