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P.N. Ross, Jr.

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LONG-RANGE STRUCTURAL EFFECTS IN THE ANOMALOUS
VOLTAMMETRY OF PT (111)

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Abstract

The history of the observation of anomalous voltammetry is reviewed and an experimental consensus on the relation between the anomalous behavior and the conditions of measurement (e.g., surface preparation, electrolyte composition) is presented. The behavior is anomalous in the sense that features appear in the voltammetry of well-ordered Pt(111) surfaces that had never before been observed on any other type of Pt surface, and these features are not easily understood in terms of current theory of electrode processes. A number of possible interpretations for the anomalous features are discussed. A new model for the processes is presented which is based on the observation of long-period ice-like structures in the low temperature states of water on metals, including Pt(111). It is shown that this model can account for the extreme structure sensitivity of the anomalous behavior, and shows that the most probable explanation of the anomalous behavior is based on capacitive processes involving ordered phases in the double-layer, i.e., no new chemistry is required.

I. A History of the Observations of Anomalous Behavior

Prior to the publication in 1980 of Clavilier's historic paper [1] reporting anomalous voltammetry of Pt(111), there had been a number of studies of the voltammetry of single crystal Pt electrodes, with some using modern methods of surface analysis (e.g., LEED or RHEED) for characterization of the structure of the crystal prior to immersion in electrolyte [2-6], and all were in qualitative agreement with the seminal work (in 1965) on Pt single crystals by Will [7]. By today's standards of surface preparation, Will's procedures for surface preparation were crude, the surface structures were not characterized by use of surface analytical instrumentation (which was neither widely available nor well developed at that time), and he employed extensive potentiodynamic cycling through the "oxide" formation potential region prior to reporting the quasi-steady state voltammetry curve, i.e., the potentiodynamic I-V curve. The studies employing surface analytical methods made a decade or more later were generally regarded as validating the major conclusions of Will's study: 1) that the relative bond strength of hydrogen on the low index surfaces of Pt are (100) > (110) > (111); 2) that the multiple features in the voltammetry curve for polycrystalline Pt in acid electrolyte are associated with adsorption on sites having the different local geometries of the (100), (110) and (111) planes. However, with respect to the quantitative details of the results, there were major discrepancies between different groups, particularly with respect to the charge under the I-V curve in the hydrogen adsorption potential region from Pt(111) surfaces, and to

the effect of potential cycling (like that employed by Will) on the amount of this charge and on the detailed shape of the I-V curve [8]. It was clear, at least to this author [2,6], that the discrepancies in the results between different groups using UHV methods were caused by the interactive effect between impurities and transformations to the surface structure caused by the potential cycling used to clean the surface of impurities. The use of oxygen atmospheres during transfer of the crystal from UHV to the electrolyte appeared to remove the impurity effect, and produced I-V curves which were essentially indifferent to potential cycling [9]. With the publication of these results, the problem of understanding the multiple states of adsorbed on Pt electrodes appeared to be fully resolved, with Will's original site-geometry interpretation upheld and further refined.

There was no precedent in the published or even unpublished history of studies with Pt electrodes (single crystal or otherwise) for the type of I-V curve reported by Clavilier [1] for Pt(111), and his observations might have been dismissed for a time had they not been defended so strongly by Parsons [10]. Motivated by subsequent communications with Parsons' on the integrity of Clavilier's results, we accelerated the pace of modifications we were making to the UHV-electrochemistry apparatus in my laboratory, converting the cell to a thin-layer type [11] with the hope of reducing the effect of electrolyte impurities on the voltammetry. With the use of this cell, we were able to produce the first corroboration of the Clavilier type voltammetry with a Pt(111) crystal prepared in UHV and characterized

by LEED as a highly ordered (111)- 1×1 surface [12]. This voltammetry is reproduced in Fig. 1a. The sensitivity of this I-V curve to the atomic scale "flatness" of the surface is illustrated by the comparison with the curve 1b, which is the same crystal ion-bombarded but not annealed. If the annealed surface is cycled potentiodynamically through "oxide" formation, the shape of the I-V curve changes rapidly, and is transformed into one resembling Fig. 1b, and many others reported previously for "cycled" (111) electrodes [4-7,9]. The features which occur in the scans for the annealed (111) surface in the potential range 600-850 mV are the anomalous features first reported by Clavilier. They are anomalous in the sense that they had never been reported before with any Pt electrode, single crystal or polycrystalline, and they occur in a potential region which from thermodynamic considerations [12] indicates they are unlikely to be either adsorbed hydrogen or adsorbed oxygen.

To obtain these startling new results with Pt single crystals, Clavilier employed a novel surface preparation technique that did not require a complex and expensive UHV system, but did require considerable skill and experience. Clavilier's original papers should be referred to with regards to the details of the method, as I shall not discuss it further here, and only refer to it subsequently as the "bead method." Because the bead method does not require UHV systems, it can be practiced by a wider number of interested electrochemists, and this has proven to be (and will continue to be) a significant factor in the development of an understanding of the anomalous vol-

tammetry, i.e., what species/processes are involved. A number of laboratories around the world were soon able to use the bead method to reproduce, in virtually every detail, Clavilier's original voltammetry, and have proceeded to use the method in studies of the chemistry of the anomalous features. The particular results with the bead method that I shall refer to in this review are from studies of the effect of anion type and concentration [13-16] and of the effect of atomic scale roughness (observed using step-terrace surface structures) on the potential region and integral charge of the anomalous features [17,18].

In contrast to the successful implementation of the bead method in studying the anomalous features, the contributions from studies with UHV-electrochemical systems has been limited to just a few. Subsequent work from our apparatus following corroboration of Clavilier's results concentrated on the effect of potential cycling through "oxide" formation potential on the surface structure [19], and later on the effect of pH and type of anion [20] on the anomalous features. Using the system in Yeager's laboratory, Hanson [21] was able to reproduce Clavilier's voltammetry not only for the (111) surface, but also the (100) and (110) surfaces as well. In spite of the relatively small number of contributions to the literature that have come from the UHV-electrochemical systems, they have made and essential validation of the bead method of surface preparation, and have verified the structure sensitivity of the anomalous features inferred from purely electrochemical observations.

II. Possible Interpretations of the Anomalous Features

Table I gives a summary of the observational data base which I shall use here for a discussion of possible interpretations for the anomalous voltammetry. The discussion here is of necessity brief, and only summarizes the detailed discussion presented in our recent paper [20]. The anomalous features are observed on well-ordered (111) surfaces in a variety of electrolytes over a wide range of pH (0-11), but the potentials at which the features appear and the detailed shapes of the I-V curves vary considerably. Specifically, the potential region (versus RHE) in which the features appear changes with anion concentration in sulphate and chloride electrolytes, but not in fluoride, perchlorate, bicarbonate or hydroxide electrolyte. In sulfate electrolyte, at constant anion concentration the region shifts (versus RHE) with varying pH, while in fluoride, perchlorate, bicarbonate and hydroxide electrolyte it does not. The use of UHV surface analytical techniques has established to a reasonable (but not definitive) extent that adventitious impurities are not involved in the anomalous process, i.e., the only species participating in the chemistry are protons/hydroxyls, water and the anions of the solute. On the basis of the pH and anion concentration dependencies, I agree with the interpretation put forward by Kolb and co-workers [15] that the anomalous features on Pt(111) in sulfate and chloride acid solutions are associated with processes of specific adsorption of these anions. The identity of the species and processes involved in the anomalous features observed on Pt(111) in sulfate and chloride acid solutions are associated with

