

effective. If these interactions are not covalent, a single catalyst could pass from substrate to substrate, as in real enzymes or in the cyclodextrin systems. The use of such artificial enzymes would change the style of synthetic chemistry. Synthesis would have moved from the age of clever functional group manipulation to a new

era in which our reactions mimic both the style and the selective results of biochemistry.

I acknowledge the experimental and intellectual contributions of my co-workers, who are named in the references. This work has been supported by grants from the National Science Foundation and the National Institutes of Health.

Electrochemistry of Well-Defined Surfaces¹

ARTHUR T. HUBBARD

Department of Chemistry, University of California, Santa Barbara, Santa Barbara, California 93106

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Reflection electron diffraction and electron spectroscopy, combined with the availability of efficient commercial ultrahigh vacuum equipment, have led to dramatic progress in gas-solid surface chemistry by permitting the preparation of atomically clean, highly ordered surfaces and by providing a means of studying the structure, electronic characteristics, and chemical reactivity of these "well-defined" surfaces. In particular, low-energy electron diffraction (LEED) provides data from which surface crystallographic structure can be determined, including the structure of the first few atomic layers of the substrate and any adsorbed material which might be present. Auger electron spectroscopy yields spectral data indicative of the identity and quantity of elements present in the surface region. All elements except H and He are determinable by means of Auger spectroscopy provided that their abundance in the surface region exceeds about 1%.

Photoelectron spectroscopy is of particular usefulness in characterizing surfaces with regard to valency and other aspects of electronic structure. Thermal-desorption mass spectroscopy is a ready source of valuable clues regarding the stability and molecular constitution of adsorbed layers. A growing number of related techniques are also available with which to explore various aspects of surface behavior; these include reflection high-energy electron diffraction, electron-stimulated desorption, with the option of determining the angular distribution of desorbed ions or neutrals, secondary-ion mass spectrometry, and electronic-vibrational analysis of surface layers by electron energy loss spectroscopy (analysis of the excitation-energy dependence of the energy distribution of inelastically reflected low-energy electrons). These techniques are the subject of a number of excellent reviews.²⁻¹²

Preparation of well-defined surfaces has been overlooked by electrochemists until recently, even in studies employing electrodes made from single crystals. This

lapse is significant. Definition of surface structure is as crucial to understanding the specific chemical

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Arthur T. Hubbard is Professor of Chemistry at the University of California at Santa Barbara. Born in Alameda, CA, in 1941, he received a B.A. degree from Westmont College and a Ph.D. degree from the California Institute of Technology. After 9 years on the faculty of the University of Hawaii, he joined the University of California, Santa Barbara, in 1976. His research interests include the theory and practice of electrochemistry with applications to surface chemistry and chemical analysis.

properties of electrodes as, say, determination of the structure of benzene was to understanding the properties of aromatic compounds. Even the colligative properties of electrodes are influenced by surface structure through variation of the number density of electrode-surface atoms in contact with the electrolyte.

Surfaces prepared in ultrahigh vacuum require direct characterization by LEED and related procedures. Indeed, cleaning a surface to the required degree is an iterative procedure. It may even turn out that the clean surface prefers a structure different from the bulk crystallographic plane to which it is parallel. This careful characterization of surfaces formed or used in contact with liquids is equally imperative since such surfaces are often unpredictable. For example, experiments in which platinum single-crystal electrodes were studied without ultrahigh-vacuum cleanliness or without surface characterization before and after electrolysis¹³⁻¹⁷ illustrate the problem. On the basis of hydrogen-electrodeposition data, Will¹⁵ concluded tentatively that electrolytic oxidation-reduction in 1 M H₂SO₄ converts a Pt surface having Miller indices (111) to Pt(110), whereas the authors of ref 16 concluded oppositely that (110) forms (111) facets, while Ross¹³ asserted that hydrogen atoms are not adsorbed on Pt(111), and Conway¹⁷ surmised that all crystal faces behaved similarly. Will's experiments were as sophisticated as possible without direct surface-structure investigation and display the correct trends, although not decisively. The situation for platinum is typical of that for other elements in the absence of direct characterization of the surface (about 400 papers); the correct trends are absent or masked by fluctuations and contradictions. The formation, direct surface-structural characterization, and use of well-defined electrode surfaces is an objective way of proceeding.

