

Electrochemical Study of Multiple-State Adsorption in Monolayers

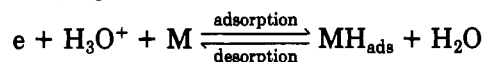
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In recent years, striking advances have been made in the surface chemistry of metals with the development of the "new spectroscopies".¹ Most of these methods are applicable only to the gas (vacuum)/metal interface. In parallel with these advances, various electrochemical methods have been developed for the study of the thermodynamic states and kinetic behavior of chemisorbed species at metal/solution interfaces. In sensitivity and resolution they are competitive with gas/solid methods but apply to radically different conditions. One of the striking features of the behavior observed is the deposition of a variety of species into multiple states of adsorption below the limit of full coverage by a monolayer. It is the purpose of this article to outline the basis and significance of electrochemical surface studies of this kind since they are rarely referred to in the usual literature of surface science.

In electrochemical studies on chemisorbed species, the monolayer is usually formed or desorbed in a Faradaic charge-transfer process involving ions or molecules in solution, e.g., for H at a metal M,^{2,3}



Such a process, in an electrochemical experiment, is controlled by means of the direction of an impressed transient current⁴ or by the direction of change of a controlled potential. Alternatively, as in chemisorption from the gas phase, adsorbed species at electrodes may arise from the solution by dissociative chemisorption of a solute, e.g., H₂, C₂H₄, HCOOH, CH₃OH.⁵⁻⁷ The chemisorbed species is then studied electrochemically by evaluation of the charge required to oxidatively desorb it⁴ or by electrochemical measurement of the sites for H adsorption that are blocked by it.

The species that can be electrochemically deposited in monolayers are often⁸ intermediates in the formation of the corresponding bulk substance, e.g., adsorbed H in H₂ evolution,^{2,3} OH or O species in O₂ or bulk oxide formation, and metal atom monolayers prior to electrocrystallization of bulk metal. The deposition of atoms or radicals over a range of potentials different from the thermodynamic potential for formation of the

corresponding bulk substance has been called "underpotential" deposition—"upd". It arises when atoms electrodeposited in a monolayer at an electrode substrate surface interact with that surface with a (free) energy numerically larger than that between the atoms themselves of the substance in its bulk state.

While Frumkin and Slygin⁹ were the earliest to characterize behavior of this type, with H and oxygen species at Pt, many examples are now known.¹⁰⁻¹⁷ One of the main characteristic features of "underpotential" deposition processes is the observation that formation of (or desorption from) the monolayer occurs in a number of usually easily resolvable stages over a potential range characteristic of both the adsorbate and the adsorbent (e.g., 0.35 V for H on Pt, 0.7 V for Pb on Au). Also the deposition and desorption directions of the surface process are often reversible^{18,19} except if surface reconstruction or alloy formation occurs.

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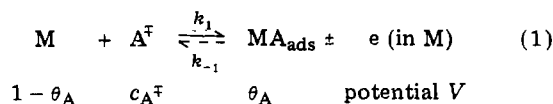
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Significance of Electrochemical Measurements on Monolayers

First, it will be useful to show how electrochemical methods provide a sensitive means for observation of monolayer surface processes and how characteristic electrochemical behavior arises in the simplest case of deposition in (or desorption from) a *single* state of adsorption. We consider a simple surface process in which a chemisorbed species A is deposited on a metal substrate M in a charge-transfer reaction:



where the line below the reaction equation defines the fractional free area $1 - \theta_A$ available on M, the concentration c_A^\mp of A^\mp species in solution from which adsorbed A originates, the occupied surface fraction θ_A , and the potential V (of electrons, e , at the Fermi level) corresponding to a given coverage θ_A attained and a given c_A^\mp . The kinetic equation for the net current i passing per cm^2 of M in reaction 1 is written^{20,21} (for a one-electron process)

$$i = q_1 \frac{d\theta_A}{dt} = q_1 k_1 (1 - \theta_A) c_A^\mp \exp[\pm \beta VF/RT] - q_1 k_{-1} \theta_A \exp[\mp (1 - \beta) VF/RT] \quad (2)$$

where q_1 is the charge required for Faradaic generation of a monolayer of A on M. In eq 2, the exp factors express⁹ how the free energy of activation in k_1 or k_{-1} is modified by the metal-solution potential difference, V , through an electrochemical Brønsted (barrier symmetry) factor^{22,23} β (≈ 0.5). Equation 2 expresses the dependence of i on V and θ_A . So long as V does not exceed the thermodynamic value for "bulk A", only the surface process 1 takes place. As the potential V is changed, i at first increases exponentially with V when θ_A is small but must (cf. eq 2) decrease as $\theta_A \rightarrow 1$. A maximum is attained at some intermediate value of θ_A , usually 0.5 if (1) is a reversible process. Also, because a surface process is involved which is limited in the case of monolayer formation by the available area, i is non-continuous and can be observed only in a non-steady-state experiment as $0 < \theta_A < 1$.