processes of specific adsorption on these anions. The identity of the species and processes involved in the anomalous features observed in perchlorate, fluoride, bicarbonate and hydroxide electrolyte remains more uncertain than in the cases of the sulfate and chloride electrolytes. Primarily by the process of elimination, i.e., hydrogen adsorption and specific adsorption of anions appear highly unlikely, the process in acidic fluoride and perchlorate electrolytes is most probably related to water dissociation, and the species are most probably surface intermediates of this process, i.e., oxygen-like. In basic electrolytes, it appears likely, by direct analogy with the process in sulfate electrolytes, that specific adsorption of hydroxyl anion is the process there. The specifically adsorbed hydroxyls ($\text{pH} > 5$) may have similar final state molecular configuration on the surface even though they derive from different initial states. It is not clear how these hydroxyl/oxygen-like species differ from the place-exchanged OH formed on the surface at higher potentials [22]. It is even more difficult to explain why the molecular configuration of any of these species would be unique to the (111) surface, nor why roughening the (111) surface should cause the process to disappear entirely. In the discussion which follows, a model is presented which attempts to resolve these difficulties within the framework of classical double-layer theory but using new concepts in ordered structures for the double-layer at Pt(111).

III. Understanding Sensitivity to Long-Range Surface Order

I know of no other examples in the surface science literature in which the adsorption of a small molecule (small in this case referring to the values of molecular/ionic radii of the adsorbate relative to the size of perfectly flat regions on the metal surface) depends critically on the existence of large regions of perfect surface structure. There are some examples of such sensitivity in the adsorption of aromatic molecules, where the "lying-down" configuration, which requires attachment to multiple points on the surface, depends critically on the existence of flat domains of size greater than the molecule itself [23]. Because these aromatic molecules provided the principal precedent for such structural effects, we spent a great deal of time in my laboratory, perhaps 2-3 man years of effort, pursuing the "impurity hypothesis" based on an adventitious organic impurity. When this hypothesis was found wanting from our studies, we turned to concepts of ordered networks in the double-layer. Fred Wagner, who worked with me on these studies of the anomalies on Pt(111), has pursued the concept of ordered networks in his own studies, as he reports in another paper in this conference. In the discussion which follows, I present a conceptual model for the double-layer at the Pt(111) surface which uses what has been learned about hydrogen bonding in adsorbed water layers from studies of water adsorption on metal surfaces at low temperature (<150 K) and extends the one-dimensional classical models [24] into a three-dimensional model. This model is then used to formulate a mechanism to explain how sulphate anion adsorption would be sensitive

to the symmetry of the surface, e.g., (111) vs. (100) or (110), and a critical level of atomic roughness in the surface, e.g., the steps and step-terrace structures.

Fortunately, the large, but diverse literature on the adsorption of water on metals has been collected in a comprehensive manner in the recent review by Thiel and Madey [25]. As shown in their review, it is now well established that water forms ordered superlattice structures at low temperatures (e.g., 100°K) on a number of metal surfaces having hexagonal symmetry, i.e., fcc(111) and hcp(001), including and especially Pt(111). The superlattice structures have $(\sqrt{3} \times \sqrt{3})$ R-30° symmetry indicated by LEED, and models have been derived showing that such symmetry is expected for long-period ice-like structures. The most detailed and convincing study of these water superlattices was by Doering and Madey [26] for water on Ru(001), the hexagonal surface for the hcp metal. They supplemented their LEED analysis with ESDIAD (electron stimulated desorption-ion angular distribution), which provided direct indication of the orientation of water molecules on the surface, and applied the Bernal-Fowler-Pauling symmetry rules for hydrogen bonding in bulk ice to derive the surface hydrogen bonded network shown in Fig. 2. In the first water layer of this bilayer structure, every other water molecule forms a bond to the surface via the oxygen lone pair and two hydrogen-bonds to the oxygen lone pairs of the water molecules in the hydrating part of the bilayer (the puckered positions). Water bilayers not directly bound to the Ru surface were not strongly bound into a regular structure, i.e., the

structure is highly ordered only in the first bilayer. There is a close match (within 1.5%) between the Ru and ice lattice parameters, but Thiel and Madey show that this epitaxial relation is not essential in forming the ice-like structure on other metal surfaces, with hexagonal symmetry provided the metal lattice parameter falls within certain limits. The ice-like structures have not been observed on fcc(100), (110) or (111)-stepped surfaces of any metal, even those that form such structures on the (111) surfaces. Thiel and Madey argue that the absence of ice-like structures on these surface is not due to the lack of appropriate epitaxial relations, but to the magnitude of the bond energy of water on the differential surfaces (and at imperfections) in relation to the strength of the hydrogen bond. On numerous fcc(111) surfaces, the metal-water bond energy is equal to twice the OH--O hydrogen bond energy (21 kJ per mole of hydrogen bonds), so that the breaking of the ice symmetry to form an additional metal-water bond (e.g., lowering the water molecules from hydrogen-bonded sites to chemisorption sites) does not result in a net lowering of the surface energy. On the more open fcc surfaces such as (100) or (110), or on "rough" surfaces, the metal-water bond energy is reported to be significantly higher, by 10-20 kJ per mole, so that the ice symmetry is not favored over a structure having a greater number of water molecules bonded to chemisorption sites on the metal surface.

There is no a-priori relationship between these ice-like structures formed on fcc(111) metal surfaces at low temperature and the structure of water in the double-layer at the same metal surfaces

in aqueous solution. One can, however, construct such a relationship starting from the classical model of Bockris and Matthews [27] for the interaction of the hydronium ion with the Pt surface and the classical model [28] of tetrahedral (ice-like) coordination of water about the hydronium ion, and apply (just) the general principles of surface bonding elucidated by Thiel and Madey that give rise to long period ice-like structures, i.e., ice-like structures will occur when the hydrogen bonding forces acting parallel to the surface balance the specific metal-water/hydronium interaction acting perpendicular to the surface. Let us use these principles and classical models to construct a picture of the process of specific adsorption of (bi) sulphate ions on Pt(111) that would explain: 1) why the specific adsorption of (bi) sulphate ion would produce the anomalous features; 2) why the adsorption does not occur to the same extent (or with the same detailed chemistry) on a Pt(100) or (110) surface, nor on a "rough" (111) surface.