Electrode-Surface Characterization and Electrolysis

Use of well-defined surfaces as electrodes has begun to yield electrochemical information of a valuable new type in which the role of substrate and adsorbed-layer structure can be clearly seen. The general goals of this work, combining ultrahigh-vacuum practices with clean electrochemical techniques, were outlined in a 1973

review of thin-layer electrochemistry¹⁸ and subsequent work has brought them into focus.¹⁹

Well-defined surfaces for use as electrodes can be prepared by orienting a single crystal with X-ray reflection photography,²⁰ polishing the crystal,²¹ and cleaning it in ultrahigh vacuum. Alternatively the electrode can be produced by epitaxial deposition on a support.²² Sample preparation is followed by direct characterization of surface structure and composition by means of the electron techniques.²⁻¹² For example, platinum single-crystal electrodes are cleaned in ultrahigh vacuum by ion bombardment with Ar⁺ ions at 1000 °C, so as to remove bulk impurities as well as surface contaminants. Surface disorder produced by ion bombardment is repaired by annealing processes occurring at the elevated temperature. The particular crystallographic structure displayed by a surface and the degree of perfection achieved are complicated and sensitive functions of many experimental variables.³ Surface-structure verification by means of LEED is an absolute necessity if the surface is to be considered well-defined. The motivation for this careful approach to electrode-surface preparation is the discovery that surface structure exerts multiple influences upon electrode behavior which cannot be ignored in fundamental studies. The valuable information concerning composition, electronic properties, and chemical reactivity of the surface region, obtained by means of the various electron techniques whose use accompanies LEED, provides further motivation.

It is also necessary to characterize the surface during exposure to solvent vapor. Restructuring of the surface and adsorbed layer occurring as a result of exposure to solvent vapor is readily observed, as are changes in the stoichiometric composition of the adsorbed layer.^{19g} Formation of ordered solvent layer structures (superlattices) at specific coverages is a common occurrence. Transitions from one superlattice structure to another may be observed as a function of coverage or temperature. Electrolytic solvents, being polar liquids, have the undesirable tendency to accumulate on the inside surfaces of the vacuum system. Accordingly, it is preferable that solvent vapor be introduced locally onto the electrode surface through a small (1 mm) nozzle at minimal flow rates (equivalent to 10⁻⁹ to 10⁻³ torr) regulated by a variable leak valve. Part of the interest in the products formed from solvent vapor and the electrode stems from the fact that they are natural precursors of the layer resulting from immersion of electrodes in solution, the compact layer. After all, exposure to vapor inevitably precedes immersion into liquid.

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Study of HCl and other hydrogen halides, carboxylic acids, nitrogenous bases, and related compounds frequently present in electrolytes is a step toward understanding the compact-layer region of the solid-liquid interface. Changes in structure, composition, or valency may accompany adsorption of solvent or solute. Reactions between solvent and solute may occur, perhaps with catalytic assistance from the electrode. Incidentally, once formed on a surface, an adsorbed solvent or solute layer tends to inhibit or totally prevent the adsorption of other species and in so doing facilitates transfer of the electrode, in uncontaminated form, into liquid electrolyte consisting of those same compounds. Stable ionic salts such as NaCl can be studied in ultrahigh vacuum (UHV) by the simple expedient of vaporization onto the surface from a heated ampule.²³

A variety of electrochemical studies of well-defined surfaces in liquid electrolytes can be performed. These include electrodeposition of hydrogen, halides, oxides, sulfides, hydrocarbons, and metals, electrode reactions of adsorbed superlattices, influence of a superlattice on the electrochemical kinetics of a dissolved species, reactions in which the electrode serves as a catalyst, and numerous others.

Studies characterizing the surface following electrolysis are also important. In particular, changes in substrate or superlattice structure resulting from exposure to liquids at open circuit or electrolysis and the structure and composition of adsorbed layers and electrodeposits are a type of fundamental electrochemical information of which there is a total lack. Some patience is necessitated by the fact that LEED patterns exhibiting discernible spots due to adsorbed material are obtained only if the adsorbed amount is exactly that required for formation of a specific superlattice; diffuse patterns will usually be observed at intermediate coverages, even when appreciable short-range order is present in the actual structure.

An intriguing aspect of electrochemical studies of well-defined surfaces is the question of how the surface properties observed in UHV compare with those existing under electrochemical conditions. (The same question might be asked regarding gas-solid surface studies at pressures above the UHV range.) The answer to this question must come from more than one type of experiment, preferably from a series of complementary experiments in which surface structure and related properties are directly determined (and thus known with certainty) before and after electrolysis.

Experimental Aspects

Electrochemical characterization of well-defined surfaces includes the following essential steps: surface characterization in ultrahigh vacuum by means of LEED, Auger spectroscopy, photoelectron spectroscopy and thermal desorption mass spectroscopy; introduction of an inert atmosphere and filling of the cell with liquid electrolyte; electroanalytical characterization of the surface; reevacuation; and recharacterization of the electrode surface and electrodeposited layers in ultrahigh vacuum by LEED and related techniques. Combined electrochemistry and electron techniques, when applied to studies of the electrode surface, require the use of an ultrahigh-vacuum system interconnecting