The kinetics of the electrochemical surface process are expressed by eq 2 while the corresponding equilibrium condition for electrochemical adsorption of A on M is given from eq 2 when $i = 0$, i.e.

$$\frac{\theta_A}{1 - \theta_A} = K_1 c_A^\mp \exp[\pm VF/RT] \quad (3)$$

where $K_1 = k_1/k_{-1}$. Equation 3 indicates that for $0 < \theta_A < 1$ there are values of θ_A , in a continuous range, uniquely corresponding to values of V , with V scaled in relation to $\ln K_1$. K_1 includes a term $\exp[-V^\circ_{\text{rev}} F/RT]$ in the standard metal/solution reversible potential, V°_{rev} , for process 1, which characterizes process 1

thermodynamically. θ_A values as $f(V)$ in eq 3 represent the electrochemical adsorption isotherm for A on M. In earlier work²⁴⁻²⁷ it was usually assumed that, on account of interaction^{24,25,27} and/or surface heterogeneity effects,²⁶ K_1 had the form $K_1^\circ \exp[-g\theta_A]$, i.e., there is a linear variation of lateral interaction energy in the monolayer with coverage characterized by a parameter g ($K_1 = K_1^\circ$ when $g = 0$ and/or when $\theta = 0$). However, results obtained by thermal desorption in gas/solid experiments and especially in electrochemical measurements show that " K_1 " is usually neither independent of θ_A nor a continuous function of θ_A ; it often has a series of *discrete* values over distinguishable small ranges of θ_A as θ_A is changed from 0 to 1. This constitutes the phenomenon of "multiple state" adsorption in monolayers. A principal feature of electrochemical techniques is that they allow the adsorption behavior to be easily differentiated with respect to potential, which has enabled excellent resolution of multiple states of adsorption, as θ_A goes from 0 to 1, to be experimentally realized.

Such a differentiation is easily performed on eq 3 with respect to V and gives,^{25,28} noting that deposition or desorption of the monolayer requires the charge q_1 (cf. eq 2), $d\theta_A/dV$ explicitly for $g = 0$, as

$$q_1 d\theta_A/dV = \frac{q_1 F}{RT} \times \frac{K_1 c_A^\mp \exp[\pm VF/RT]}{(1 + K_1 c_A^\mp \exp[\pm VF/RT])^2} = C_\phi \quad (4)$$

where C_ϕ is seen to have the nature of a capacitance. In the general case ($g \neq 0$),

$$q_1 d\theta_A/dV = \left(\frac{q_1 F}{RT} \right) \frac{\theta_A (1 - \theta_A)}{1 + g\theta_A (1 - \theta_A)} = C_\phi \quad (5)$$

C_ϕ , which is usually called the adsorption "pseudocapacitance", is to be distinguished from the electrostatic double-layer capacitance,²⁹ C_{dl} , that arises at all electrode interfaces. Normally, $C_\phi \gg C_{\text{dl}}$.

C_ϕ is a useful quantity since it represents the differential coefficient of the adsorption isotherm 3 and can be directly measured experimentally by means of the current density, i , generated in a voltage sweep. This is easily demonstrated if we write

$$i = q_1 d\theta_A/dt \equiv q_1 (d\theta_A/dV)(dV/dt) = C_\phi dV/dt \quad (6)$$

Thus, if the electrode potential is modulated in a single or repetitive sweep, linearly in time ($dV/dt = \text{constant} = s$, say; see below), C_ϕ is directly measured as i/s , giving the differential isotherm for adsorption of A. This is very convenient as evaluation of C_ϕ therefore provides, among other things, a sensitive method for characterizing adsorption when the latter occurs in *multiple* states as $0 < \theta_A < 1$. The sensitivity arises on account of the differential nature of C_ϕ . Equation 6 also distinguishes a simple surface process from one involving diffusion for which $i \propto s^{1/2}$, or one involving coupled chemical steps for which i is a complex $f(s)$,³⁰

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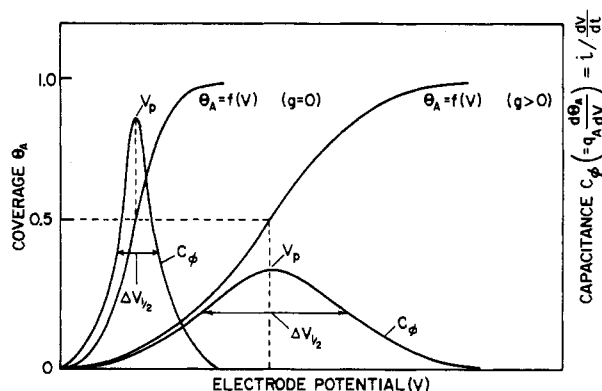


Figure 1. Adsorption pseudocapacitance (C_ϕ) profiles corresponding to reduced current-density (i/s) vs. potential (V) relations for a simple (single state) surface process in which a monolayer is deposited or ionized (schematic). Cases for Langmuir conditions ($g = 0$) or when lateral repulsive interactions are significant ($g > 0$) are shown together with the corresponding isotherms for θ_A as $f(V)$ (based on ref 20, 25, and 30).

as observed for some reactions.

Some general features of a simple single-state process (i.e., with a unique value of K_1 or K°_1) are next to be noted: a single peak in C_ϕ arises at $\theta_A = 0.5$ at a corresponding peak potential, V_p , as illustrated in Figure 1. In the general case, when $g > 0$, the peak height is diminished but its breadth is increased (Figure 1); in fact, the width at the half-height (the "half-width", $\Delta V_{1/2}$ ^{20,31}) is almost linearly proportional to g , and this gives a useful and accurate way of characterizing the lateral interaction energy parameter, g , for the monolayer.^{24,25,27,31} If attractive interactions are involved ($g < 0$), the peak is narrowed.

