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Publication Date

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of the American Vacuum Society, Baltimore, MD,
October 17-31, 1986; and to be published in
Journal of Vacuum Science and Technology

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August 1986

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STRUCTURE-PROPERTY RELATIONS FOR
SURFACE PROCESSES AT THE METAL/SOLUTION INTERFACE

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ABSTRACT

The recent development of special apparatus coupling electroanalytical cells directly to UHV surface analytical chambers has made possible definitive determination of structure-property relations for processes at metal electrode surfaces. The results have been surprising. The process of submonolayer metal ion deposition (so-called underpotential deposition) exhibits unexpected sensitivity to long-range order in the substrate, indicating that lateral bonding forces are of the same magnitude as the perpendicular bonding force. On a well-ordered Pt(111) surface, unexpected new surface processes have been observed that are unique to this surface, i.e. are not seen on either (100) or (110) surfaces, nor on polycrystalline surfaces. It appears that the new processes are associated with atomically flat regions of the (111) surface with a critical region size that is quite large, at least 2 nm. It is suggested that cooperative interactions in the double-layer form a critical ensemble that react to form the new surface species. However, much further study utilizing in-situ spectroscopy will be required to understand this new surface process in Pt(111).

INTRODUCTION

Within the last decade, a number of electrochemical research groups around the world have developed a new type of research apparatus uniting UHV surface analytical techniques with electroanalytical cells (1-6). At the same time, Clavilier and co-workers (7-9) developed what we now call the "bead-method" for preparing clean, well-ordered surfaces of the low-index planes of platinum and gold by laboratory methods (not requiring UHV systems and the usual methods of ion-sputtering and thermal annealing). Independent analyses of the structure of "bead-method" surfaces with LEED by other groups has confirmed the clean, ordered structure of these surfaces. The development of the bead-method has enabled a larger spectrum of electrochemists (not having or wanting UHV systems) to contribute in a meaningful way to single crystal electrochemistry. Together, the combined progress produced by these developments in experimental methods has made possible the definitive determination of structure-property relations for a number of electrode processes at metal surfaces. The growth in the number of such studies has been so rapid in recent years that it is not possible to review them all here without doing injustice to some important areas. Instead, I will emphasize new results from the study of selected electrode processes at the low-index surfaces of platinum that have come out of several laboratories world-wide in the last decade. In particular, I will review: i.) surface structure transformations produced by anodic film formation; ii.) evidence for strong lateral interaction in

submonolayer metal-ion deposition (or underpotential deposition, UPD) processes; iii.) anomalous adsorption phenomena on Pt(111).

ANODIC FILM FORMATION ON PLATINUM

The details of the process of anodic oxidation of platinum surfaces in aqueous electrolytes has long been sought after by electrochemists, and the volume of literature on the subject is staggering (a bibliography can be found in the recent review paper by Conway (10)). Using purely electroanalytical methods and carefully constructed arguments, Conway and co-workers (11) established a model for anodization which has served as a guidepost for studies in the past decade. This model proposed a series of oxidation steps which change as a function of electrode potential and time at a fixed potential. As shown in Fig. 1, the initial oxidation (in acidic solution) in the potential region 0.8 - 0.93 V(RHE[†]) was ascribed to reversible hydroxylation (i.e. chemisorbed OH) of the surface. Above 0.93 V, place exchange between adsorbed hydroxyls and Pt surface atoms occurs, and kinetic irreversibility sets in, together with attendant complex aging phenomena. Concomitant with place exchange is an oxidative deprotonation of hydroxyls to form -OOH type surface species.