to an electrochemical-cell apparatus through a suitable vacuum interlock. The essential feature of the ultrahigh-vacuum apparatus is the absence of components which would leak or vaporize to a degree detectable at 10^{-10} torr (for instance, moving seals, porous materials, fluids, and most plastics). The apparatus must be baked to dislodge adsorbed gases from interior surfaces. Compatibility with electron- and ion-emitting devices dictates the use of materials which can withstand the powerful "redox" action of energetic charged particles and prompts elimination or careful placement of magnetic and insulating materials to prevent them from influencing particle trajectories. Valuable general descriptions of ultrahigh-vacuum theory and practice will be found in ref 6, but several points should be emphasized in the present context: Partial pressures of surface-active residual gases must be kept within ultrahigh-vacuum limits throughout the experiment, in the atmospheric as well as spectroscopic experiments, by selective gettering of reactive gases. Frequent use of corrosive reagents dictates that the conventional copper gaskets be gold plated²⁴ to prevent disruptive interior contamination by copper-corrosion products. A sample-isolating vacuum interlock should be provided to isolate the electron optics from the electrode during the electrochemical procedures. "Triode" pumps which operate by ionization of residual gases are an excellent means of maintaining ultrahigh vacuum in a system which is operated under normal loads. However, cryogenic pumping is preferable immediately following electrolysis when the gas load is high and electrode contamination by plasmas or reactive fragments from ionization pumping could be severe. The entire electrode surface should be oriented,²⁰ polished,²¹ and characterized in order that all faces will be crystallographically equivalent and thus immersible; surface contamination of electrodes sealed into glass or plastic is always a likely possibility.

Electrochemical characterization of surfaces should utilize the essential features of modern electroanalytical methodology: "potentiostatic" circuits which can automatically record the potential of the couple formed by the single-crystal electrode and a reference-electrode half-cell (such as AgCl/Ag/KCl) and control this potential by applying current between the single-crystal electrode and an inert auxiliary electrode.²⁵ (Mixing of the fluid environment of the single-crystal electrode with that of the other two electrodes is prevented by suitable barriers which minimize accidental contamination.) The observed variation of current with potential resulting from application of a potential varying linearly with time (cyclic voltammetry) contains a peak for each electrochemical couple present in the system. Peak height and position are descriptive of electrode reaction rate and energy; the voltammetric curve is an "electrochemical spectrum", locating and defining interfacial charge-transfer processes. Ultra-pure water (preferably less than 10^{-6} M of surface-active impurities)²⁶ and high-purity electrolytes are vital to obtaining reproducible and interpretable results. Air should be

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removed and excluded from the solutions. Electrolytic cells constructed of glass are usually satisfactory and Teflon does not noticeably contaminate the atmosphere above the solution.

In general, the sensitivities with which electroanalytical and electron-spectroscopic techniques detect surface impurities are comparable. Also, the abilities of the two classes of techniques to remove and exclude *unintentional* impurities are comparable. In fact, the electrochemical procedures may hold somewhat of an advantage in this category in spite of being rather simple, inexpensive, and old. However, the electrolytic solution and various compounds which it forms with the electrode must be tolerated as *intentional* contaminants of electrode surfaces cleaned by electrolysis. That is, the absolute surface cleanliness which facilitates preparation of well-defined surfaces in ultrahigh vacuum is not possible in electrolysis. Accordingly, correlation between single-crystal-electrode orientation and electrochemical reactivity is neither observed nor expected without surface preparation and characterization in ultrahigh vacuum.

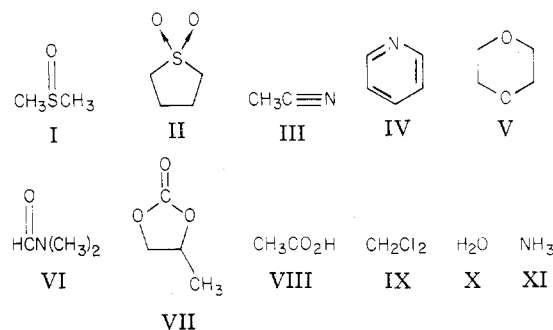
Electrochemical techniques offer a number of unique capabilities for the study of surfaces after preparation in ultrahigh vacuum. These include precise correlation of redox reaction rate (current) with interfacial potential difference (electrode potential), sensitive and quantitative determination of adsorbed species, and preparation of special surface structures or coatings by electrodeposition or electrocrystallization.²⁷ Electrochemical theory is usefully applicable to a wide range of interfacial and surface chemical problems, including thermodynamic²⁸ as well as kinetic²⁹ aspects. Related aspects such as interfacial mass transfer³⁰ and coupling of bulk-phase chemical reactions to electrochemical reactions³¹ are also nicely treated. Interfacial charge attracts, to the electrode, reactants of opposing electrostatic charge, favoring the reactions of these materials. The charge density can be usefully altered by attaching ionic species to the surface by means of hydrocarbon chains having a suitable combination of anchoring and ionizable substituents.³² Acid-base and metal-ion complexing behavior can likewise be utilized.³³ Determination of metal-surface properties is facilitated by the use of a "thin-layer electrode" in which the electrolytic solution is confined to a thin (10^{-3} cm) compartment surrounding the electrode.^{18,34} Be-

cause the volume of the thin-layer compartment is very small, the contribution of surface processes to the total charge required for the electrolysis is comparatively large, and contamination of the surface by trace impurities of the solution is controllable. The thinness of the solution layer also permits mass-transfer equilibrium to be closely approached, so that complications related to diffusion are avoided.