Experimentally Measurable Quantities

From the nature of Faraday's laws, currents for surface processes integrated over time give a sensitive measurement of changes of coverage (e.g., of the species A in eq 1) with changing potential. Hence C_ϕ and, after integration, θ_A as a function of potential, V , can be accurately derived. Thus

$$q_1 \theta_A = \int_0^t i dt = \int_{V_i}^{V_t} \frac{i}{s} dV \propto \int_{V_i}^{V_t} C_\phi dV \quad (7)$$

where V_i is the initial potential in a potential-sweep and V_t some other potential. C_ϕ can be directly measured, according to eq 6, by the potential-sweep method¹³ or by differentiation of voltage transients arising from controlled-current pulses applied to an electrode.³ The following are indications of the sensitivity of these electrochemical methods: (a) A monolayer of H on Pt corresponds to an easily measurable charge of 2.10 ~ 2.20 C m⁻² of real surface, depending on the orientation of the crystal plane. (b) Currents, corresponding to C_ϕ , are normally in the range 5 μ A to 50 mA cm⁻², depending on dV/dt , and are thus accurately measurable. (c) Accuracies of charge determination, and hence of θ , are ca. 1~2%. (d) Binding free energies of adsorbed species can be determined as peak potentials in a potential-sweep experiment with an accuracy of 10 mV (or

20~25 when overlapping peaks arise), i.e., ca. 1 KJ mol⁻¹. (e) Distinguishable adsorption states can be resolved for ΔG° differences ≥ 2 kJ mol⁻¹, i.e., when multiple state adsorption is observed. (f) Kinetic data can be derived³² from experiments over a sufficiently large range of s values (see section on Kinetics).

The study of monolayers or thin films at electrode surfaces can also be made by in situ reflectance techniques (relative reflectance, $\Delta R/R$, and ellipsometry giving the Δ and ψ parameters) which are particularly convenient at electrodes on account of the ease of modulating the potential and hence the state of the surface. This allows the reflectivity to be studied under potential-sweep or alternating voltage (av) conditions using signal-averaging techniques in sweep experiments^{33,34} or lock-in, phase-sensitive amplification in av modulation³⁵ experiments. A qualitatively striking result is found for H adsorption: the signs of $d(\Delta R/R)/d\Delta V$ are different for the strongly and weakly bound H regions of the i - V profile^{33,36} at Pt electrodes (see Figure 3).

While good sensitivity can be achieved by these methods, interpretation of reflectivity changes due to monolayers is complex³³ owing to contributions from double-layer ion accumulation, water orientation and electrostriction, and the potential-dependent refractive index of the surface electron plasma as well as uncertainties about the complex refractive index of the monolayer itself (bulk properties cannot be assumed).

Main Features of Interest in Monolayer Processes at Electrodes

Multiple-State Adsorption in Monolayers. The most striking feature of nearly all i - V profiles for electrochemical surface processes is that multiple states of adsorption of the deposited species are observed below the limit of monolayer coverage, as is sensitively revealed by cyclic voltammetry^{13,18} (Figure 2a,b).

In cases where resolution is good, the *individual* peaks have almost Langmuir character,²⁰ i.e., $g \simeq 0$ (eq 5), in the multiple state assembly constituting the monolayer.

In early work,^{9,13} two main states ("weakly" and "strongly" bound) of H adsorption were distinguished, as also seen in relative reflectivity profiles³³⁻³⁶ (Figure 3). However, 4 or 5 H states at comparable coverages are resolved at Pt or Ir in clean,³⁷ sufficiently dilute¹⁸ solutions, 7 for Pb on Au (Figure 2b), and 3 for OH on Pt,¹⁹ etc. These results parallel those of temperature-programmed desorption at gas/solid interfaces, e.g., CO on W. Except when surface alloying occurs, the desorption and adsorption i - V profiles are usually reversible. With surface oxide films, however, both reversible and irreversible processes can be resolved¹⁹ (see Kinetics).

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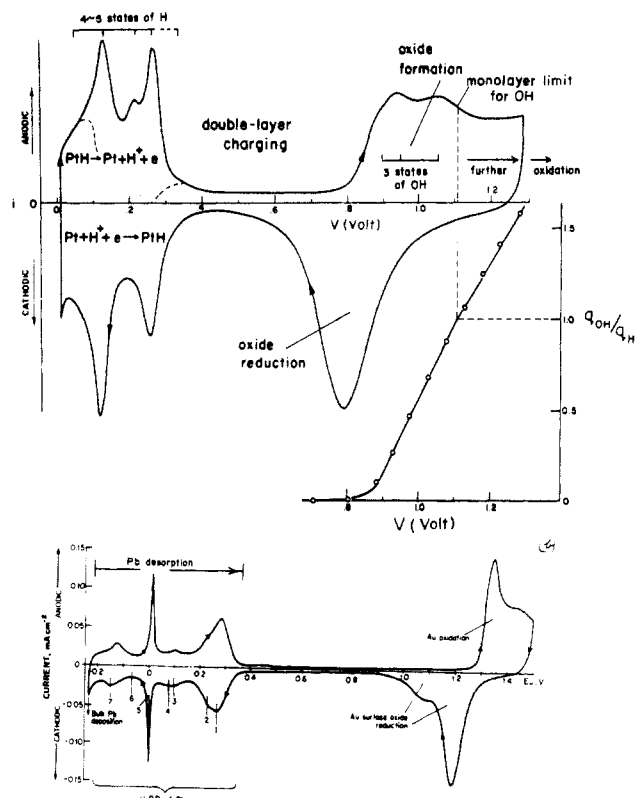