Recent work with UHV analytical techniques have produced results which are consistent with many aspects of the Conway model, particularly with respect to the place-exchange process. LEED analysis (3,12) of the surface after anodization has been used to

[†]RHE, a reversible hydrogen electrode in the same electrolyte.

identify unambiguously the onset of the place exchange process, and to give new insight into the process. The results of the LEED analysis of Wagner and Ross (12) for Pt(100) are summarized in Table I. The critical amount of anodic charge for the onset of place-exchange was found to be equal to that for a monolayer of an -OH type species, i.e. place-exchange is the process by which more than one -OH per Pt surface atom is accomodated. No evidence has been found by LEED that the place-exchanged layer is ordered, in fact it appears that place-exchange produces a disordered structure. Upon cathodic reduction following place-exchange, the displaced Pt atoms do not return to their original positions in the surface lattice, but they occupy fcc lattice positions on top of the original surface. Place-exchange only involving displacement of atoms from the surface layer necessarily creates a three-level structure, the displaced-atom level, the original surface plane, and a vacancy level. The LEED spot profile analysis indicated a high degree of correlation in displaced-atoms and vacancies, which Wagner and Ross (12) have interpreted as an island-hole structure, i.e. cathodic reduction leaves adatoms and vacancies that migrate and nucleate into islands and holes, respectively. As might be expected from this picture, anodization to higher charges causing displacement of more than one layer leads to a more than three level structure and the evolution of a randomly stepped surface with a substantial degree of vertical displacement of atoms originally in the surface plane.

Spectroscopic analyses have complemented these LEED studies in developing a more detailed understanding of the chemical nature of the

anodic surface layer on platinum. A number of different surface analytical methods have recently been used for the analyses of emersed Pt electrodes, and the results have been in substantive agreement with respect to the chemical nature of the anodic layer. Among the methods that have been used are XPS (13,14), AES (16), TDS (14,16), SIMS (16), EELS (15,17), and EMIRS (18). These methods have not all be used in the same study, but even when applied independently have provided complementary information on stoichiometry (TDS, AES, SIMS), valence (XPS), and functional groups (EELS, EMIRS). These spectroscopic methods have clearly established that the anodic layer formed on Pt in acid electrolytes in the potential region from 1.2 - 2 V (RHE) is an hydroxyl (-OH) structure, and little or no evidence for either an oxyhydroxide (-OOH) or hydrated oxide (-O.H₂O) has been found. As we have emphasized before (3), and I re-emphasize here, ex-situ surface analytical methods can only be used to study surface species that are irreversibly bound due to the very nature of the emersion process, and in the case of anodic layers on Pt this limits the use of these methods to the study of only the irreversible (i.e. place-exchanged) state. Unfortunately, none of this recent spectroscopy provides direct evidence for the identity of the kinetically facile species formed at potentials below ca. 1 V (the potential region of interest for fuel cells). Direct identification of these species will have to come from in-situ spectroscopies yet to be developed. It is still unclear exactly how the place-exchanged film grows, and what stoichiometry the film has as a function of thickness. Peukart and co-workers have suggested a model in which the film grows as the

progressive expansion of Pt (+IV) nuclei evolving into a Pt(OH)₄ structure upon extensive anodization, i.e. there is no intermediate (+II) hydroxide stage as postulated in the models of Conway and co-workers.

UNDERPOTENTIAL DEPOSITION OF METALS

When a metal-ion is either partially or completely discharged at the surface of a dissimilar metal, it is often the case that the free energy of formation of the adatom state is more negative than the free energy of formation of the bulk phase of that metal. In such cases, the discharge occurs at a potential "under", i.e. cathodic to, the potential for the deposition of the bulk phase, giving rise to the terminology underpotential deposition (UPD). Electrochemists have been interested in the details of this electrode process both because of its possible technological consequences in electrocatalysis (19) and metal deposition (20) and also because it is interesting surface chemistry in and of itself. The early studies of UPD employed polycrystalline electrodes on which one usually observed multiple states, leading to the reasonable supposition that the multiple states were related to the heterogeneity of a polycrystalline surface. Single crystal studies of UPD appeared in the electrochemical literature before the general availability of UHV systems and LEED, and prior to 1980 there were no reports of UPD studies that used UHV prepared single crystal surfaces (with surface structures confirmed by LEED analysis). The utility of the studies with mechanically polished x-ray (Laue) oriented crystals is therefore