Results Obtained with Well-defined Platinum Surfaces

Recent LEED-EC studies of well-defined electrode surfaces have concentrated on Pt, although the techniques are broadly applicable.

1. Electrolytic Solvents. The interaction of well-defined platinum surfaces with the vapor of a variety of typical solvent materials (I–XI) was investigated by



low-energy electron diffraction, Auger spectroscopy, and thermal-desorption mass spectroscopy. The basal (hexagonal) plane, Pt(111), was employed for these initial studies since facets of this stable orientation constitute a major portion of the surface area of practical platinum electrodes. Interfacial concentration (coverage) was measured by AES.^{19c} The compounds are listed in order of decreasing coverage at comparable exposure. Compounds I–VIII were strongly adsorbed from vacuum. Compounds IX–XI were not adsorbed to an appreciable extent (less than 10^{-2} molecule per surface Pt atom) at nozzle-beam dosages equivalent to a pressure of 10^{-3} torr. On the basis of AES data, the adsorbed materials possessed the same stoichiometries as the free molecules. That is, any molecular rearrangement which might have accompanied adsorption did not result in a loss of material into the vacuum. Compounds I–IV (as neat liquids and dilute aqueous solutions) reacted with polycrystalline Pt to produce strongly adsorbed layers able to interfere with the electrolysis of dissolved reactants.³⁵ Compounds V–IX and XI were not chemisorbed appreciably from aqueous solution and did not interfere with electrolysis, in keeping with their lesser affinity for Pt surfaces in UHV.

LEED patterns obtained for Pt(111) surfaces after exposure in UHV to compounds I–VIII revealed a surprising trend: Each of these compounds produced a sharply defined Pt(111)[2×2] structure at a coverage of one solvent molecule per four surface Pt atoms ($\theta = 0.25$) (Figure 1). (Surface crystallographic nomenclature is discussed in ref 36.) For example, Pt(111)[2×2]-sulfolane denotes an adsorbed layer structure whose two-dimensional unit-cell vectors are twice those of the

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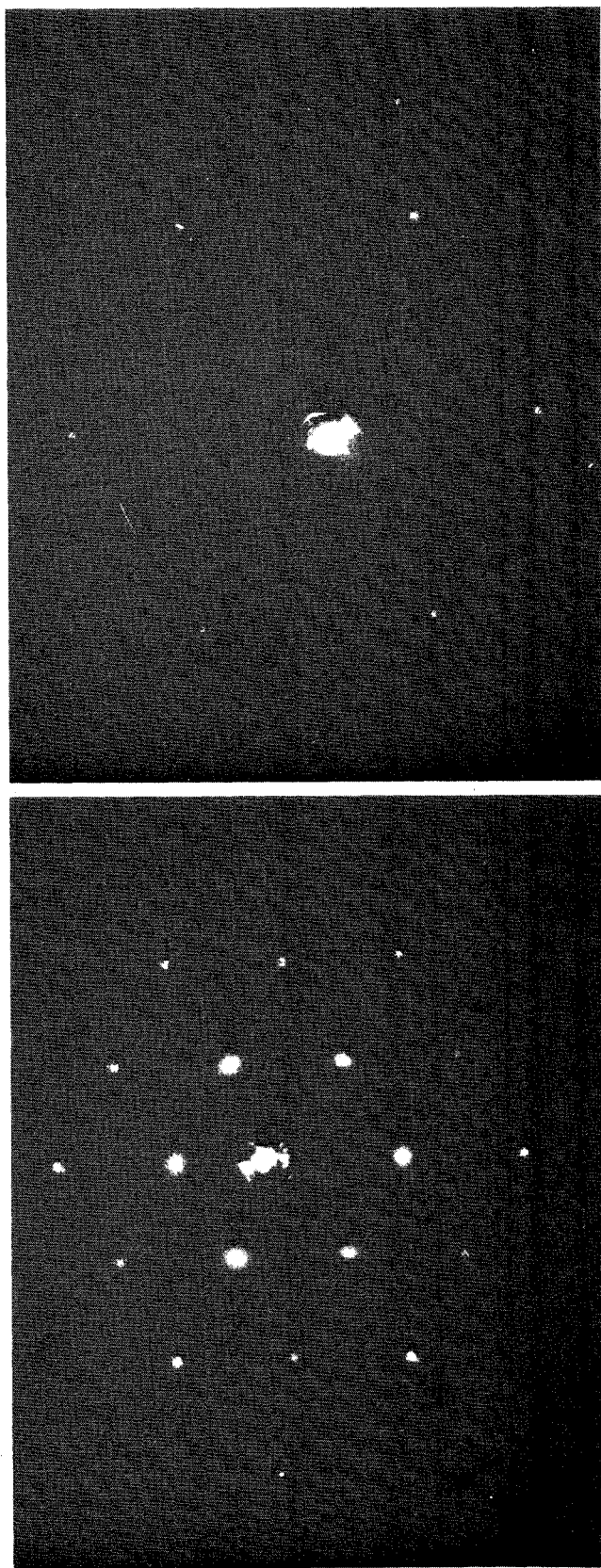