Figure 2. Examples of underpotential deposition and desorption involving multiple adsorption states; cyclic-voltammograms taken at 25 mV s^{-1} for (a) electrochemical deposition and desorption of H and OH/O species at Pt in $0.5 \text{ M H}_2\text{SO}_4$ (inset shows integral isotherm for deposition of OH as charge required relative to that for H monolayer); (b) electrodeposition and desorption of Pb at Au in seven distinguishable states below a monolayer, also found on single crystal surfaces.⁴³

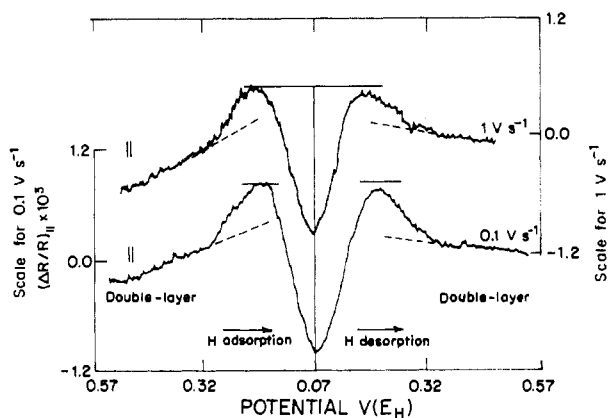


Figure 3. Relative reflectance change, $(\Delta R/R)_{||}$, vs. potential profiles for H underpotential deposition and desorption at Pt in $0.5 \text{ M H}_2\text{SO}_4$ showing two regions of $\Delta R/R$ having different signs. $\Delta R/R$ is measured relative to the reflectance at 0.5 V E_H in the double-layer charging region, where neither H nor OH/O species are on the electrode.

The critical question concerning multiple-state adsorption is whether, or to what extent, it is due to surface heterogeneity since all of the earlier work was done on polycrystalline metals, especially Pt.^{19,30} However, in 1966, Will³⁸ showed that two or three states of H adsorption could still be distinguished on (100), (110), and (111) planes but in relatively different amounts. The multiple-state adsorption was attributed

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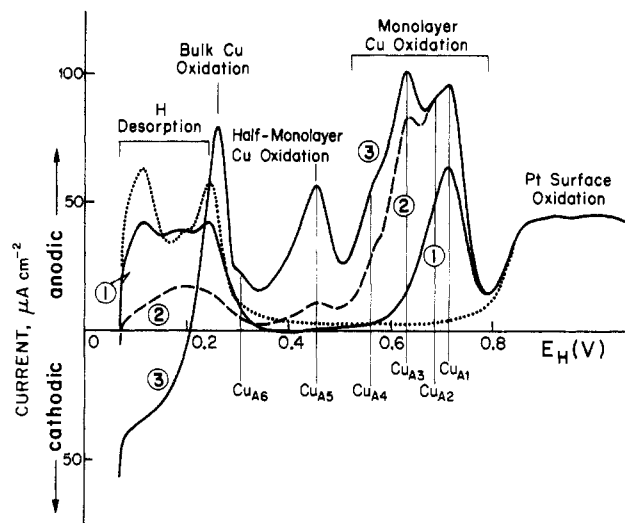


Figure 4. Relation between current vs. potential (V) profiles for anodic desorption of H adsorbed in several states at polycrystalline Pt in the presence of previously codeposited Cu atoms and the current vs. potential profiles for desorption of those atoms in various states in the same anodic sweep (ref 17, 18). Cu₁₋₄ states of Cu desorption profile correspond to a monolayer of Cu; Cu₅ and Cu₆ peaks are for oxidation of second half-monolayer; "A" represents "anodic" desorption. (---) $0.5 \text{ M H}_2\text{SO}_4$ support electrolyte; $0.5 \text{ M H}_2\text{SO}_4$ + (1) $5 \times 10^{-5} \text{ M CuSO}_4$, (2) 10^{-4} M CuSO_4 , (3) $2.5 \times 10^{-4} \text{ M CuSO}_4$ used in the previous cathodic sweep where diffusion-controlled deposition of the Cu species took place.

to residual nonuniformity of the surfaces.

More recently, in situ LEED examination of single-crystal electrode surfaces has been combined³⁹⁻⁴¹ with electrochemistry done in the LEED chamber or by transfer to an attached chamber. The general results are³⁹⁻⁴¹ that the (111) Pt surface is associated with the weakly bound H states (0.0–0.18 V) while the (100) surface is associated with more strongly bound species (0.18–0.35 V E_H). However, on these well-characterized single-crystal surfaces, the i - V profiles still show³⁹⁻⁴¹ more than one component of H adsorption in nontrivial (viz., 20–30%) amounts. Multiple-state adsorption is also found for upd of Pb or Tl on single crystals of Au⁴² or Ag.⁴³ A recent paper by Clavilier⁴⁴ also describes multiple-state adsorption of H on supposedly well-characterized single-crystal Pt surfaces. Similar conclusions for adsorption of H or CO from the gas phase on to Pt were reached by Somorjai, who stated⁴⁵ that "... even a single crystal plane is heterogeneous when viewed by the adsorbed species", in the sense indicated in (iv) below. The "critical question" is not yet finally answered and awaits further careful discriminatory work.