questionable, and key systems will have to be re-examined with the new analytical systems now available. UPD studies from the period prior to 1980 have been reviewed by Kolb (21) and by Lorenz and Juttner (22). In spite of the uncertain reliability of these studies, they have helped to define the key issues in what is really a much more complex chemical process than the stoichiometry would suggest. Certain common features were apparent when UPD on low index single crystals was compared with observations on polycrystalline electrodes: i.) multiple states were observed even on well-ordered structurally homogeneous surfaces; ii.) the isotherm for a given state exhibited a narrower than Langmuirian distribution function; iii.) assuming complete discharge of the ion, the coverage by adatoms at potentials approaching bulk deposition was often much less than a monolayer. The complexity of the UPD process indicated by these early single crystal results produced an expected divergence of views on the interpretation, e.g. two-dimensional nucleation, phase transitions, solvation changes, etc., with the missing critical factor that would discriminate among these models being the structure of the adatoms on the surface. It was anticipated that UHV surface analytical methods might provide this critical structure determination at least for some "classic" cases.

The use of UHV analytical systems for structure determination of UPD adlayer surfaces has an intrinsic problem in that one cannot be certain that the structure observed in UHV is the same as the structure the adlayer has in solution. The problems and uncertainties arise due to the process of "emersion" (removal of the crystal from solution with loss of potential control) and vacuum evaporation of retained electrolyte from

the surface. In this author's view, it is essential to use the UHV and electrochemical techniques one has in these systems to study the stability of the UPD adlayer to the emersion/evacuation process. We have outlined the methods that can be used to test the stability of UPD adlayers and have given some examples of stability tests in another review (3). The most extensive use of ex-situ LEED analysis for the determination of the structure of UPD layers on Pt single crystal surfaces has come from Art Hubbard's group (23-25). Hubbard's group paid careful attention to the question of stability of the UPD adlayer to the emersion/evacuation process, and found that it was necessary to "protect" the adlayer by doing the deposition in the presence of iodide, an anion that is very strongly adsorbed on platinum surfaces. In supporting electrolyte with non-adsorbing anions like perchlorate, Hubbard's group found that even copper and silver adatoms (whose corrosion potentials are relatively anodic) are unstable, and are discharged during emersion/evacuation. Presumably, adlayers of metals having lower corrosion potentials than either copper or silver, such as the electrocatalytically interesting systems with Pb, Tl, Sb, Sn and Ge (19), would be unstable in electrolytes not containing iodide. The mechanism by which iodide "protects" the adlayer from discharge is not clear, nor is it known whether other anions less strongly interacting with platinum, e.g. chloride or sulfate, would have a similar effect. There appears to be considerable skepticism in the electrochemical community concerning the general utility of ex-situ LEED analysis for UPD adlayer (or double-layer) structure determination because of these stability questions.

There are other ways in which the new UHV/electroanalytical systems have been used for the study of UPD phenomena that for the most part avoid the problems and uncertainties related to the emersion/evacuation process. One is the relatively simple and straightforward use of the UHV analytical system to prepare the surface of the metal single crystal, characterize the UHV surface structure, and provide clean transfer of the crystal to an electroanalytical cell so that at the instant of physical contact with electrolyte the surface has a homogeneous well-defined structure. Another application is the use of post-test LEED analysis to look at "footprints" electrode processes "leave" on the surface. An example of both these applications in the study of the UPD of copper on platinum single crystal surfaces (26) can be seen in the results shown in Figs. 2 and 3. Figure 2 shows the voltammetry for copper deposition/dissolution from the three low index faces of platinum surfaces prepared in UHV and characterized by LEED (for the non-electrochemist reader, voltammetry is analogous to thermal desorption spectroscopy in gas-phase studies, with the potential bias applied to the electrode changing the surface energy analogous to the effect of temperature on surface energy). The results were dramatically different (Fig. 3) from the same crystals if they were ion-bombarded but not annealed, as seen by comparison of Figs. 2 and 3. Although the binding energies (the potential of the UPD peak maxima) were affected only slightly, the widths of both the deposition and dissolution peaks were greatly increased, and in the case of the (111) surface the multiplicity seen on the well-ordered surface was essentially wiped out by the introduction of disorder. LEED spot-profile analysis made after several