To use the general force-balance principle, we need to make some assumptions about the relative strengths of interactions of the various molecules involved: 1) on the atomically flat Pt(111) surface, the $\text{Pt}9\text{P}_3\text{O}^+$ bond is somewhat stronger than the $\text{Pt}(\text{H}_2\text{O})$ bond (there is some evidence for this in the recent EELS study by Wagner and Moylan [29]; 2) the $\text{Pt}-\text{HSO}_4^-$ bond energy is intermediate between that for $\text{Pt}-\text{H}_2\text{O}$ and $\text{Pt}-\text{H}_3\text{O}^+$; 3) the $\text{Pt}-\text{H}_2\text{O}$ and the $\text{Pt}-\text{H}_3\text{O}^+$ bonds are somewhat structure sensitive, with H_2O (H_3O^+) bonding slightly more strongly at steps and (100) or (110) surfaces; 4) the $\text{Pt}-\text{HSO}_4^-$ bond is strongly structure

sensitive, with the anion bond much more strongly at steps and at (100) and (110) surfaces. Following the classical model of Bockris and Matthews [24], at the potential at the minimum in the voltammetry curve between the charge for "normal" adsorbed hydrogen and the charge from the anomalous features (ϕ_{\min}), the inner Helmholtz layer is formed by H_3O^+ hydrated (according to the Boering-Madey argument for the hydrogen bonding in water) into a long-period ice-like bilayer, as depicted in Fig. 3. The incorporation of H_3O^+ into a Doering-Madey type ice-like structure is previously suggested by Wagner and Moylan [29] in their study of the coadsorption of water and HF on Pt(111) at low temperature. The orientation of H_3O^+ in such structures is consistent with the enhanced symmetric/asymmetric bend intensity ratio seen in EELS vibration spectra. Chemical intuition and charge compensation suggest the anions form the outer Helmholtz layer by occupying the high symmetry sites in the pure H_2O bilayer, as shown in Fig. 4. Note that the anions only partially charge compensate the hydronium ions, so that one could refer to this structure in classical terms as "super-equivalent" hydronium ion adsorption. The structure of successive layers forming the diffuse double-layer would logically become progressively less ordered, since the anion layer (the OHP) becomes the ordering template, but the anions are only weakly hydrated and the ordering force is dissipated. There is ample precedent for the formation of charge compensated bilayers on Pt(111) in this potential region indicated in the studies by Hubbard and co-workers [30-32]. As the potential is made anodic to this potential (ϕ_{\min}),

protons are driven out of the IHP and the anions are drawn towards the metal surface due to the (+) potential field from the Pt surface. The hump in the I-V curve corresponds to the change in capacitance of the inner-layer due to this deprotonation. According to the structural model of Fig. 4, the charge under this hump could be as high as $1/3 e^-$ per Pt atom (or about $85 \mu\text{C}/\text{cm}^2$) depending on the interaction of the proton on H_3O^+ with the Fermi sea of the metal at ϕ_{min} . In the limit of strong interaction, this model corresponds to the original Clavilier interpretation of the hump as "hydrogen desorption." As the potential is made cathodic to ϕ_{min} , protons are discharged and adsorb onto the Pt surface in the classical manner [24]. However, since classical electrochemical "pictures" of the interface did not depict the structure parallel to the surface, it was not widely appreciated that at any instant in time one-third of the surface atoms are not coordinated to a water molecule, i.e., even if one does not invoke the ice-like structure for water in the double-layer, the water molecules cannot be more densely packed in the plane of the surface than in this structure. Thus, if the bonding of hydrogen to the surface is affected by interaction with water molecules in the double-layer, then it is easily seen from Fig. 3 that there are three different energetic states for hydrogen on Pt(111), one having no direct association with a water molecule. It is not merely coincidental, therefore, that a significant fraction of the hydrogen on the Pt(111) surface has exactly the same heat of adsorption in solution as in vacuum [9]. Returning again to the capacitive hump anodic to ϕ_{min} , the deprotonation of

the inner-layer is followed, at more anodic potentials, by displacement of water from the inner-layer as well and the "contact adsorption" of the (bi)sulphate anion. As shown in Fig. 4, the model structure indicates that the sharp spike in the anomalous feature is the contact adsorption of the anion with the Pt surface, 1 anion being adsorbed for every 9 Pt atoms, into a (111)-3 x 3 ordered anionic superlattice.

I cannot emphasize too strongly an important aspect of the model presented here: there are no processes occurring in the anomalous features that do not occur on all Pt surfaces!! What is different about the well-ordered (111) surface from all other Pt surface morphologies is that these processes occur in a much narrower potential region. The narrowing of the potential region where these processes occur is due to the ordered structure of the double-layer at the well-ordered (111) surface, a structure which does not occur on other surface morphologies, as will be discussed in greater detail below. As the structural model presented here indicates, the anomalous processes are all phase transitions, and the capacitive current observed in the I-V curve corresponds to the change in the concentration of ionic charge in the inner layer, from 5.4×10^{14} hydronium ions per cm^2 to 0.2×10^{14} (bi)sulphate anions per cm^2 . It is difficult to make the model quantitative at this stage, because the absolute values of the capacitance and the capacitive currents depends on more precise knowledge of the degree of interaction of these ions with the electron sea of the Pt surface. Back-of-the-envelope type calculations suggest the model produces capacitance and capacitive

currents consist with experiment. Consider the change in ionic concentrations cited above, and assume the change in "effective charge" in the inner-layer is $50 \mu\text{C}/\text{cm}^2$ (the maximum possible value is $115 \mu\text{C}/\text{cm}^2$). On a polycrystalline Pt surface, these same capacitive processes occur in the normal "double-layer potential region, from 0.3 V to 0.8 V (RHE). Then, we can approximate the capacitance as $C = dq/dV = 50/0.5 = 100 \mu\text{F}/\text{cm}^2$, and the characteristic current at 0.1 V/s as $10 \mu\text{A}/\text{cm}^2$. These are typical of the capacitance and current in the double-layer region observed with polycrystalline Pt. On the well-ordered (111) surface, these same capacitive processes occur over a much narrower potential, about 100 mV, so $C = 50/0.1 = 500 \mu\text{C}/\text{cm}^2$ and $i = 50 \mu\text{A}/\text{cm}^2$ at 0.1 V/s. Note these estimated capacitive currents are, respectively, characteristic of the current for the sputtered (111) surface (Fig. 1b) and for the anomalous features on the annealed (111) surface.

The discussion of anion adsorption from dilute sulphuric acid has used the term (bi)sulphate to refer to the anion. The ambiguity is intentional. The local pH of in the IHP is therefore much lower than in the bulk and the predominant anion species in the OHP may then be sulphate, rather than the bisulphate anion, which is the predominant anion in the bulk. It is, however, not obvious which of these species is adsorbing, and thus the ambiguous designation.

Why are the anomalous features so specific to the well-ordered (111) surface, and not to (100), (110), or a (111) with a critical level of roughness? The answer to this question, in terms of the

model presented here, was alluded to above, but is worth discussing in further detail. The key to the structure sensitivity, indeed to the entire phenomenon itself, is the formation of the ordered hydronium ice-like network in the double-layer. The formation of this network requires that a delicate balance be achieved between relatively weak bond forces, as articulated so elegantly in the discussion of water on metals by Thiel and Madey. The hydrogen bonds are very directional and very sensitive to bond length. The points of attachment of network to the metal atoms must therefore have hexagonal symmetry, a condition which cannot be met on the (100)-1 x 1 (the unreconstructed) surface. As Thiel and Madey have shown, it is possible to construct a ice-like network on an unreconstructed fcc(110) surface like Ag(110), but the Pt(110) surface is reconstructed to a 2 x 1 "missing row" [33] structure which is stable even in acid electrolyte [9]. The missing row structure is a sawtooth-type structure, and the vertical articulation of the surface makes it impossible to form the hydrogen-bonded network. In the case of step-terrace structures [17,18], where the anomalous features are seen to depend on a critical length of the (111) terraces, apparently there is a critical ensemble size to form not only the hydronium network inner-layer but the full ordered double-layer. Note in Figs. 3-4 that a complete (bi)sulphate 3 x 3 unit cell requires a perfectly flat Pt domain six atoms on a side, which is consistent with the experimental observation of 5 or more as the critical terrace length.