These important results thus indicate that the interesting multiple-state adsorption in upd may not be

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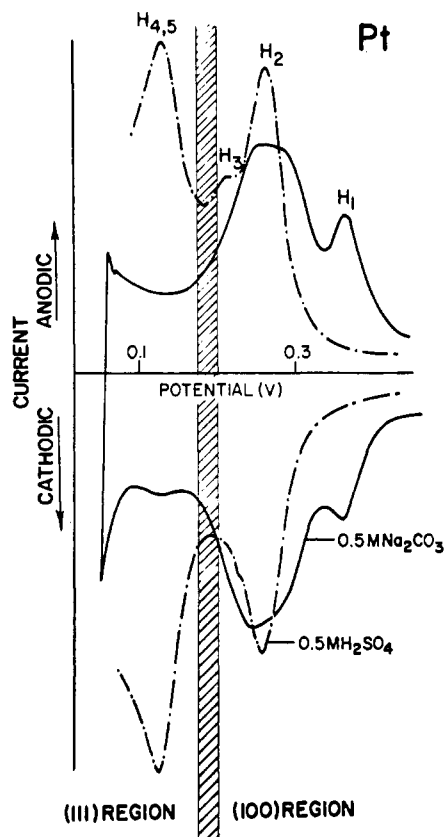


Figure 5. Current vs. potential profiles for H deposition and desorption at Pt at 25 mV s^{-1} in acid and alkaline solutions in relation to the behavior (ref 39-41) at (111) and (100) single-crystal surfaces showing apparent "transfer" effect between (110) and (100) regions.⁴⁰ H_1, H_2 etc., represent the distinguishable states of adsorbed H in the monolayer. Reproduced with permission from B. E. Conway et al., Proceedings of the Third Symposium on Electrode Processes. Copyright 1979, The Electrochemical Society.

due simply to the presence of a variety of crystal planes on which atoms are deposited with various standard free energies of adsorption. However, some fine structure in the i - V profiles evidently can be attributed to the presence of step edges⁴¹ or facets,⁴⁰ as shown by Ross⁴¹ and Hubbard,⁴⁰ and the distribution of H among various states is certainly dependent on the principal orientation of the surface.

In cases where both H and metal monolayers can be studied at the same metal, e.g., Pt,^{17,18} it is found that the sequence of blocking of the H adsorption states by the deposited metal atoms does not correspond to the sequence of deposition of metal atoms into adsorption states in the metal monolayer itself with respect to ranges of electrode potentials over which the metal atoms are deposited or desorbed. This suggests that each type of monolayer has a characteristic "spectrum" of chemisorption states not determined only by the incidental presence of steps, edges, facets, etc., on the crystal surface. Examples are shown in Figure 4 for Cu and H at Pt where the progressive blocking of H states by Cu does not correspond to the order of appearance of the four monolayer Cu states.

If the multiplicity is not due entirely to heterogeneity, then other factors must be considered; various possibilities have been examined, as follows: (i) use of various hybrid orbitals on the surface as θ_A approaches an epitaxial or a geometric limit of 1 (surface d-orbital energy splitting with change of θ_A); (ii) modification of

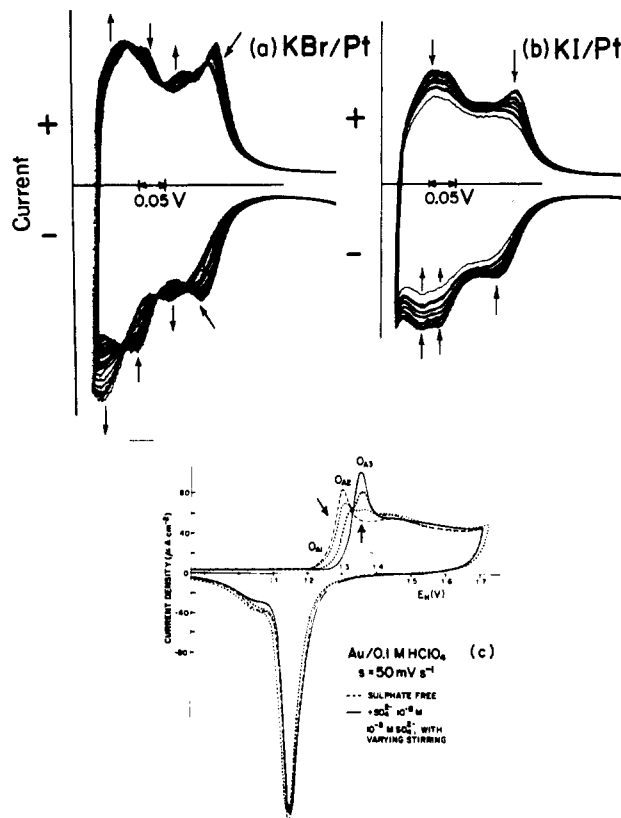


Figure 6. Effects of (a) Br^- , (b) I^- ions/concurrent vs. potential profiles for H deposition and ionization at Pt with successive increases of concentration from 10^{-8} to 10^{-6} M of Br^- or 10^{-9} to 10^{-7} M of I^- in $0.1 \text{ M H}_2\text{SO}_4$, 298 K. Cl^- effect is similar to that of Br^- . Arrows indicate direction of change with increasing anion concentration. (c) Effects of SO_4^{2-} ion (10^{-8} M) on initial stage of surface oxidation of Au in 0.5 M HClO_4 , 298 K. $\text{O}_{a1}, \text{O}_{a2}, \text{O}_{a3}$ are successive stages of surface oxidation. Arrows show directions of effect of increasing mass transfer of SO_4^{2-} ion and consequent increased adsorption.

the electronic properties of the surface in a communal way⁴⁶ by all the adatoms at a given θ_A as θ_A increases from 0 to 1. (iii) Long-range electronic interactions between adatoms on the surface;⁴⁶ (iv) occupation, successively, of various different coordination positions on the surface¹⁸ [this presumably would be a result of (i) and/or (v)]; (v) successive development of ordered overlay lattice structures with characteristic standard free energies, as coverage increases towards unity;^{18,19,47} and (vi) reactive reconstruction of the substrate/adsorbate layer as $\theta_A \rightarrow 1$ with development of successive lattices⁴⁷ involving both adsorbate and adsorbent.

