

Atomic-Resolution Electrochemical Scanning Tunneling Microscopy: Evidence of I–Pd Place Exchange in the $I_{(Ads)}$ -Catalyzed Dissolution of Pd(111)

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It is known that a single chemisorbed layer of zerovalent iodine atoms catalyzes, at ambient temperatures, the anodic dissolution of Pd (to Pd^{2+} species) even in *inert* (halide-free) electrolyte. Early experiments based on low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) showed that, regardless of the rate or duration of the corrosion reaction, the composition and long-range order of the $Pd(111)-(\sqrt{3} \times \sqrt{3})R30^\circ-I$ adlattice, *before* and *after* the dissolution, were essentially identical. Follow-up studies based on medium-resolution electrochemical scanning tunneling microscopy (EC-STM) demonstrated that, *at very low rates*, the layer-by-layer dissolution occurred exclusively at steps rather than on terraces (where dissolution would necessitate I–Pd place exchange). The present study introduces atomic-resolution EC-STM images that show I-atom-constituted but Pd-atom-deep pits on terraces at more positive applied potentials (i.e., at much higher dissolution rates); such uniquely proportioned pits suggest I–Pd place exchange on terrace sites in which underlying Pd atoms are segregated to the surface prior to their dissolution; that the pits increase laterally but remain one Pd atom deep indicates a layer-by-layer dissolution sequence immediately after an initial place-exchange mechanism. When the potential is reverted back to the double-layer region, the pits disappear, and in conformity with the LEED experiments, the well-ordered $Pd(111)-(\sqrt{3} \times \sqrt{3})R30^\circ-I$ adlattice is regenerated; such a process implies a *reverse* I–Pd place exchange in which the embedded iodine is transported back to the uppermost layer.

Introduction

Palladium electrodes pretreated with a single chemisorbed layer of iodine atoms undergo anodic dissolution in inert (halide-free) sulfuric acid solutions; no dissolution takes place in the absence of iodine.¹ This unusual type of corrosion was first explored by ultrahigh-vacuum (UHV) methods [low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES)]; it was shown that the initial-state (prior to dissolution) and final-state (after emersion) structural and compositional features of the iodine-on-palladium adlattice were unperturbed by the corrosion process, regardless of the rate or duration of the dissolution reaction. On the basis of these observations, it was conjectured that the dissolution took place one layer at a time; otherwise, the LEED patterns would have deteriorated. However, it could not be ascertained whether the dissolution occurred at steps, defects, and/or at terraces; Pd dissolution at a terrace, without removal of the adsorbed iodine, can happen only via an iodine/palladium place-exchange mechanism.

To address fundamental issues such as the actual dissolution mechanism, tandem electrochemistry (EC) and scanning tunneling microscopy (STM) was later invoked.² The ordered adlattices studied by (medium-resolution) EC-STM were those spontaneously formed upon immersion of the Pd single-crystal surface to a dilute solution of iodide: $Pd(111)-(\sqrt{3} \times \sqrt{3})R30^\circ-I$, $Pd(100)-c(2 \times 2)-I$, and $Pd(110)$ -pseudo-hexagonal- I .³ The adsorbed-iodine-catalyzed corrosion of Pd was found to be a structure-sensitive reaction, decreasing in the order $Pd(110)-I > Pd(111)-I \geq Pd(100)-I$. *At very low dissolution*

rates, it was observed that the corrosion of $Pd(100)-I$ and $Pd(111)-I$ occurred exclusively at step edges in a layer-by-layer sequence without deterioration of the iodine adlattice structure at the terraces.

The question remains as to how the dissolution transpires at more positive potentials (i.e., at much higher reaction rates). To support the higher corrosion rates, an alternative mechanism could become operative. For example, an iodine–palladium place exchange may occur on a terrace site to expose a Pd atom and enable its dissolution. Once a pit (defect) is formed, layer-by-layer dissolution at the pit steps can then proceed; in such a scenario, the pits should become larger in width yet remain constant in depth. It is toward this possibility that the present investigation, which necessitates atomic-resolution EC-STM, has been addressed.