Let us now extend the long-period hydronium ice-like model for the IHP on Pt(111) to explain the observations in electrolytes other than sulphate. In acid chloride, both the observations and the model carry-over directly from the case of sulphate. In fluoride, perchlorate, bicarbonate and hydroxide, in which the anomalous features shift considerably in both potential and appearance (especially in the basic media) from sulphate, another model is needed. Both (bi)sulphate and chloride are large weakly hydrated anions, and in the double-layer model of Figs. 3-4, they interact strongly with both the hydronium ions and the Pt surface. The contact adsorption of these anions screens the net (+) image charge on the metal surface from the water molecules in the OHP, so that much higher fields (anodic potential) are required to cause water dissociation and "OH" formation on the surface. Fluoride especially is a small strongly hydrated anion, which does not interact strongly either with hydronium ion or the metal surface, and does not screen the potential field of the metal atoms from the water in double-layer. To account for these fundamental differences in physical properties, it is necessary to construct a double-layer model which retains certain basic elements of Figures 3-4, but is very different in essential features. Because the fluoride ion has weak charge compensating properties, the "super-equivalent" hydronium ion layer cannot form the IHP. Instead, I suggest formation of a Doering-Madey long-period ice-like layer with hydronium ions alternately in the first and second bilayers and insertion of fluoride ions into the more dense 2X2 packing positions in the second

bilayer. The latter achieves a nearly charge compensated double-layer at ϕ_{\min} , and the view of this structure parallel to the surface would look a great deal like the classical DBM [24] double-layer model. Thus, replacement of (bi) sulphate ion with fluoride ion has two effects on the double-layer structure: a) it reduces the interaction of hydronium ion with the Pt surface because this interaction is intrinsically a cooperative interaction; b) the potential field from the metal is relatively unscreened by the anions. The consequence of these effects are to eliminate the phase transitions in the IHL at ϕ_{\min} due to deprotonation and anion adsorption, and instead cause phase transitions at higher potential associated with dissociation of the water molecules in the IHL to form ordered OH structures. As before with sulphate, I argue that no electrode processes take place on Pt(111) in fluoride electrolyte that do not also occur on other Pt surfaces in the same electrolyte. The crucial difference between these processes on Pt(111) and on other Pt surfaces is again the squeezing of the potential region in which these processes take place due to the ordered structures, i.e., transitions from one ordered phase to another in a narrow range of potential (I resist the temptation to give these transitions an order, e.g. first order phase transition, until more is known about them). Potential cycling experiments [20] that progressively roughen the surface clearly show that of the 80-90 $\mu\text{C}/\text{cm}^2$ under the anomalous features at 0.6-0.8 V, about 25% of that charge reappears in the "normal" hydrogen region, while the remaining charge is spread anodically into the "oxide" formation po-

tential region. This redistribution of charge with loss of surface order is consistent with the model. Roughening breaks the long-period ice-like structure of the double-layer, which changes the association between water and adsorbed hydrogen producing a redistribution of charge among the three different states of hydrogen on the (111) surface, and some increase in total charge due directly to the increase in the roughness. The "OH" formation process, which could be termed a UPD state of oxygen, moves towards the oxygen Nernst potential due to a lowered free energy of formation on the disordered versus the ordered surface. The process is also no longer a transition between ordered phases, and the charge becomes smeared out in potential.

IV. The Path to Definitive Models of the Anomalous Processes

The path of discovery in the great period of atomic physics from ca. 1920-1940 has become a model for the process of intellectual discovery which social scientists term "the scientific method." Briefly stated, the inquiry begins with the observation of anomalous behavior, e.g., the Stark effect, so termed because the observations are totally new and the results inexplicable in terms of current theory. Others try to duplicate the observations, with usually contradictory results, and a period of controversy ensues until eventually a consensus emerges defining the nature of the phenomena. Hypothetical models are presented which attempt to explain the new behavior, and theorists and experimentalists alternate in disproving one hypothesis and bringing forth a new one, until eventually a model evolves that explains all observations. The purpose of this talk has been to put

the study of the anomalous electrochemical behavior of Pt(111) into that same type of intellectual framework. Following a period of controversy concerning the experimental observations, there has emerged a consensus concerning the valid data set that describes the anomalous behavior, which was summarized here in Table I. We are now at the stage of inquiry where hypothetical models are needed to initiate the next stage in the process of discovery. I have attempted to present such a model here. I hope that this model will stimulate theorists to use it as a basis for calculations of free energies of formation of the ordered phases and the corresponding capacitances. These calculations should give rise to new and more refined models, and guide experiments designed to test the new theory. The key to activating this traditional cycle of theory and experiment is entry of theorists, who have so far remained on the sidelines while the experimentalists sort out the valid observations.

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Table I. Summary of observations of the anomalous features.

o	Appearance of anomalous features on Pt(111) requires critical degree of long-range order, e.g., perfectly ordered domains 12-25Å
o	Potential region depends on the type of anion, and anion concentration and pH as follows:
In sulfate and/or chloride	cathodic shift with increasing C_{A^-} at constant pH no shift vs. SCE at constant C_{A^-} with varying pH
In perchlorate fluoride, carbonate and/or hydroxide	no shift with increasing C_{A^-} at constant pH 59 mV/pH vs. SCE at constant C_{A^-} with varying pH
o	In sulfate and/or chloride, there is a conservation of charge integrated under the potential region for "normal hydrogen" and the anomalous features with $Q \approx 280 \mu\text{C}/\text{cm}^2$. Roughening causes the normal hydrogen charge to increase with a commensurate decrease in charge for anomalous features.
o	In fluoride, perchlorate and/or hydroxide, there is no simple conservation of charge between the normal hydrogen region and the anomalous features. Roughening causes redistribution of charge both anodic and cathodic to anomalous features.