Potential-sweep i vs. V profiles, especially for H, are dramatically affected by coadsorption of both the anions⁴⁸ and, to a lesser extent, the cations^{18,49} of the electrolyte. The nature of these effects aids in understanding the significance of multiple-state adsorption.

Change of pH from an acid to alkaline value produces a striking redistribution of the states of adsorbed H at

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Pt (Figure 5). In relation to underpotential deposition of H at (100) and (111) Pt surfaces,³⁹⁻⁴¹ Figure 5 shows that H is apparently "transferred" in a substantial quantity from the "(111)" weakly bound region to the "(100)" strongly bound region with the total charge remaining the same ($\pm 5\%$). A transfer effect in the opposite direction occurs upon adsorption of halide ions (Figure 6a for Br⁻). With I⁻ ion (Figure 6b), only a blocking effect arises similar to that with neutral atom adsorption, e.g., with Hg. This is because I⁻ is adsorbed as a neutral particle, with charge transfer.⁵⁰

If the two regions of Figure 5 correspond to H adsorption on (111) and (100) planes, respectively, it is difficult to see how such a major "transfer" of H between the states could arise since there is no evidence (as there is in the oxide region) for surface reconstruction in going to pH 13. Change of pH to alkaline values moves the potential range for H up negatively relative to the potential of zero charge (pzc), causing diminished anion adsorption. This change could also cause¹⁸ reorientation of H₂O dipoles from a direction in which oxygen atoms are adjacent to the metal surface to a direction in which hydrogen atoms are adjacent to the surface of the metal. These two effects could produce the observed redistribution.

At sufficiently low concentrations ($10^{-5} \sim 10^{-4}$ M) of chemisorbed anions such as Cl⁻, Br⁻, SO₄²⁻, the quantity of H or OH species which can be electrodeposited at Pt in the most strongly bound state is *diminished* but that in the next lower energy state is correspondingly *increased*, giving rise to an "isosbestic" (isopotential) point. This implies an almost 1:1 transfer of the electrodeposited species from one bound state to another; e.g., see Figure 5a for H on Pt and especially 5c for SO₄²⁻ adsorption effects on surface oxidation of Au. It is difficult to account for this type of behavior in terms of the distinguishable states of chemisorption of H or OH on Pt being associated only with different crystal planes. On the other hand, it is possible qualitatively to understand how this behavior can come about in terms of a lattice model¹⁹ where occupation of sites of one overlay lattice (see b below) partially by anions instead of by OH allows development of the next ordered structure to occur at a higher potential, as appears to occur at Au (Figure 5c).

Two-Dimensional Ordered Overlay Lattice Structures. Beyond 0.78 V E_H at Pt, three peaks for surface oxidation are resolved¹⁹ in clean solutions³⁷ over $0 < \theta_{OH} \leq 1$. Beyond this region, an unstructured profile for the further oxidation step Pt/OH \rightarrow Pt/O + H⁺ + e is seen.^{19,30}

Kozłowska, Conway, and Sharp¹⁹ proposed that the three peaks corresponded to development of successive ordered overlay lattices of OH on Pt with, for example, ratios of OH to Pt sites having values 1:4 ($\theta_{OH} = 0.25$), 1:2 ($\theta_{OH} = 0.5$), and 1:1 ($\theta_{OH} = 1$) on the (100) plane. On account of repulsive interactions among the electrodeposited polar OH species, the adlayer will tend to minimize its free energy by progressively establishing a series of two-dimensional lattice structures. Experimental evidence for behavior of this kind has been given from LEED studies⁴⁷ on O monolayers on Ni. It is of interest that the multiple capacitance peaks observed⁵¹ in charging TiS₂ with Li⁺ have been explained

on a similar basis but with a succession of *three-dimensional* ordered structures. The two-dimensional structure model of Kozłowska et al.¹⁹ has been taken up by various authors^{10,43,52} for the interpretation of up profiles of metal adatoms, including the phase change that appears to arise in the multistate Pb monolayer on Au.^{11,42,43}

State of Charge of Electrodeposited Species. In the deposition of atoms in electrocrystallization of metals, it was recognized by Lorenz⁵³ that there would be some ionic character ("adions") to the deposited "atoms", together with corresponding hydration, before they were completely incorporated into the growing crystal lattice.

This idea was extended to underpotential deposition where the fractional extent of charge transfer in a cathodic or anodic surface process was defined⁵⁴ as the electroadsorption valency, γ , e.g., $A^{\mp} + M \rightarrow MA^{(1-\gamma)\mp} \pm \gamma e$. When $\gamma < 1$, the adsorbed A species bears a partial electron charge. Correspondingly, a similar situation can arise with spontaneous specific adsorption of ions: $X^{-} + M \rightarrow MX^{(1-\gamma)-} + \gamma e$ (in M). Thus, for I⁻ adsorption on Pt, experiments show that $\gamma \approx 1$ so the adsorbed I is almost a neutral atom⁵⁰ (Figure 6b) (cf. the converse situation where Na adsorbed on W is in the form of cations). A series of examples where $\gamma < 1$ has been given,⁵⁴ together with its effect on g (eq 5).