Experimental Section

Single-crystal surfaces of palladium were prepared by the Clavilier method.⁴ A Pd wire of 99.995% purity was melted in an oxygen-rich hydrogen flame and slowly cooled to obtain, at the end of the wire, a single-crystal bead 3 mm in diameter. Eight facets (0.2 mm in diameter), oriented in the (111) plane, and six smaller facets (0.08 mm in diameter), oriented in the (100) plane, appeared on the single-crystal bead in octahedral and hexagonal arrangements, respectively. Final treatment and/or regeneration of the clean and ordered surfaces consisted of flame annealing, slow cooling (in a stream of high-purity inert gas), and immersion in ultrapure water (to prevent environmental contamination).

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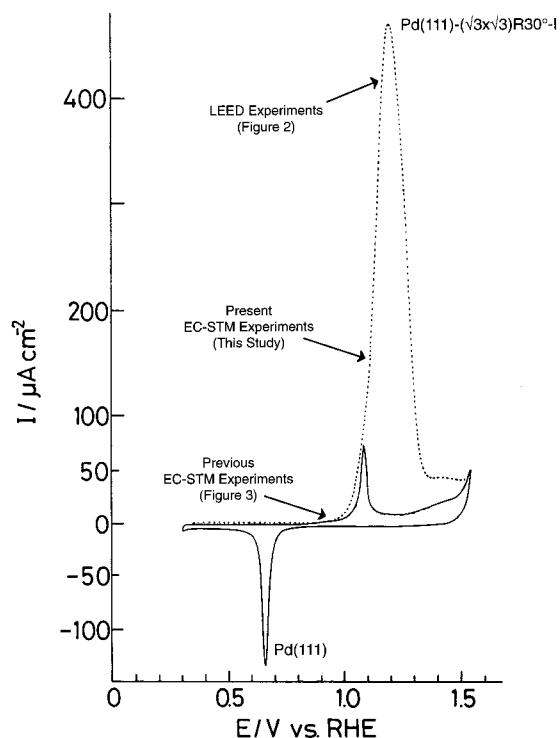


Figure 1. Current density vs potential curves in the surface-oxidation region in 0.05 M H₂SO₄ for a Pd(111) facet on a single-crystal bead, clean (solid curve) and I-coated (dashed curve). Potential sweep rate, $r = 10 \text{ mV s}^{-1}$. The arrows indicate the potentials at which the data in Figures 2 (LEED), 3 (EC-STM), and 4–6 (atomic-resolution EC-STM) were taken.

Iodine pretreatment was accomplished simply by immersion of the clean electrode, without potential control, in an aqueous 1 mM solution of iodide for 5 min. Unadsorbed iodide was removed by rinsing with pure water. All solutions were prepared from double-distilled-grade H₂SO₄ (Aldrich Chemicals, Milwaukee, WI), KI (99.99% pure; Aldrich Chemicals, Milwaukee, WI), and Milli-Q Plus water (Millipore Systems, Houston, TX). Potentials were referenced against the reversible hydrogen electrode (RHE).

In situ STM was carried out with a Nanoscope E microscope (Digital Instruments, Santa Barbara, CA) equipped with a custom-built Kel-F electrochemical cell. The tunneling tips were prepared by electrochemically etching a tungsten wire, 0.25 mm in diameter, in 1 M KOH at 15 V_{AC}; the tips thusly formed were then sealed with transparent nail polish to minimize the faradaic current. The background current of the STM tip at a potential in the double-layer region was less than 20 pA. Experimental details have been presented elsewhere.^{2,3,5}

Results and Discussion

Figure 1 shows the current–potential curve for a clean and an iodine-coated Pd(111) facet, formed on a single-crystal bead, in *halide-free* 0.05 M H₂SO₄. The exceedingly large anodic peak at about 1.2 V represents the Pd_(s)⁰-to-Pd_(aq)²⁺ anodic stripping reaction that occurs only when interfacial iodine is present. It is important to mention that, if the potential is held just below 1.2 V, the current, as expected from a material-limited dissolution process, does not decay but remains constant. Indicated in this figure are the potentials at which previous LEED¹ and EC-STM^{2,3} experiments were carried out; the latter was done only at potentials where the dissolution rate was very