deposition cycles, i.e. where less than a monolayer was deposited and stripped several times, indicated no change in the platinum surface structure had occurred as a result of these processes. However, when more than a monolayer was deposited and stripped, LEED spot-profile analysis clearly showed displacement of platinum surface atoms from their original positions in the low index surface, i.e. a "footprint", indicating that place-exchange between the deposited copper atoms and platinum (surface alloying) occurred during the growth of multilayers of copper.

The sharpness of the voltammetry peaks for copper UPD on Pt(111) and (100) are a challenge to current theory (27). While current theory can explain peaks somewhat narrower than Langmuirian by use of nearest-neighbor interaction models, the occurrence of peaks with an FWHM of only 15 mV and coverages of less than half a monolayer cannot be accounted for with such models. In addition, the strong dependence of the FWHM on the size of atomically flat regions of the surface suggests long-range interactions as very important phenomena in some types of electrode processes is one of the principle new conclusions to be derived from recent work with single crystal metal electrodes.

Few would argue that an in-situ method for electrode surface structure determination is preferable to an ex-situ method, and there are now a rapidly growing number of research groups pursuing the development of in-situ methods. Among the methods being pursued are scanning tunneling microscopy (STM), grazing incidence x-ray diffraction (GID), and extended x-ray absorption fine-structure analysis (EXAFS). Electrochemists are not, of course, the only surface scientists

not yet enough results from these new studies to review here, but the preliminary findings from several groups have shown promise and there are reasons to be optimistic about the eventual development of these techniques for the study of electrochemical interfaces. In particular, I mention preliminary results on copper UPD on gold single crystal surfaces from two different groups, from Jim McIntyre and Ian Robinson of Bell Laboratories using GID and Joe Gordon and Owen Melroy from IBM (San Jose) using EXAFS, that have at least demonstrated feasibility of the methods.

ANOMALOUS ADSORPTION PHENOMENA ON Pt(111)

Using an unconventional (to surface scientists) method of surface preparation, Clavilier (7) produced voltammetry curves (Fig. 4) for Pt(111) surfaces in dilute acid solutions that showed anomalous features never before reported for any Pt surface. There was reason to question the validity of this report, as the method of surface preparation seemed unlikely to produce a clean well-ordered (111)-1x1 surface. However, Wagner and Ross (5) were able to reproduce Clavilier's voltammetry with UHV prepared and LEED characterized single crystals, and subsequently other groups (6, 28-31) have reproduced these curves using both UHV preparation and Clavilier's original method now commonly referred to as the "bead-method". There is no question that these features are associated with a clean well-ordered Pt(111) surface, but there is significant disagreement as to what electrode process produces these features. There are three unusual properties to these features: i.) they are kinetically very fast ($k \gg 1$ cm/sec); ii.) the potential at