The energy of the bond of electrodeposited species, e.g., H, to the electrode metal is dependent on the work function, Φ , of the adsorbent metal. As was shown by Conway and Bockris,³ this is because the polarity of the surface bond is related to the electronegativity difference between adsorbate and adsorbent. This approach was applied by Kolb et al.⁵⁵ to the energy states of electrodeposited metals in monolayers: a linear relation between the underpotential shift, $V_{\text{bulk}} - V_{\text{monolayer}}$, and the work function difference, $\Delta\Phi$, between the substrate and monolayer metal was found as in the case of adsorption of H at electrodes.³

Entropy and Volume of H Species Chemisorbed at Pt. When electrochemical experiments are conducted at various temperatures^{5,56} or pressures,⁵⁷ the entropy and volume of electrodeposited H can be conveniently derived from measurements on the dependence of peak potentials of the various adsorption states of H referred to the potential of an H₂/H⁺ electrode in the same solution. For three of the four H states, the entropy corresponds to H in a *mobile* monolayer, but the fourth state, which is influenced in aqueous H₂SO₄ by HSO₄⁻ adsorption, has much lower entropy.⁵⁶ Corresponding experiments at high hydraulic pressures⁵⁷ give a normal covalent volume for adsorbed H of 5.1 ± 1.0 cm³ mol⁻¹. At Pd, where H is *absorbed*, the volume is less, corresponding to a partially protonic state of H in the lattice, as known from other work.

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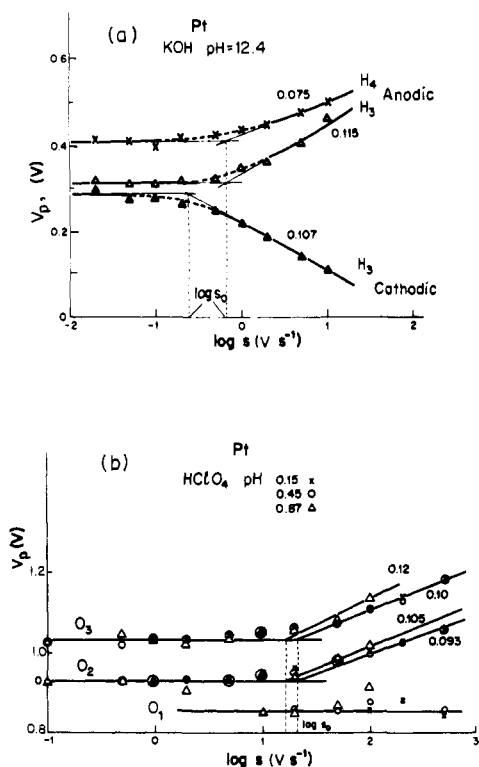


Figure 7. Evaluation of the reversibility parameter s_0 and the Tafel slope for H and OH monolayer surface processes at a Pt electrode³² from the shifts of peak potentials V_p with \log [weep-rate, s , $V s^{-1}$]. (a) For two of the submonolayer states of H denoted by H_3 and H_4 at Pt in anodic and cathodic sweeps in aqueous KOH and (b) for three submonolayer states of OH denoted by O_1 , O_2 , and O_3 at Pt in aqueous $HClO_4$ at 3 pH's in anodic sweeps. Numbers on lines give Tafel slopes in V for the irreversible regions.

Kinetics, Reversibility, and Hysteresis in Monolayer Deposition and Desorption Processes

In underpotential deposition of metal and H atoms, the cathodic and anodic i - V profiles are almost mirror images (Figure 2) at sufficiently low sweep rates. Deviations arise from irreversibility in coadsorption of anions. At high sweep rates, however, the processes themselves become irreversible because they cannot keep up with the rate of change of V . Under these conditions the peak potentials, V_p , become shifted in proportion to $\log s$. Extrapolation of an experimental line of V_p vs. $\log s$ to the reversible peak potential gives³² a quantity, $\log s_0$, where s_0 is the maximum value of s , called the "reversibility parameter", within which the process remains reversible. s_0 is related to the exchange current density, i_0 , by

$$s_{0,p} = i_{0,p} / C_{\phi,r,p} \quad (8)$$

for the peak (p) of an i vs. V profile where $C_{\phi,r,p}$ is the observed capacitance at the peak when the surface process behaves reversibly. s_0 has the advantage that its evaluation, unlike i_0 , does not require knowledge of real surface area of the electrode. It is thus a parameter specially suited for kinetic evaluations of surface processes.

The shift of (cathodic) peak potential with $\log s$ follows the relation (when $g = 0$)³²

$$V_p - V_{p,r} = \frac{RT}{\beta z F} \log s_{0,p} - \frac{RT}{\beta z F} \log (-s) \quad (9)$$

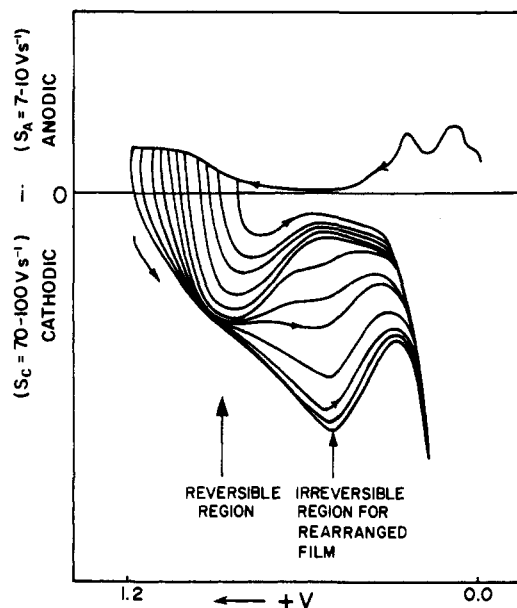
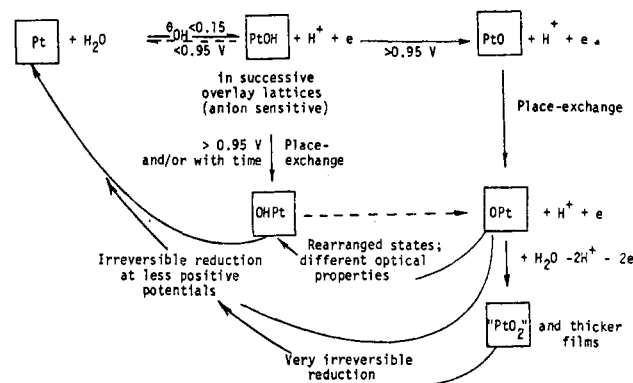