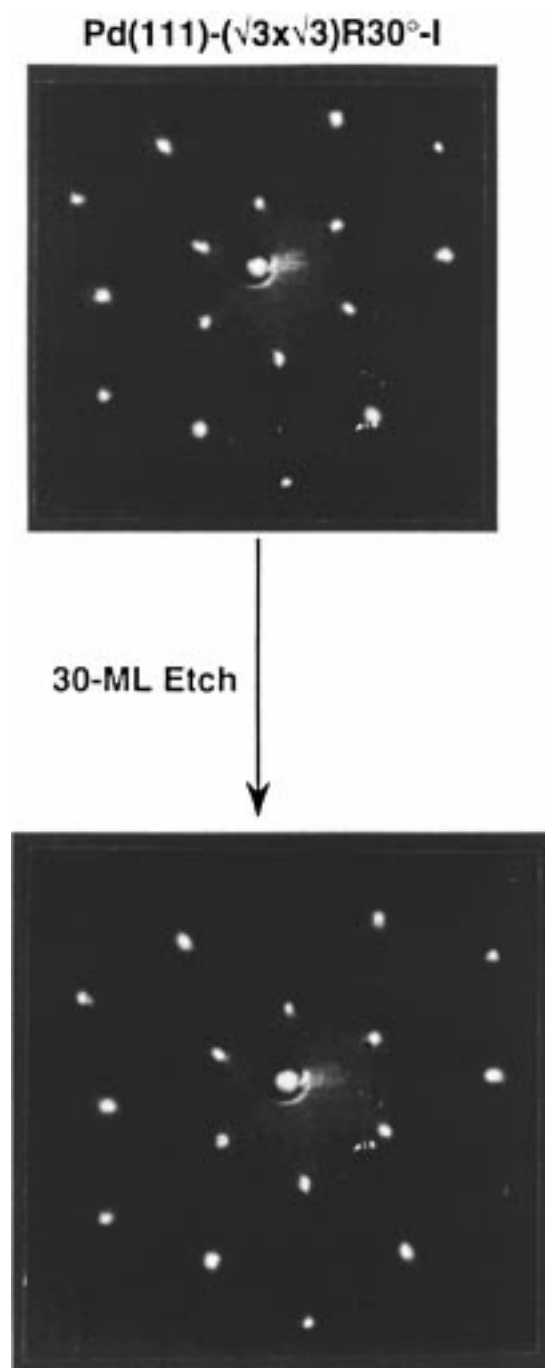


Figure 2. Low-energy electron diffraction (LEED) patterns for a Pd(111)–($\sqrt{3} \times \sqrt{3}$)R30°-I adlattice before and after anodic dissolution of approximately 30 monolayers of Pd surface atoms at the potential indicated in Figure 1.¹ The beam energy and beam current were nominally 60 eV and 2 μA , respectively.

low, whereas the LEED studies included potentials where the corrosion occurred at much higher rates.

Figure 2 shows photographs of LEED patterns for Pd(111)–($\sqrt{3} \times \sqrt{3}$)R30°-I prior to and after removal of about 30 monolayers of Pd surface atoms.² In this experiment, the potential was held close to but not past the anodic dissolution peak; that is, the corrosion was carried out at a fairly high rate. The LEED data clearly show that the postcorrosion I-coated Pd surface remained as well-ordered as it was prior to the dissolution reaction. Since only initial-state and final-state *emersed* structures are obtained, no information on the actual dissolution mechanism could be extracted from the LEED