Figure 1. LEED patterns of Pt(111)-sulfolane. (A, upper) Clean Pt(111) surface; (B, lower) Pt(111)[2×2]-C₄H₈SO₂. Experimental conditions: clean Pt(111) surface in UHV was exposed at room temperature to nozzle beam of sulfolane, C₄H₈SO₂, equivalent to a pressure of 10^{-8} torr; incident-beam energy 60 eV; current 0.33 μ A.

ideal Pt(111) crystallographic plane but have the same direction. Rotation of the unit-cell vectors of the adsorbed layer with respect to those of the substrate is indicated by the letter R and the angle of rotation; for example, Pt(111)[$\sqrt{3} \times \sqrt{3}$]R30°. Sulfolane (II) displayed a Pt(111)[$\sqrt{3} \times \sqrt{3}$]R30° pattern at $\theta = 0.33$ and a Pt(111)[1×1] pattern at $\theta = 1.0$. Dimethyl sulfoxide (I) also gave a Pt(111) pattern at $\theta = 1$. The remaining compounds proceeded from $\theta = 0.25$ to coverages as high as $\theta = 0.55$ without producing other definitive patterns at room temperature. Heating of the adsorbed layer in each case produced a series of transitions in structure and composition, leading eventually to a refractory layer which persisted at red heat.^{19g} From these results we learn that polar solvents tend to form an ordered first layer, a superlattice, in response to the structure of the electrode surface. Solvents adsorbed on the hexagonal (rhombic) Pt(111) surface are arranged hexagonally, in registry with the substrate. The size of the superlattice unit cell decreases as coverage increases, reaching an apparent limit of one solvent molecule per surface platinum atom.

2. Calibration of Auger Electron Spectroscopy.

Quantitative electrochemical analysis of adsorbed material has been utilized to calibrate Auger spectroscopy for adsorbed layers.^{19c} This involved comparison of the current of emitted Auger electrons with coverage determined by thin-layer coulometry. Compounds having one substituent capable of anchoring the molecule to the surface by adsorption (the carbon double bond) and a second substituent containing additional elements whose Auger emission was to be calibrated, such as allylamine (CH₂=CHCH₂NH₂), were employed. Exposure of the electrode to the hydrocarbon vapor and detection of the Auger electron current were followed by measurement of the charge required for electrochemical oxidation of the hydrocarbon layer. It was assumed that the elemental compositions of the hydrocarbon materials employed were not altered by adsorption. This assumption is supported by electrochemical studies which indicate that these hydrocarbons retain their functional integrity (such as acid-base, redox, or chelating behavior) after adsorption.^{32,33} Calibration data demonstrate that the Auger electron current from a chemisorbed layer is governed in a simple way by the abundance of each element (atoms/cm²) and by the ionization cross section of the initially ionized level. The energy of emitted electrons varies noticeably with chemical factors but the yield does not. This calibration applies generally to the technique and not merely to one spectrometer. Accordingly, the elemental composition of an adsorbed layer can be determined in any laboratory equipped with a conventional Auger spectrometer by applying these results.

3. Iodine and Hydrogen Iodide.

I₂ and HI each interact with Pt(100) and Pt(111) in UHV to form an interesting series of LEED patterns and structures (Figures 2 and 3). In spite of the square arrangement of Pt atoms in the Pt(100) plane, the iodine superlattices formed on that surface are nearly hexagonal (rhombic), with only slight distortion.^{19e,f} Quantitative AES corroborated the iodine-atom abundances inferred from the structures. Mass spectra demonstrated that thermal desorption produces predominantly I atoms. Identical structures were observed with I₂ and HI, ex-

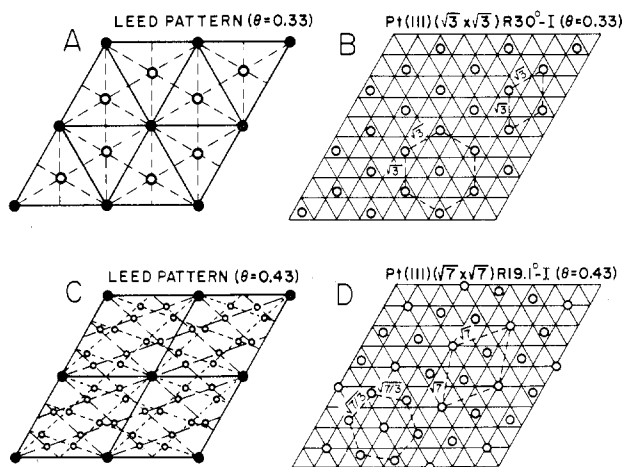
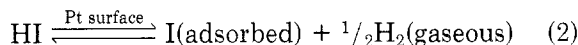
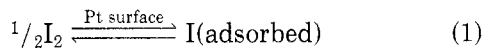