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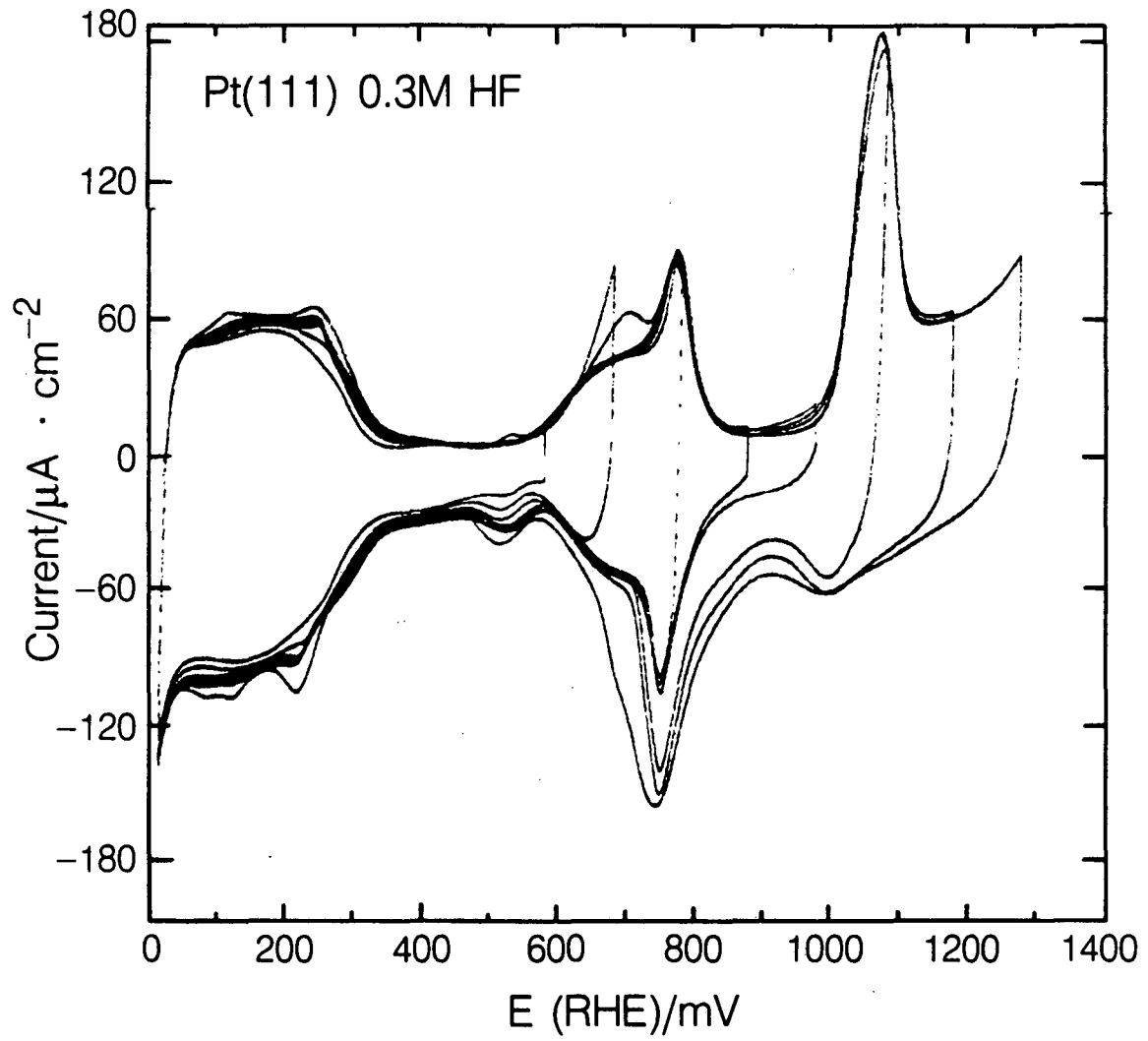
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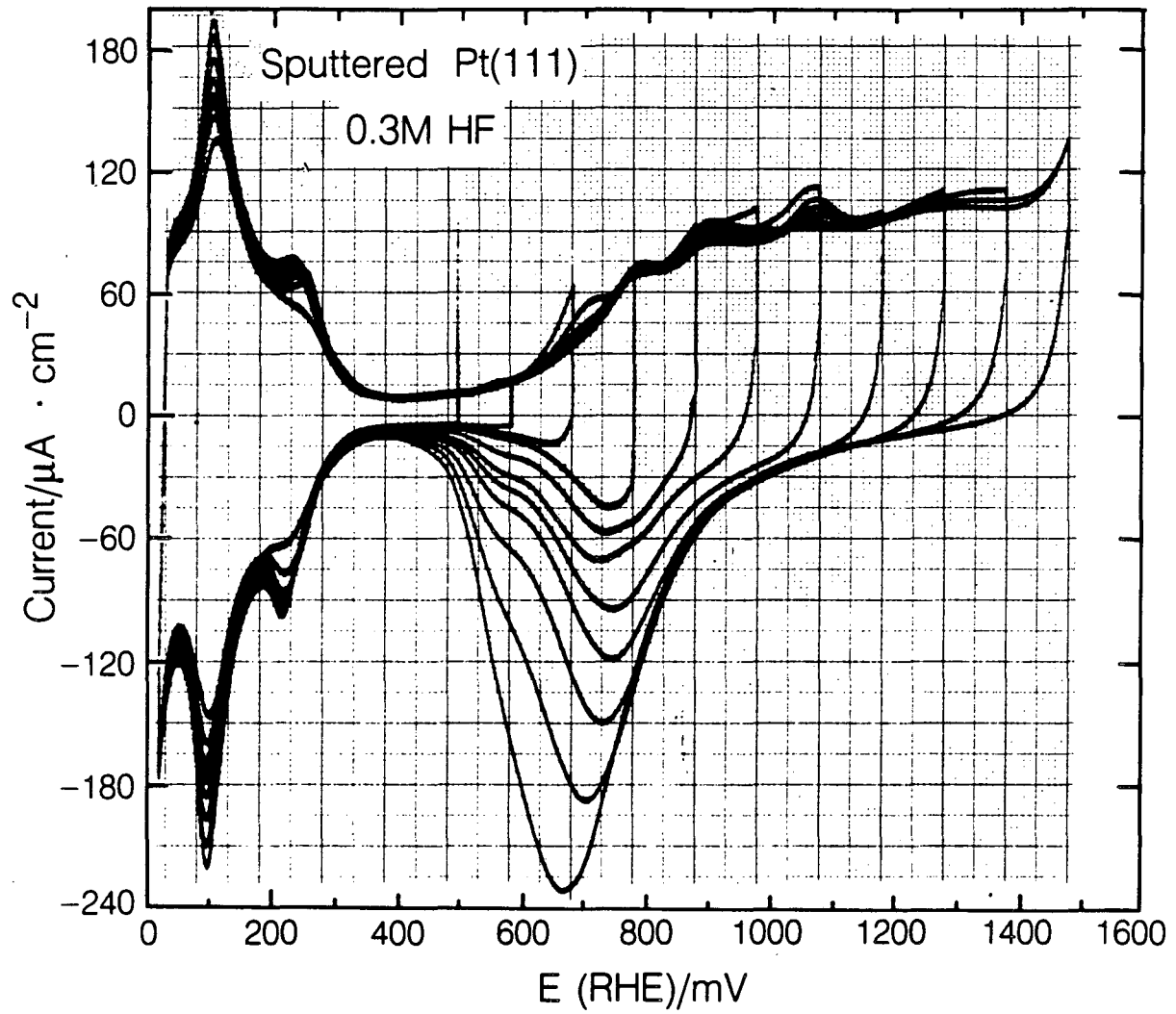
Figure Captions

- Fig. 1. a) Cyclic voltammetry curve recorded from a UHV prepared, well-annealed Pt(111) crystal in dilute HF electrolyte. Crystal was immersed under potential control at 0.6 V (RHE) and swept cathodically to the limiting potential; b) same experiment performed with the same crystal but not annealed after ion-bombardment.
- Fig. 2. Model for long-period ice-like structures on fcc (111) or hcp (001) surfaces proposed by Doering and Madey [26]: a.) view perpendicular to fcc (111) surface; b.) view parallel to (111) plane.
- Fig. 3. Model for a hydronium ion inner layer on the Pt(111) surface derived from the long-period ice-like structures of water on metals at low temperature.
- Fig. 4. (a.) Model for the double-layer structure on Pt(111) as viewed both normal to (111) plane and parallel to the surface at the potential ϕ_{\min} . The potential ϕ_{\min} is defined in the voltammetry curve (b.).
- Fig. 5. Model showing deprotonation of the inner layer as the potential in the potential region between ϕ_{\min} and ϕ_{dip} . Protons are transferred to outside the OHP by the conventional Grotthus mechanism.