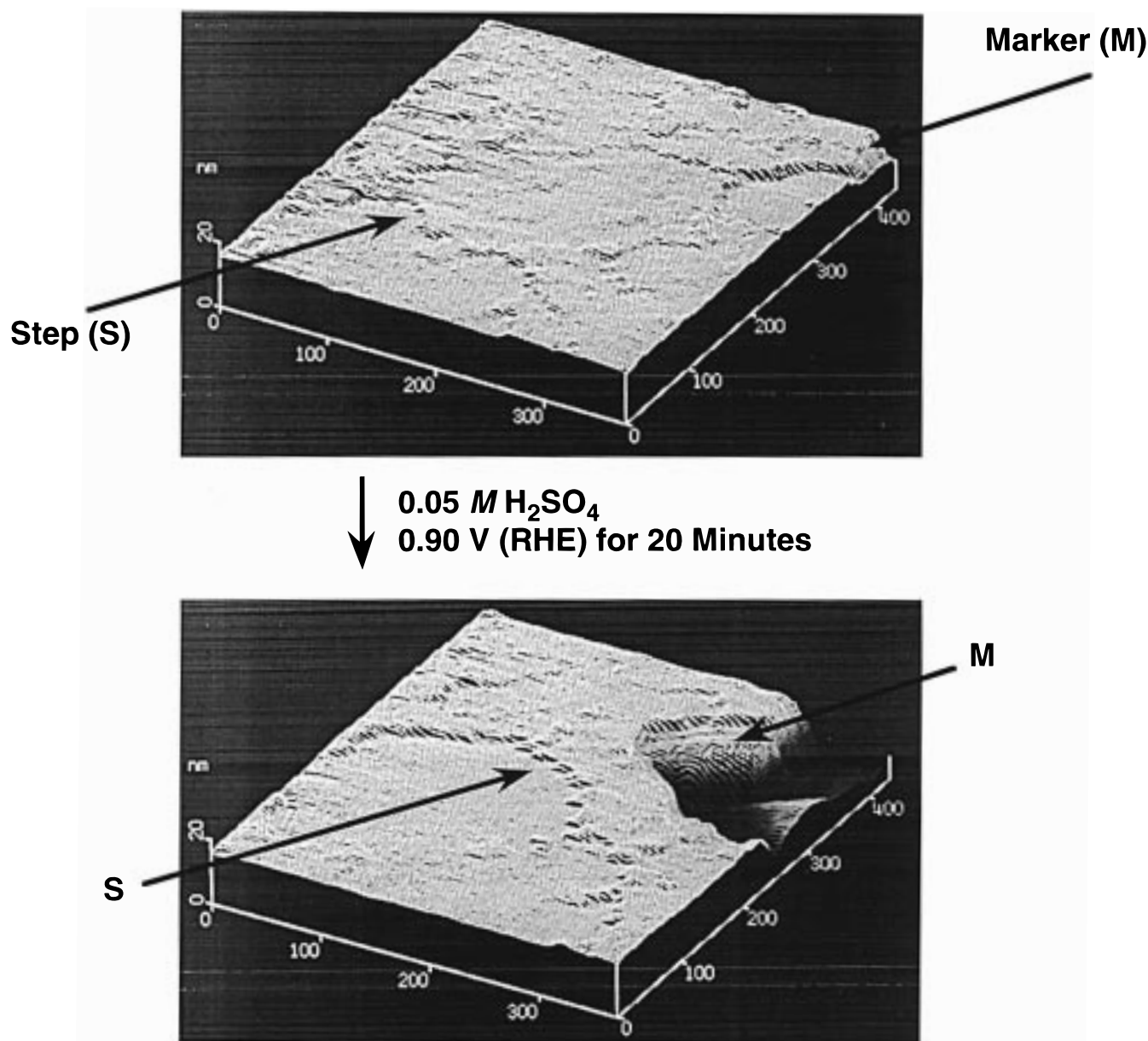


Figure 3. Wide-area electrochemical scanning tunneling microscopy images of a Pd(111)-($\sqrt{3} \times \sqrt{3}$)R30°-I facet on a single-crystal bead at two preselected stages of adsorbate-catalyzed dissolution:² M, marker; S, step. The potential of the tip was held at 0.9 V; the tunneling current was 1 nA.

measurements, although it can be argued that a layer-by-layer sequence had to occur; otherwise, the LEED patterns would have deteriorated after multilayer corrosion. For mechanistic-type information, in situ STM experiments had to be undertaken.

Figure 3 shows typical medium-resolution STM-EC images of Pd(111)-($\sqrt{3} \times \sqrt{3}$)R30°-I before and after I-catalyzed dissolution.^{2,3} The top photograph was obtained prior to dissolution; the step, monatomic and diatomic in height, that was monitored during the dissolution process is marked S. The bottom photograph was taken after 20 min of *mild* oxidative dissolution at a potential just at the foot of the anodic stripping peak. It can be seen in the latter image that (i) the step has receded toward the marker and (ii) an enlarged smooth terrace has been formed. STM images such as these^{2,3} clearly demonstrate (i) layer-by-layer dissolution and (ii) step-selective corrosion, at least under the present conditions of mild dissolution. The formation of wide-area smooth terraces is in agreement with the sharp LEED patterns such as those shown in Figure 2.