which they are observed is strongly dependent on the anion of the supporting electrolyte; iii.) the very existence of the features depends critically on the domain size of atomically flat regions, which appears to be a relatively large size like 2 nm. Clavilier concluded from the rapid kinetics of the process that it must correspond to hydrogen adsorption/desorption, this representing a strong bound state of hydrogen which derives additional stability by virtue of lateral hydrogen bonding that occurs only on a well-ordered (111) surface. At least two other groups disagree with the hydrogen-adsorption interpretation. Wagner and Ross (5) argued that thermodynamic calculations indicate that such strongly bound hydrogen (ca. 30 kcal/mol) is unlikely. Scherson and Kolb (29,32) have argued that the displacement of the features seen in perchlorate by the introduction of sulfate ion indicate that the features do not represent a very strongly bound species, certainly nothing like the ca. 30 kcal/mol required by the hydrogen-adsorption interpretation. They argued further that since the qualitative shape of the anomalous feature is very like that observed for anion adsorption on Au(111), it is likely that the species is an anion, possibly hydroxyl ion. There is a consensus among the aforementioned workers that the strong dependence of the anomalous features on the scale of atomic flatness of the surface is most probably indicative of a hydrogen-bonded structure of some kind. At the present time, it is my opinion that the Scherson and Kolb interpretation is on the right track, but that the details need extensive filling out, i.e. what exactly is meant by a hydrogen-bonded hydroxyl ion structure, how does anomalous hydroxyl ion adsorption differ from conventional -OH formation, why does it only occur on the (111) surface.

FUTURE DIRECTIONS IN STRUCTURE-PROPERTY RELATIONS

In some sense the dynamism of a field of physical science is indicated by the extent to which new experiments conducted with more refined apparatus and method produce unexpected (or even anomalous) results that challenge the conventional wisdom in the field. By that measure the new structure-property relations portend a dynamic period for electrochemical science, and it should be apparent that the revisions to current theory necessary to account for the new results will have a substantial intellectual impact on electrochemistry as a whole. The current thinking on the constitution of the double-layer at metal surfaces, and on electrosorption phenomena at metal surfaces, are derived rather directly from classical models developed from studies with mercury electrodes. By its very nature as a liquid metal, there is no long-range order in the mercury surface, local bond forces are predominant, and models of the double-layer are concerned only with structure in the direction normal to the surface. It is not surprising that these models could be taken directly to polycrystalline metals, whose surface structure could in a sense be said to have "liquid-like" randomness in the coordination parallel to the surface. Thus, theory for metal surfaces could ignore interactions parallel to the surface plane and appear to account satisfactorily for the properties of polycrystalline metal surfaces. Even early work with single crystal metals did not appear to require more elaborate theory, but we now know that most results obtained from that period probably did not represent phenomena occurring at surfaces having regular two-dimensional periodicity. However, recent

work with clean well-ordered metal surfaces has shown the need to include strong lateral bonding (ordering) forces parallel to the surface in addition to the strong bonding forces perpendicular to the surface, i.e. forces acting parallel to the surface are of the same magnitude as forces acting perpendicular to the surface. Some theorists have already anticipated the importance of lateral interactions for double-layers at metal surfaces, in particular Guidelli (33). Guidelli's treatment anticipates the formation of superlattice structures and critical phenomena (superlattice phase transitions) that are indicated in recent studies with single crystal metals. There is not yet a sufficient body of experimental work with well-ordered metal surfaces to know how important lateral bonding forces will be for electrode processes in general, i.e. they are clearly important in adsorption of ionic species but they may have no effect on the adsorption of molecular species. The technological implications of the new results with single crystals are also unclear, but potentially exciting. One can speculate that the effect of surface order on electrode kinetics for some reactions may be analogous to the effect of crystal perfection on the performance of semiconductor devices, and that new electrochemical technologies might evolve that use single crystal electrodes fabricated by analogous methods. In this author's opinion, the advent of "true" single crystal electrochemistry presages a dynamic new period of discovery with potentially significant intellectual and technological impact.

ACKNOWLEDGMENT

The author is pleased to acknowledge the continuous support for single crystal studies from the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Storage and Distribution of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Table I. Summary of LEED Observations on the Effect of Cyclic Electrolytic Oxidation/Reduction on the Surface Structure of Pt(100). From Wagner and Ross (12).