Figure 2. LEED patterns and I atom structures formed by exposure of Pt(111) to HI. (A) LEED pattern, $\theta = 0.33$; (B) structure Pt(111)[$\sqrt{3} \times \sqrt{3}$]R30° - I, $\theta = 0.33$; (C) LEED pattern, $\theta = 0.43$; (D) structure Pt(111)[$\sqrt{7} \times \sqrt{7}$]R19.1° - I, $\theta = 0.43$. LEED patterns: (O) fractional-index spots. Structures: (O) I atoms; intersections of solid lines, Pt atoms.

cept for the Pt(100) surface at coverages above $\theta = 0.50$, for which disordered LEED patterns were obtained and thermal desorption produced HI or I. Evidently, adsorption of I₂ and HI is dissociative up to $\theta = 0.50$ (eq 1 and 2). No previous studies of halogens or hydrogen



halides on well-defined Pt surfaces have appeared. Studies of halogens (X₂) on well-defined surfaces of Ag, Cu, Ni, and W, however, have revealed a propensity for the M(111)[$\sqrt{3} \times \sqrt{3}$]R30° - X structure at $\theta = 0.33$; structures formed at other coverages are more varied.³⁷

Exposure of the Pt(100)[$c(\sqrt{2} \times 2\sqrt{2})$]R45° - I and Pt(111)[$\sqrt{7} \times \sqrt{7}$]R19.1° - I superlattices to an H₂O vapor beam equivalent to 10⁻³ torr for prolonged periods produced no change in LEED patterns or Auger spectra. Slight desorption occurred during prolonged soaking in liquid H₂O at open circuit. This considerable durability of Pt-I superlattices facilitated observation of their electrochemical reactivity^{19e} by means of the following experiments: Voltammetric current-potential curves for the oxidation (in perchloric acid electrolyte) of adsorbed I atoms to dissolved IO₃⁻³⁸ appear in Figure 4. The Pt(111)[$\sqrt{7} \times \sqrt{7}$]R19.1° - I structure shown in Figure 2 yielded a single peak, C. The Pt(100)[$c(\sqrt{2} \times 2\sqrt{2})$]R45° - I structure (Figure 3) produced a pair of peaks at more positive potentials, A. Whether the doublet is due to sequential oxidation of the Pt(100)-[$c(\sqrt{2} \times 2\sqrt{2})$]R45° - I and Pt(100)[$c(2 \times 4)$] - I structures (Figure 3) or to other causes is a question presently under study. Since electrooxidation removes I atoms from the surface by dispersing them in the solution (in the form of IO₃⁻ ions), later voltammetric curves are simply those characteristic of well-defined