The data in Figure 3 demonstrate that step-selective dissolution is the predominant mechanism. But the question can be raised as to whether corrosion occurs exclusively at the steps or whether other reaction pathways become operative at much higher reaction rates.

The question remains as to whether dissolution occurs via the same step-selective mechanism or by other reaction pathways at much higher reaction rates. To tackle this issue, atomic-resolution EC-STM experiments were performed in which an oxidation potential was applied up to 200 mV more positive than that employed in Figure 3. The results are shown in Figures 4–6.

Figure 4 displays EC-STM images for a Pd(111) single-crystal surface, at potentials within the double-layer region, before (1×1) and after [$(\sqrt{3} \times \sqrt{3})$ R30°-I] iodine chemisorption; these images are similar to those reported previously.^{2,3} Figure 5 gives EC-STM images when the Pd(111)-($\sqrt{3} \times \sqrt{3}$)R30°-I adlattice is sequentially subjected to potentials at more positive than 0.9 V. The top image was obtained approximately 5 min after the

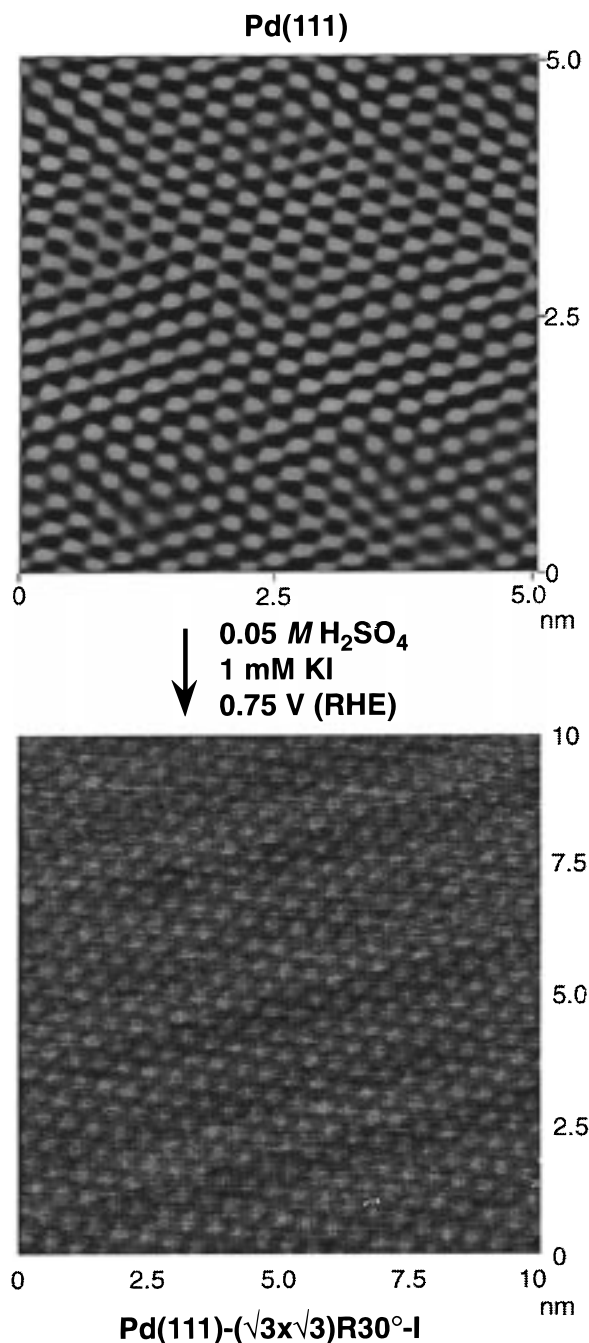


Figure 4. Atomic-resolution EC-STM images of a Pd(111) facet on a single-crystal bead before and after exposure, at a potential within the double-layer region, to dilute aqueous KI. Experimental conditions were as described in the text.