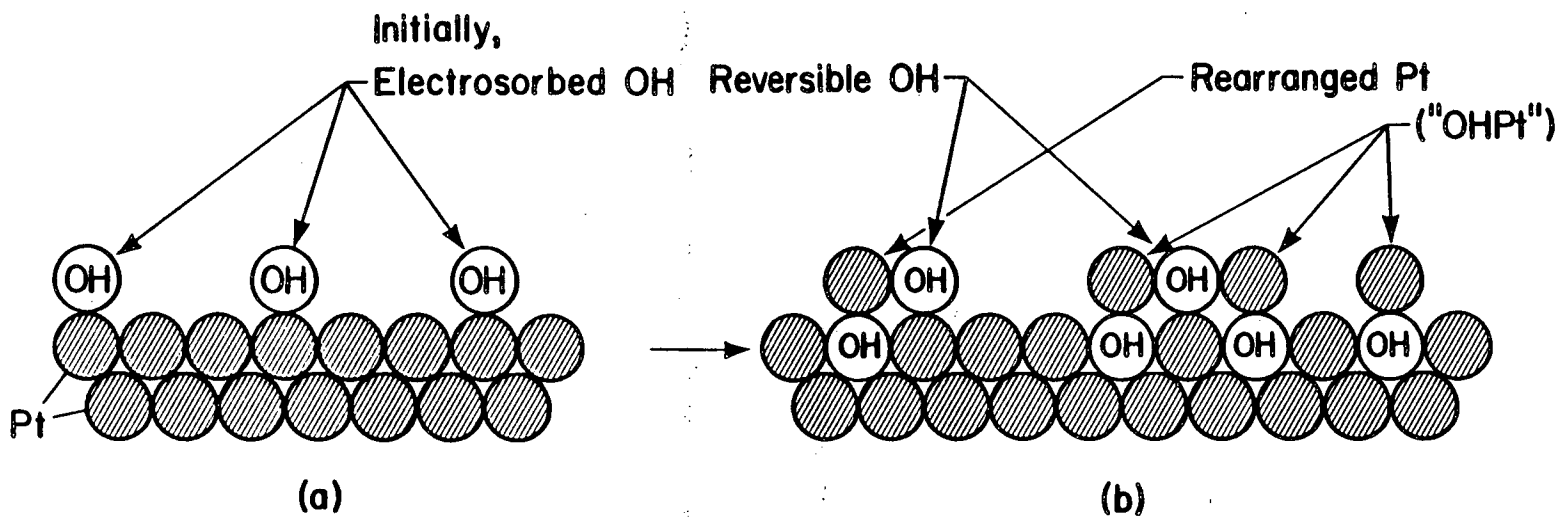
Anodic Potential Limit (V)	Charge per Cycle ($\mu\text{C}/\text{cm}^2$)	LEED Pattern
< 0.8	< 40	(1x1) sharp at all beam energies
1.0 - 1.3	250 - 450	Sharp spots alternating with sharp central spots with halos at characteristic beam energies; halo intensity increases with q^\dagger
1.3 - 1.6	< 500	Sharp spots alternating with diffuse spots at characteristic beam energies; diffuseness increases with Q^\ddagger

† q , charge per cycle

‡ Q , total integrated charge for all cycles

FIGURE CAPTIONS

- Figure 1. Schematic representation of the place-exchange process occurring on Pt surfaces during anodization in acidic solution, following Angerstein-Kozłowska et al. (11): a.) kinetically reversible -OH species formed in potential region 0.8 - 0.93 V; b.) place exchange between Pt and -OH resulting in displaced Pt adatoms and kinetically irreversible -OH.
- Figure 2. Cyclic voltammetry of copper deposition (cathodic) and dissolution (anodic) on UHV prepared and annealed Pt single crystal electrodes. From Andricacos and Ross (26). 1 mM Cu (II) in 0.3 M HF, 10 mV/s.
- Figure 3. Same as Fig. 2, but with single crystals that were ion-bombarded and not annealed.
- Figure 4. (a.) Cyclic voltammetry on UHV prepared and annealed Pt(111) in 0.3 M HF, 50 mV/s; (b.) same after ion-bombarding, but not annealing the Pt(111) crystal.