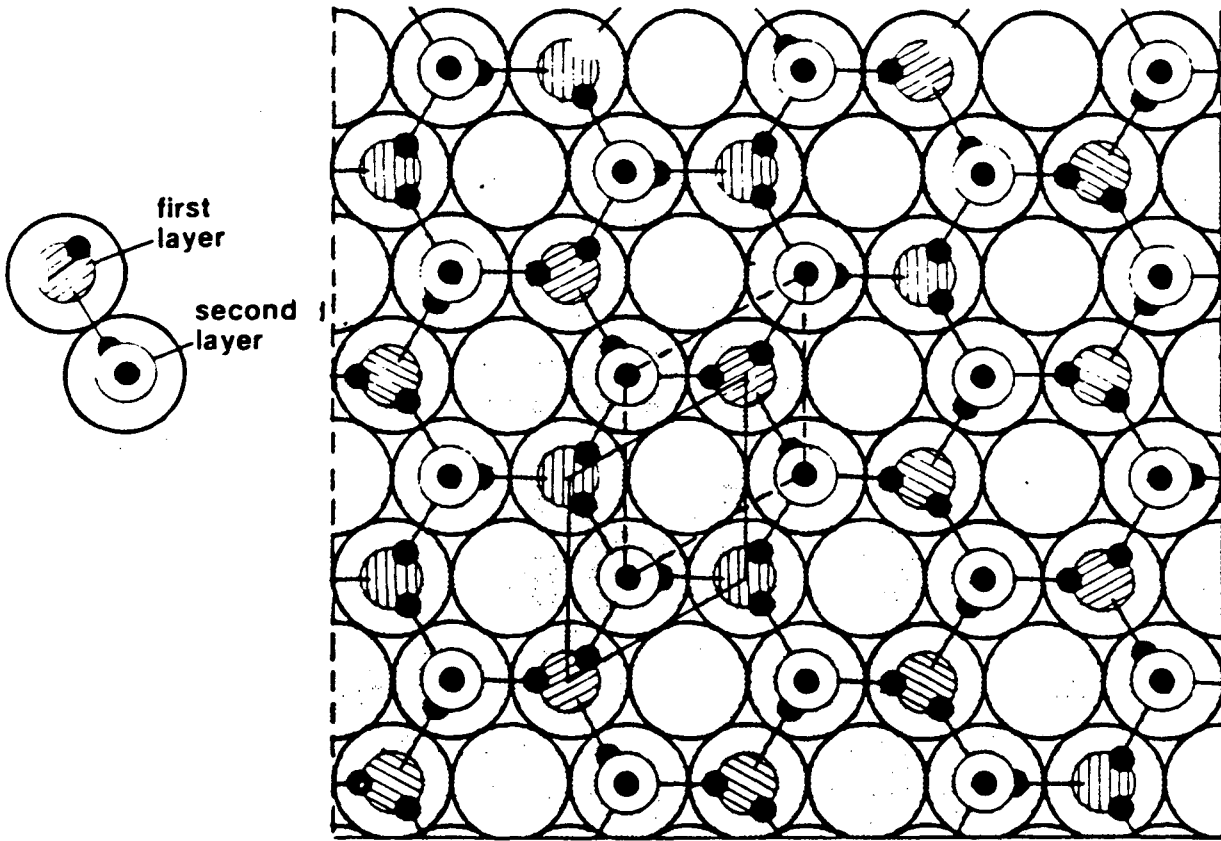
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Fig. 1 a