potential was poised at 1.1 V. Two important features are to be noted in this image: (i) The erstwhile smooth terrace has become strewn with small-size pits, the widths of which are equivalent to approximately 2–5 iodine atoms. (ii) The section profile of the pits indicate step heights of ca. 0.23 nm, a value indicative of a Pd-atom, *not an I-atom*, vacancy. These two features strongly suggest an iodine–palladium place-exchange process in which underlying Pd atoms are segregated to the very top of the surface to facilitate their dissolution. That most of the pits are no deeper than one Pd atomic step indicates a predominantly layer-by-layer dissolution process. It is important to mention that, for extended corrosion times, the lateral size

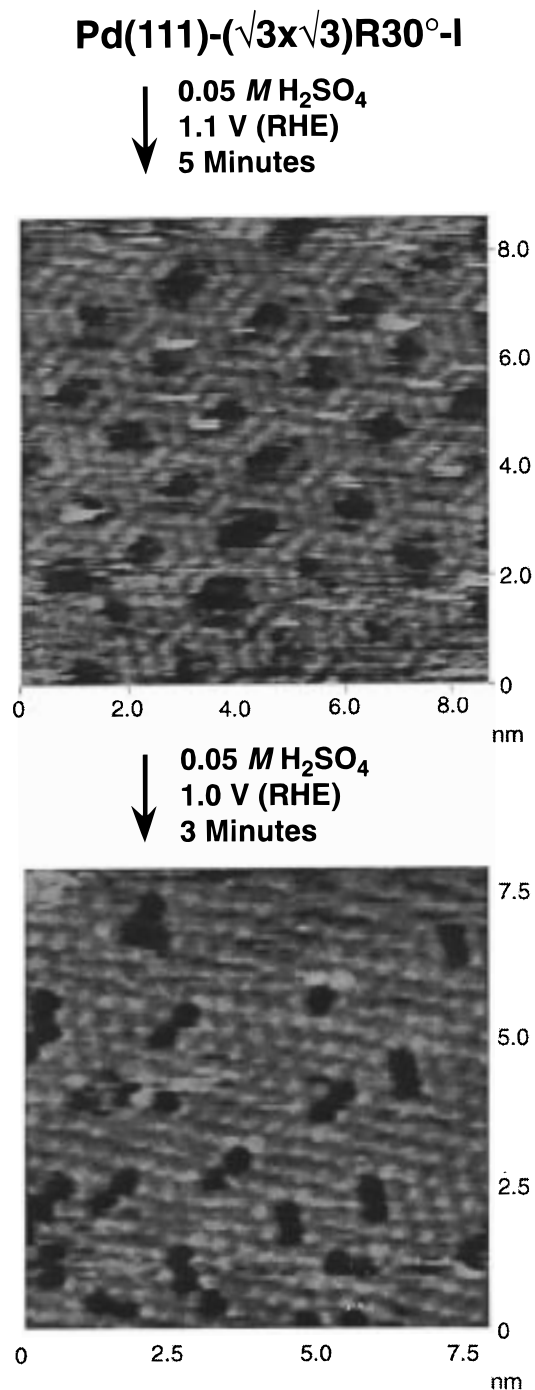


Figure 5. Atomic-resolution EC-STM images of a Pd(111)–($\sqrt{3} \times \sqrt{3}$)R30°-I facet on a single-crystal bead after (medium-rate) anodic dissolution at two different potentials. Experimental conditions were as described in the text.

of the pits become larger, but the depth remains constant. In addition, the structure of the (iodine) adlattice inside the enlarged pit is identical to that on the upper terrace, Pd(111)–($\sqrt{3} \times \sqrt{3}$)R30°-I. The emergence of this alternative dissolution mechanism is presumably necessitated by the demand for higher corrosion currents: the I/Pd place exchange exposes steps (defects) that make possible higher dissolution rates.

It is interesting to note in Figure 5 that, at 1.1 V, pit formation does not occur randomly but appears to follow a near-hexagonal pattern. The reason for such preferential I/Pd place-exchange sites is presently not understood.