Figure 8. Resolution in fast cathodic sweeps of OH species deposited reversibly and irreversibly at Pt in experiments at low temperature (243 K) in 5 M H_2SO_4 . Cathodic sweep rates are 10 times faster than anodic ones in a series of successive sweeps taken to progressively increasing positive potentials, $+V$ (from ref 19).

Scheme I: Schematic Cycle of Processes in Formation and Reduction of Oxide Monolayers on Pt



Plots of the left-hand side vs. $\log (-s)$ give the Tafel slope $RT/\beta z F$ of the surface process. Examples of the evaluation of s_0 and the Tafel slope for the surface process are shown in Figure 7 for the distinguishable states of H and OH adsorption at Pt.

With noble metals, there is always hysteresis between the processes of formation and reduction of the monolayer oxide film. Depending on the metal, the potential, pH, and anion adsorption, an initially kinetically reversible formation and reduction of a submonolayer of OH can, however, be detected¹⁹ (θ_{OH} from 2% at Au to 25% at Pt). At higher potentials, increased hysteresis develops however slow the sweep is conducted. This is due to a "postelectrochemical" process of field-assisted reconstruction of the initially deposited submonolayer of OH, or later O, species which occurs by a "place-exchange" mechanism schematically illustrated in ref 19. This process eventually leads to thickening of the oxide film and is anion sensitive.

By making fast sweep experiments at low temperatures, the irreversible stages of surface oxidation can be clearly distinguished¹⁹ (Figure 8) from the low-cov-

erage reversible component. Resolution of the latter is very sensitive to anion adsorption which blocks it but it is also resolved in relative reflectivity measurements.³⁴ The overall process of surface oxide formation and reduction is represented in Scheme I where the reversible and irreversible stages, which lead to hysteresis, are shown schematically.

This hysteresis in surface oxide formation and reduction plays a major role in the kinetics of electrocatalytic oxidation reactions at Pt and other noble metals,

e.g., in oxidation of H₂ and small reactive organic molecules such as HCOOH, CH₃OH, etc. In such reactions, the initial reversibly formed species in the oxide film are reactive while the rearranged state of the film is usually inhibitory. For H₂ oxidation, however, all states of the film at Pt are inhibitory.

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Infrared Multiphoton Decomposition: Photochemistry and Photophysics

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Chemical kineticists often search for experimental tools that allow the preparation and study of molecules with energy distributions other than thermal. Thus, experiments using photochemical and chemical activation are common. Also sought are techniques whereby short-lived species, such as free radicals, may be created under conditions where their reactions may be studied. In this Account, we report on some experiments in which we have employed an infrared laser to achieve both of these results.

In the past 10 years,¹⁻³ experiments have indicated that polyatomic molecules can be decomposed when subjected to radiation from a high-power infrared laser under conditions where no molecular collisions are possible. Infrared optical pumping is thus a nonthermal energization process.

Three aspects of this phenomenon have been of great interest. First, the molecular decomposition can lead to reactive species, such as free radicals, and thus is a rapid method for preparing such species for chemical and physical study. Second, the optical pumping process may be mode specific, i.e., as many photons are absorbed, they may excite a given molecular vibration to a continually greater degree. This is quite different from collisional excitation which is statistical. Because of this difference, it is conceivable that chemistry induced by laser excitation would be considerably dif-

ferent from that induced by thermal collisional excitation. Finally, since similar molecules with different isotopically substituted molecules absorb infrared radiation of different frequencies, the infrared laser-induced dissociation process is a natural method for isotopic separation. Indeed, these last two points have furnished the major impetus for recent research in this area.

Kinetic Model

A model for infrared laser pumping of molecules which has received general acceptance is illustrated in Figure 1. In this particular case, the first two photons are absorbed in a given isolated vibrational mode with the anharmonicity being compensated for by $\Delta J = \pm 1$, leading to allowed transitions. In Figure 1 we depict a situation where the coupling of energy from $v = 2$ of the isolated vibrational mode to the other quantum states of the molecule at this energy is sufficiently strong that we describe the molecule in terms of an energy level, rather than a specific state. At this energy and higher, the density of levels is so great that the resonant absorption of the specific laser photon is assured. This energy region is called the quasicontinuum. Above some barrier to chemical decomposition, a true continuum exists and molecules have lifetimes given by $(k(E))^{-1}$, where $k(E)$ may be computed via RRKM theory or other models for unimolecular decay. The exact nature of pumping in any given molecule is thus strongly dependent on energy-level and wave-function details. If we desire to understand the time history of population in the molecular quantum states, we need to solve the time-dependent Schrödinger equation. It is well-known⁴ that under certain conditions the

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