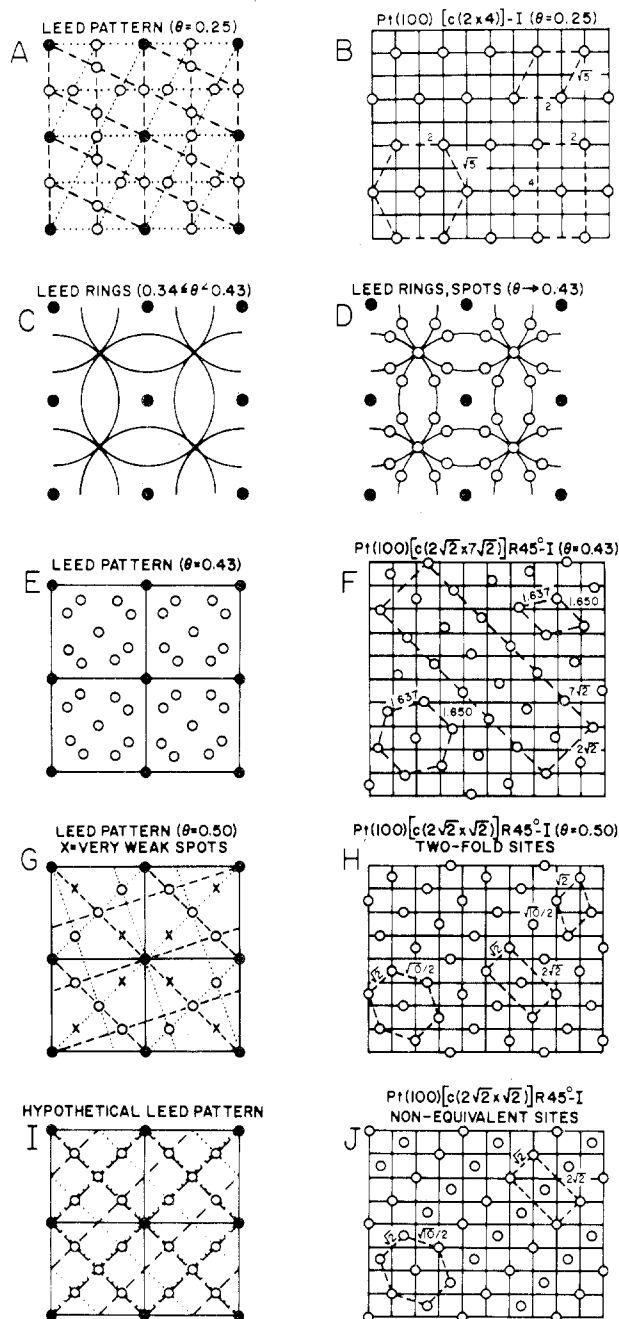


Figure 3. LEED patterns and I atom structures formed by exposure of Pt(100) to HI. (A) LEED pattern, $\theta = 0.25$; (B) structure Pt(100)[$c(2 \times 4)$] - I, $\theta = 0.25$; (C) LEED rings, $0.34 \leq \theta < 0.43$; (D) LEED rings, with spots, θ approaching 0.43; (E) LEED pattern, $\theta = 0.43$; (F) structure Pt(100)[$c(2\sqrt{2} \times 7\sqrt{2})$]R45° - I, $\theta = 0.43$; (G) LEED pattern, $\theta = 0.50$, X = very weak spots; (H) structure Pt(100)[$c(2\sqrt{2} \times 2\sqrt{2})$]R45° - I, $\theta = 0.50$, I atoms in twofold sites; (I) LEED pattern expected from twofold structure shown in figure 3J; (J) structure Pt(100)[$c(2\sqrt{2} \times 2\sqrt{2})$]R45° - I, I atoms in nonequivalent sites. LEED patterns: (O) fractional-index spots. Structures: (O) I atoms; intersections of solid lines, Pt atoms.

Pt(100)[1×1] and Pt(111) surfaces. The adsorbed material formed by treating the Pt(100) and Pt(111) electrodes with a saturated aqueous I₂ solution contained coverages slightly greater than $\theta = 0.5$, based upon I atoms, gave no fractional-index LEED spots characteristic of ordered adsorbed layers, and yielded a single voltammetric peak at potentials intermediate to those for the superlattices (Figure 4B and 4D). Structural characterization, in UHV, of adsorbed layers

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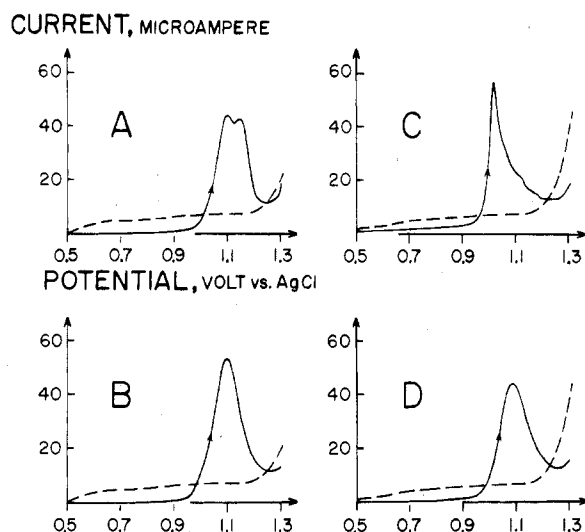


Figure 4. Linear potential scan voltammetry of iodine adsorbed on Pt(100) and Pt(111). (—) Iodine overlayer; (---) clean surface. (A) Pt(100) - I maximum coverage; (B) Pt(100) surface after treatment with saturated aqueous iodine solution; (C) Pt(111)[$\sqrt{7} \times \sqrt{7}$]R19.1° - I ; (D) Pt(111) surface after treatment with saturated aqueous iodine solution. Experimental conditions: electrode area of Pt(100) = 0.536 cm², Pt(111) = 0.453 cm²; rate of potential scan 10 mV/s; supporting electrolyte 1 M HClO₄; temperature 23 ± 1 °C; the surfaces were cleaned by alternate oxidation (1.2 V NaCE) and reduction (0 V) in 1 M HClO₄, immersed in 1 M HClO₄ saturated with I₂ under nitrogen, and rinsed prior to recording curves B and D in 1 M HClO₄.

formed from solution, is in progress. These results illustrate once again the substantial dependence of electrochemical reactivity of adsorbed material upon substrate and adsorbed-layer structure.

4. Electrodeposition of Atomic Hydrogen. When exposed to liquid water, the complex structure characteristic of clean Pt(100) undergoes structural rearrangement to form the [1 × 1] structure corresponding to the ideal (100) plane of platinum.^{19b} The (1 × 1) structure of clean Pt(111) persists when Pt(111) electrodes are immersed in water. The immersed (1 × 1) structures withstood the 10 or more cycles of electrolytic oxidation and reduction applied to them.^{19d} Such durability permitted their study in liquid electrolytes, as follows: Reduction of H⁺ to adsorbed hydrogen in aqueous acid occurs at distinctly different potentials on well-defined Pt(100) and Pt(111) electrodes.^{19d} That is, reversible electrodeposition and dissolution of hydrogen, eq 3, is sensitive to metal-surface structure.