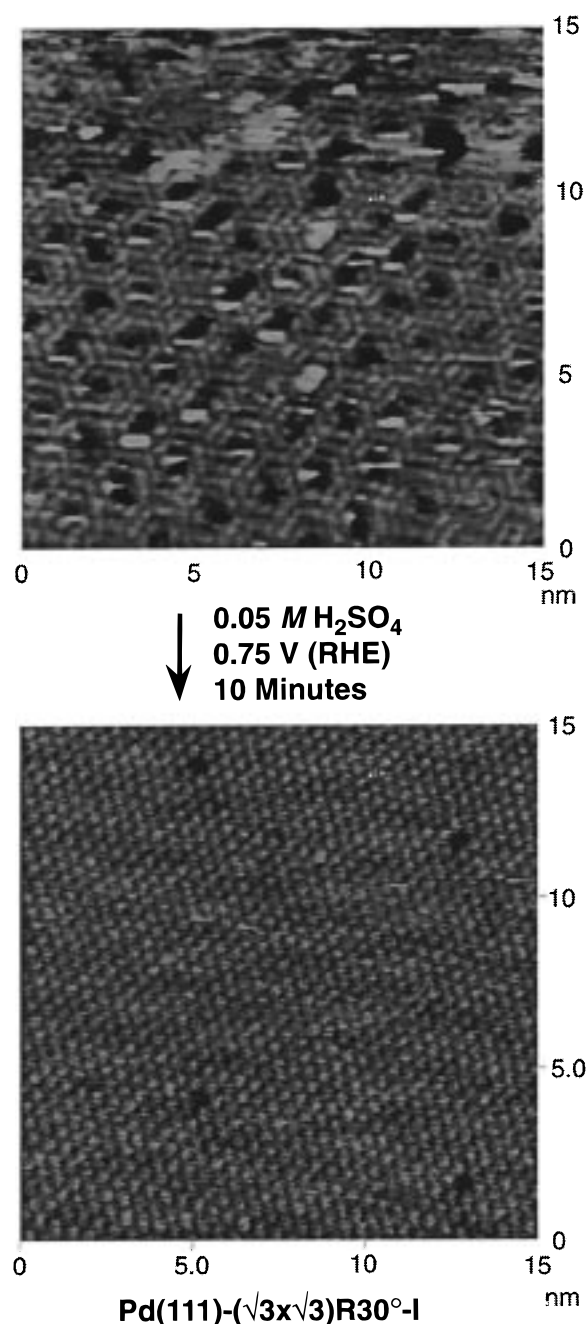


Figure 6. Atomic-resolution EC-STM images of a Pd(111)-($\sqrt{3} \times \sqrt{3}$)R30°-I facet on a mildly corroded single-crystal bead before (top) and after (bottom) restoration of double-layer-region potentials. Experimental conditions were as described in the text.

When the potential was then lowered to 1.0 V, the bottom image in Figure 5 was obtained. Two changes are conspicu-

ous: (i) the number of terrace pits have decreased, and (ii) the sizes of the pits have been diminished to the equivalent of no more than two iodine atoms. Section profile measurements of the pits continue to indicate an atomic step height characteristic of palladium, not iodine. The atomic-resolution images in Figure 5 provide evidence that the extent of I-Pd place exchange is dependent upon the applied potential (i.e., reaction rate); the incidence of place-exchange-induced monatomic pits increases as the dissolution rate (or applied potential) is increased.

Figure 6 shows high-resolution EC-STM images when the potential applied to the highly pitted (corroded) surface (top image) is lowered to values just within the double-layer region. It is most striking to note that, within a few minutes, the terraces have become virtually pit-free and reverted back to their original well-ordered Pd(111)-($\sqrt{3} \times \sqrt{3}$)R30°-I structures. Evidently, a decrease in electrode potential induces a *reverse* place-exchange process in which all embedded iodine atoms are transported back to the uppermost layer.

The structural "relaxation" toward pit-free, atomically smooth terraces upon termination of the anodic stripping reaction helps rationalize the original LEED results, namely, that highly ordered adlattices were retained even after prolonged, high-rate dissolution.¹ Apparently, the disruption of the applied oxidation potential upon emersion leads to the disorder-to-order place-exchange "relaxation". Nevertheless, a layer-by-layer dissolution sequence, even under conditions where the place-exchange mechanism is operative, is indicated by the results of the present study. This is as expected since, as soon as a pit is formed, defects are exposed that enable the kinetically favored step-selective mechanism to proliferate.

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References and Notes

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