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Fig. 1 b



Side View Adsorbed Ice I_h

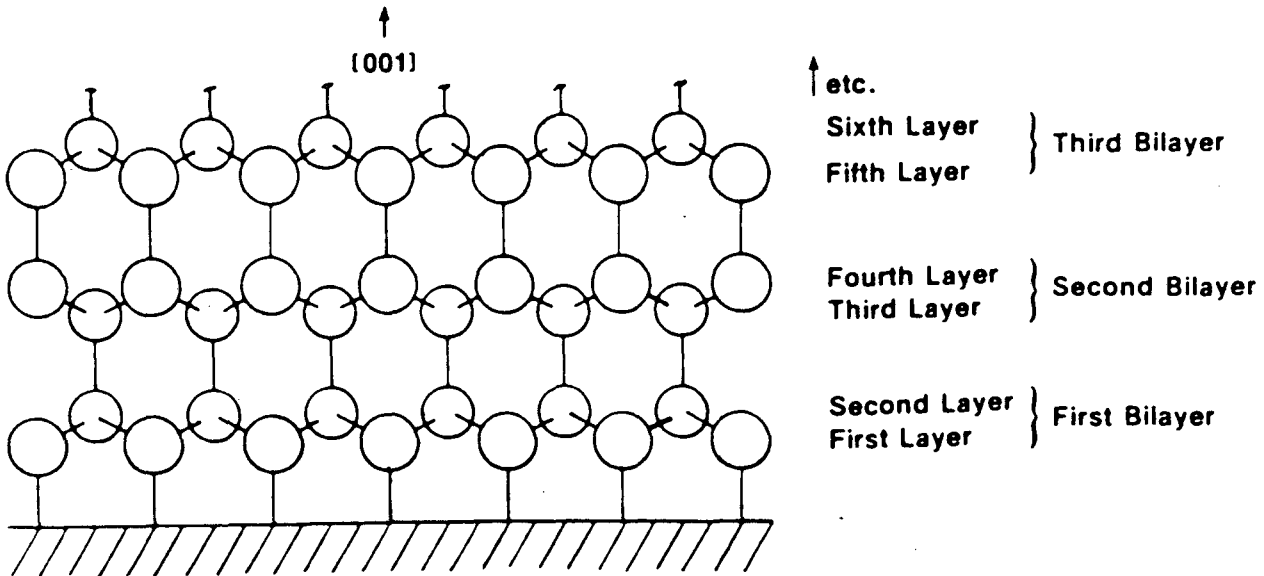


Fig. 2 a & b

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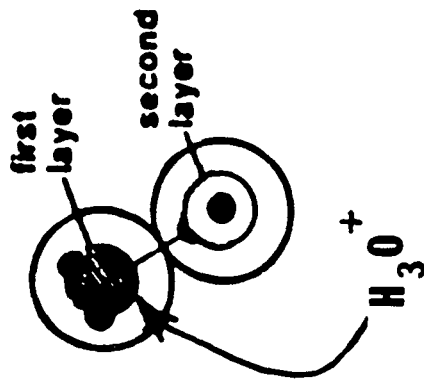
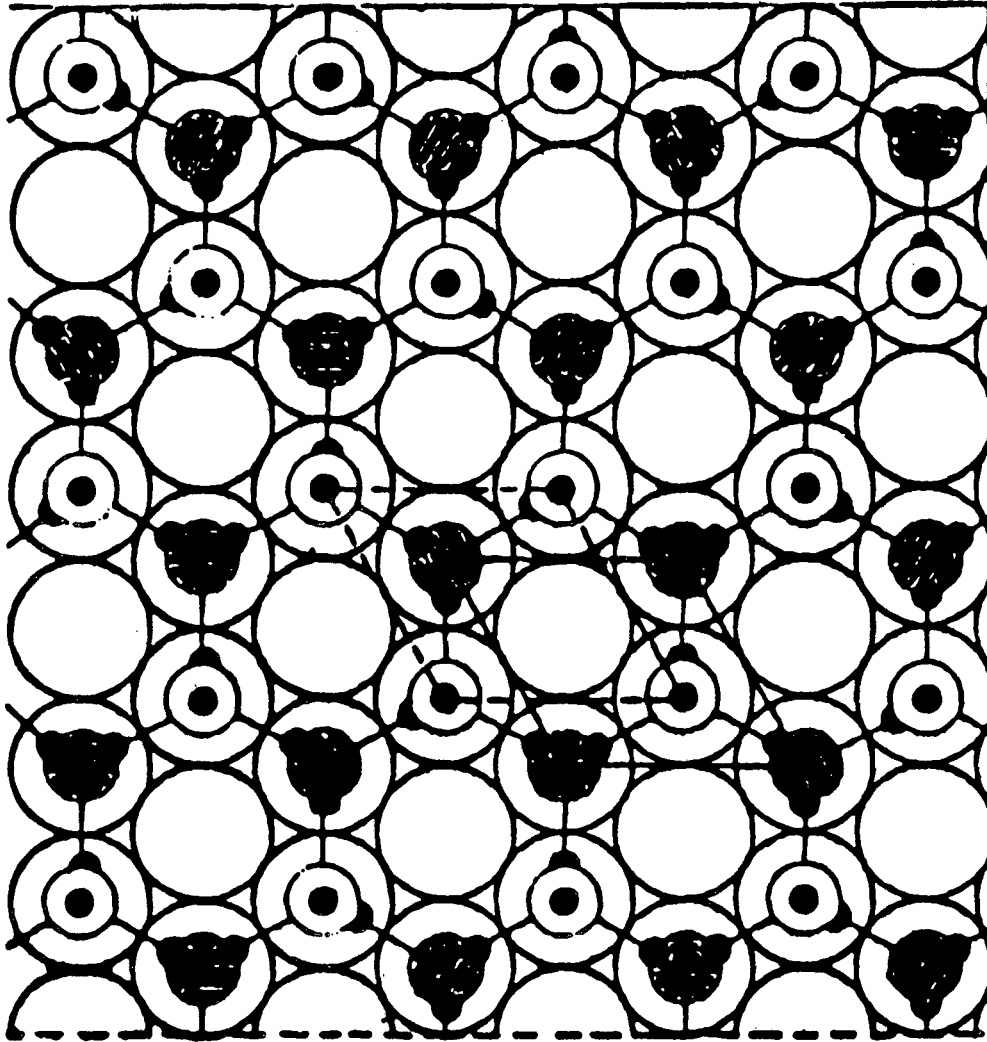
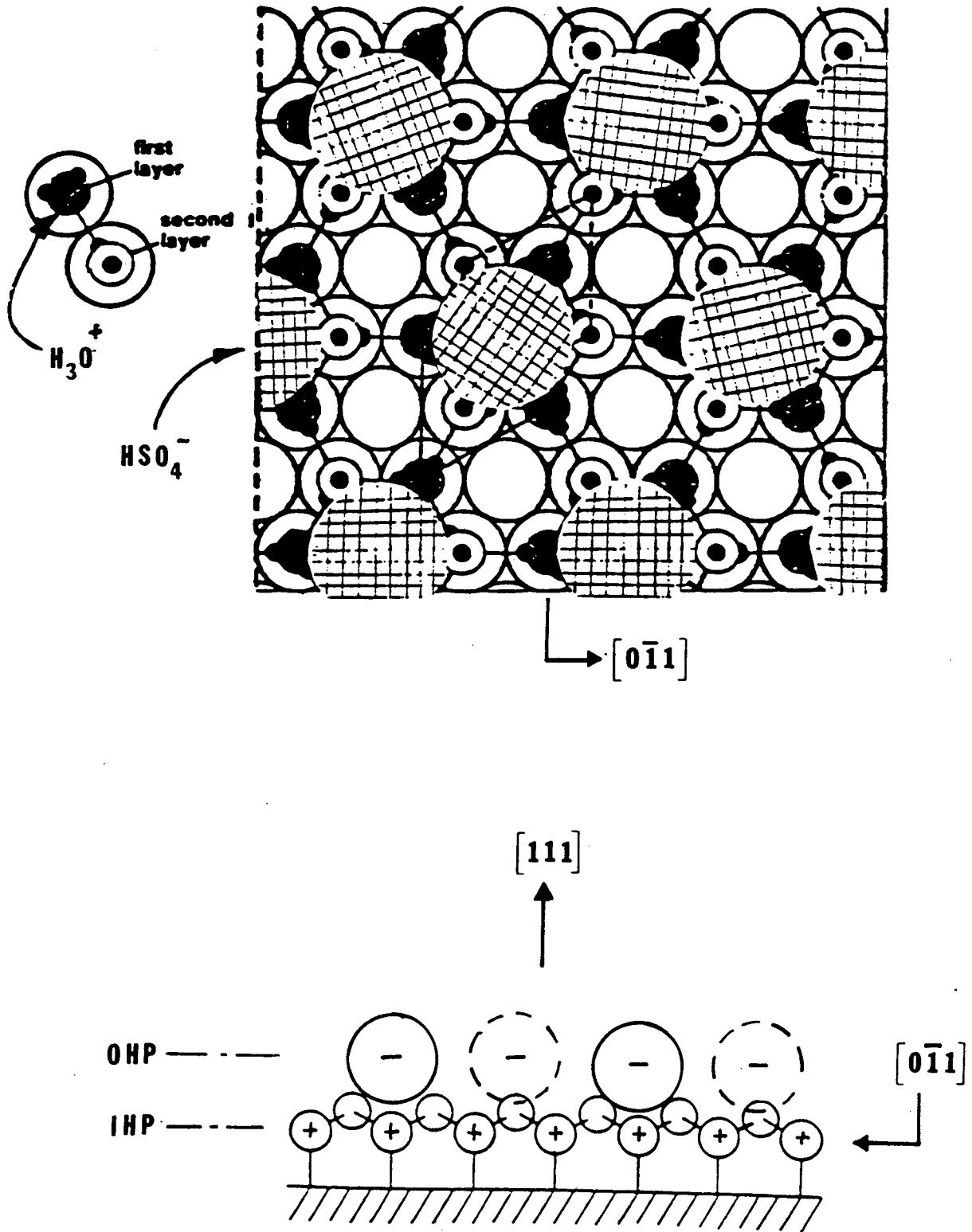
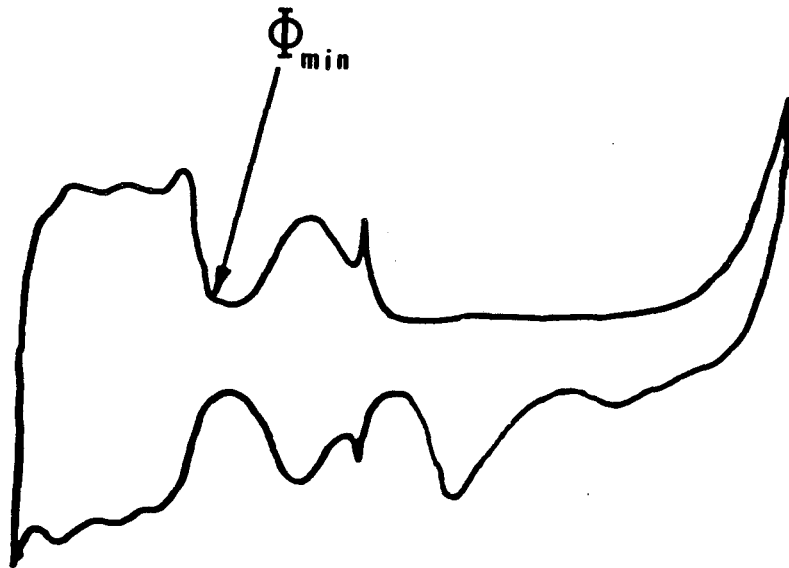
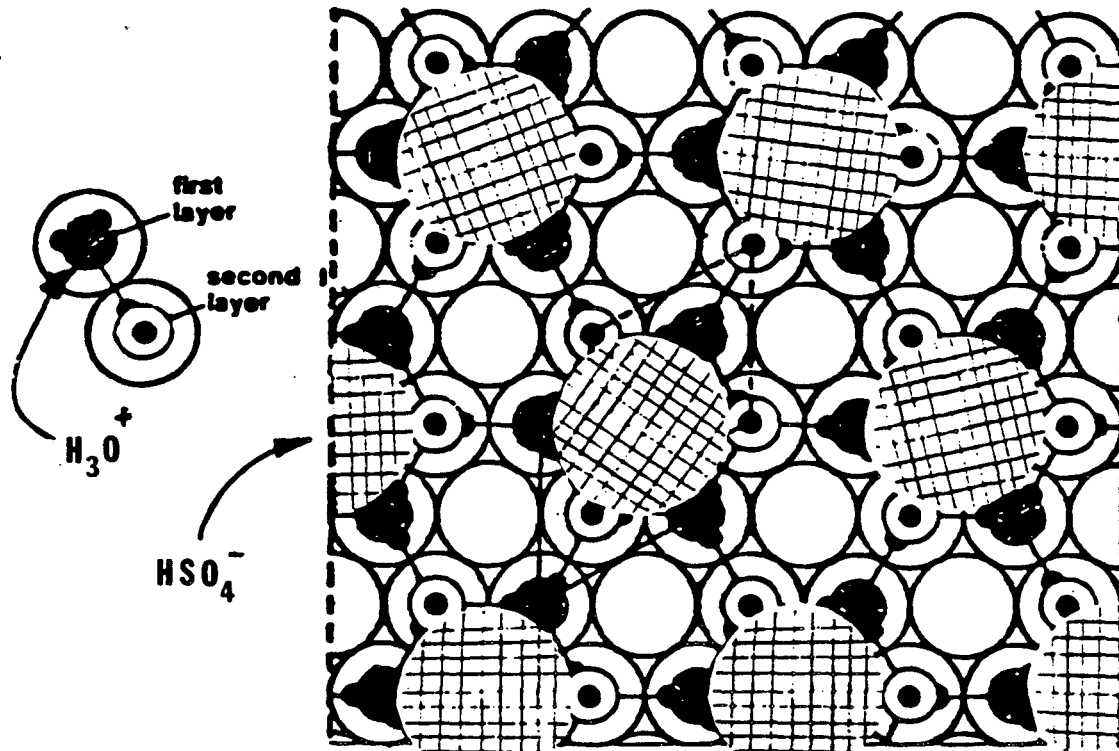