Evidently, the standard potential, E° , eq 4, and/or the

$$E = E^\circ + \frac{RT}{F} \ln \frac{a_{\text{H}^+}}{a_{\text{H}_{\text{ads}}}} \quad (4)$$

activity coefficient for adsorbed H atoms are different for the Pt(100) and Pt(111) planes (Figure 5). The unexpectedly large variations in the widths of voltammetric peaks for H-atom deposition suggest that there is strong coupling between the adsorbed atoms. Additional small peaks appearing in the voltammetric curves are due, perhaps, to deposition of hydrogen preferentially at structural faults of the Pt surfaces. Polycrystalline Pt electrodes pretreated conventionally (by electrochemical oxidation and reduction in 1 M HClO₄ or H₂SO₄) behave, toward deposition of hydro-

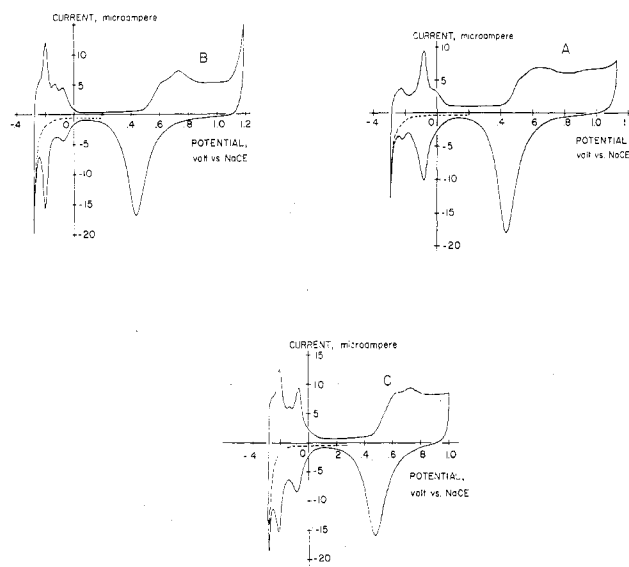


Figure 5. Cyclic current-potential curves for Pt electrodes in 1 M H₂SO₄. (A) Pt(100) rectangular solid single crystal; (B) Pt(111) parallelepiped single crystal; (C) Polycrystalline Pt electrode. Experimental conditions: sweep rate 10 mV s⁻¹; solution temperature 23 °C; electrode area (A) 0.622, (B) 0.579, (C) 0.800 cm². (Reprinted with permission from ref 15d. Copyright 1965, Elsevier Sequoia S.A., Lausanne.)

gen, as a 0.55:0.45 mixture of Pt(111) and (100) planes. Accordingly, results obtained with well-defined Pt surfaces are descriptive of practical electrode performance at individual facets of conventionally prepared surfaces. Incidentally, such voltammetric curves may prove to be a convenient, non-UHV test of surface orientation. LEED-EC studies have been described by Ross¹³ and O'Grady, Hagans, Woo, and Yeager,¹⁴ who have described some H-deposition experiments.

Conclusions and Prospects for the Future

Studies of well-defined electrode surfaces are at a very early stage and the prospects are more numerous than the conclusions. Nevertheless, the experiments performed recently with platinum electrodes have yielded significant results and, of course, a type of information not previously available for electrodes. Detailed results will certainly vary with electrode material, but the following generalizations are appropriate: When an electrochemical reactant is initially present in an ordered adsorbed layer (superlattice), its reaction rate parameters will depend significantly upon the structure of the superlattice. Energies of electrode reactions at equilibrium vary substantially with electrode-surface crystallographic structure when at least one of the participating species is present in an adsorbed state. Adsorbed amounts are influenced by electrode-surface structure and accordingly the electrical double layer is surface-structure dependent. Polar solvents tend to adsorb strongly on electrode surfaces; the adsorbed material is present in superlattice form at certain coverages (including saturation coverage in some instances). Well-defined surfaces display, in favorable cases, sufficient durability to permit their use in solution, including electrolysis. Conventionally pretreated polycrystalline platinum electrode surfaces consist of mixtures of (111) and (100) planes and fault structures characteristic of those planes; similar results are expected for other noble metals, but the behavior of

well-defined non-noble-metal surfaces as electrodes is unknown at present.

Analytical applications of electrodes to messy systems, for instance in brain research,³⁹ require electrodes which are easy to prepare or refurbish, but development of such electrodes is a continuing process in which surface characterization permits direct objective diagnosis of problems as they arise. It is surprising that electrochemists and others studying photoactive electrodes of potential usefulness in solar-energy devices have not reported systematic studies of the spectroscopic properties of their electrodes. Industrial applications of electrolysis are numerous;⁴⁰ while many of

these processes operate under mass-transfer-limited conditions in which the surface is ignored so long as it conducts, the remainder are surface sensitive. Electrocatalysts, fuel cells, electrosynthetic reactions, and materials processes (e.g., corrosion, embrittlement) are in this latter category. Elemental assay of the surface is now routine. Simple experiments such as work-function measurement²⁷ provide clear evidence for such otherwise elusive phenomena as chemisorption at surface faults.⁴¹ Reactivity of the surface and adsorbed material toward light, heat, ionizing radiation, and chemicals is readily monitored. In brief, the future holds a gold mine in store for the well-defined electrode, of which classical techniques have only scratched the surface.

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