Fig. 3.



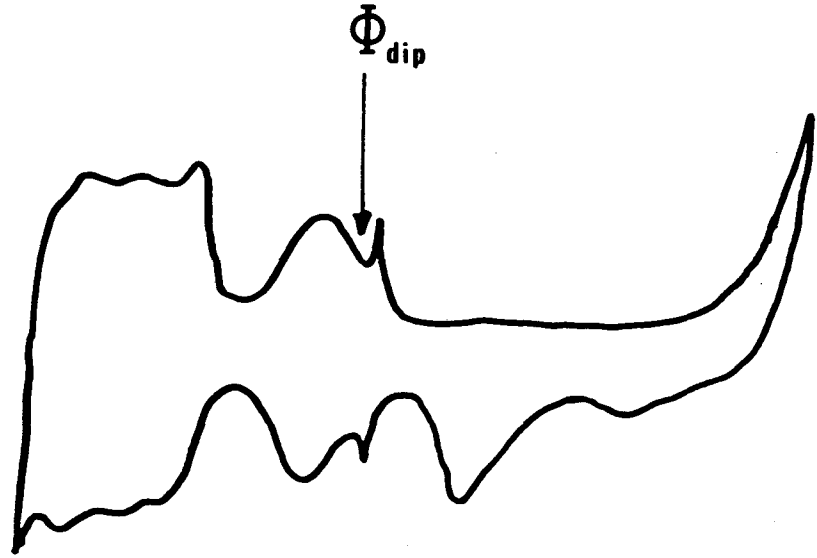
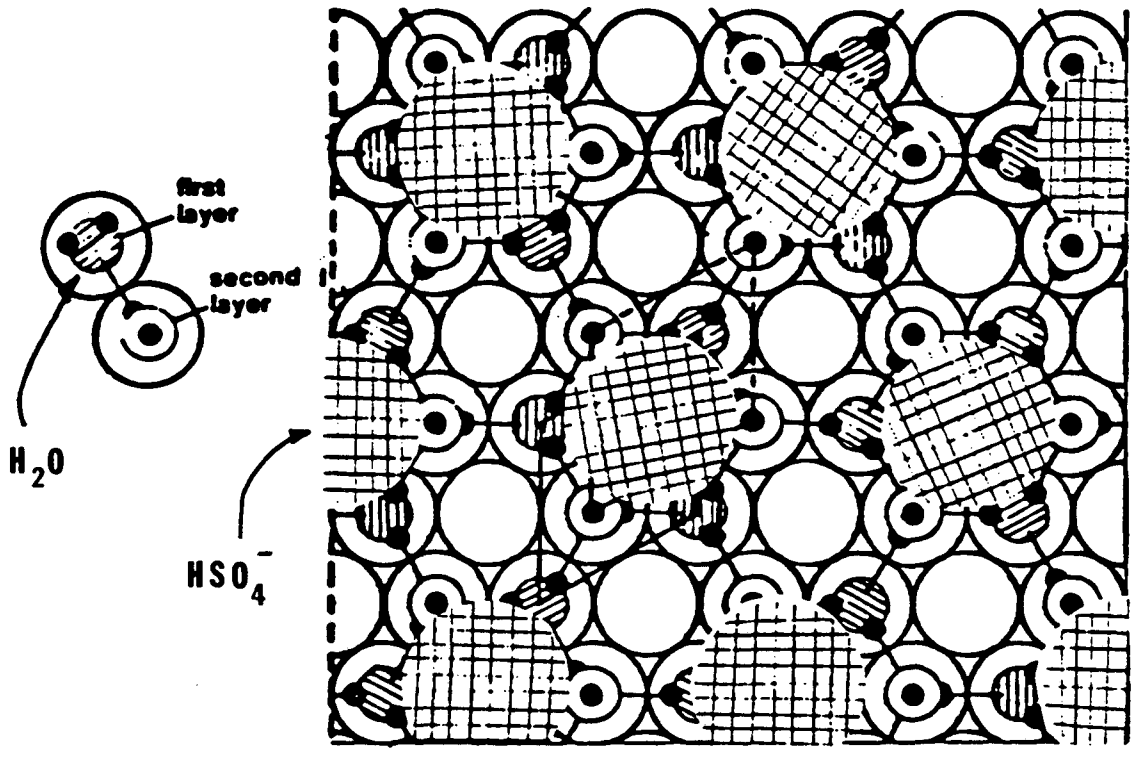
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Fig. 4 a



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Fig. 4 b



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Fig. 5

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