XBL 818-1222

Fig. 1

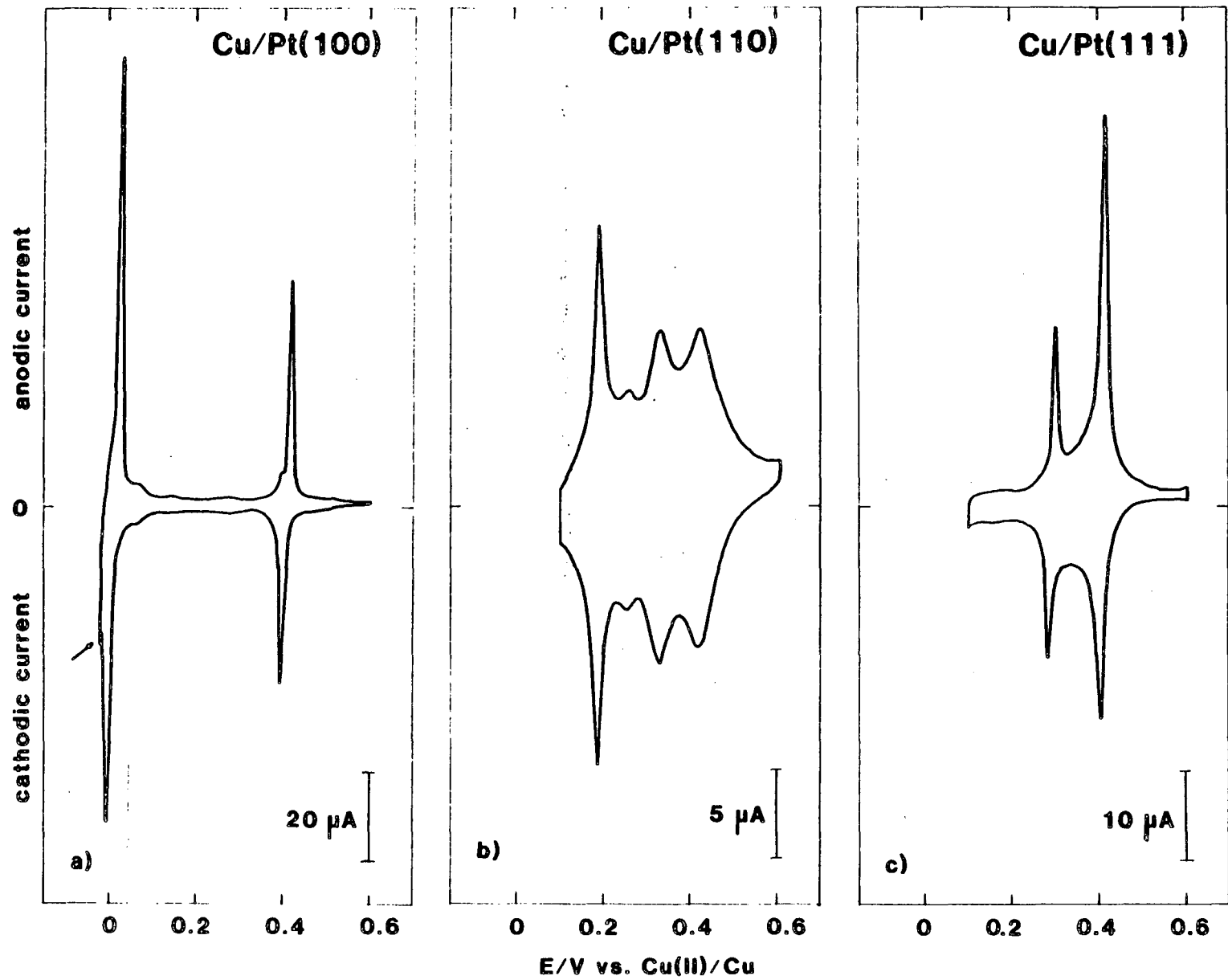


Fig. 2

XBL 841-267

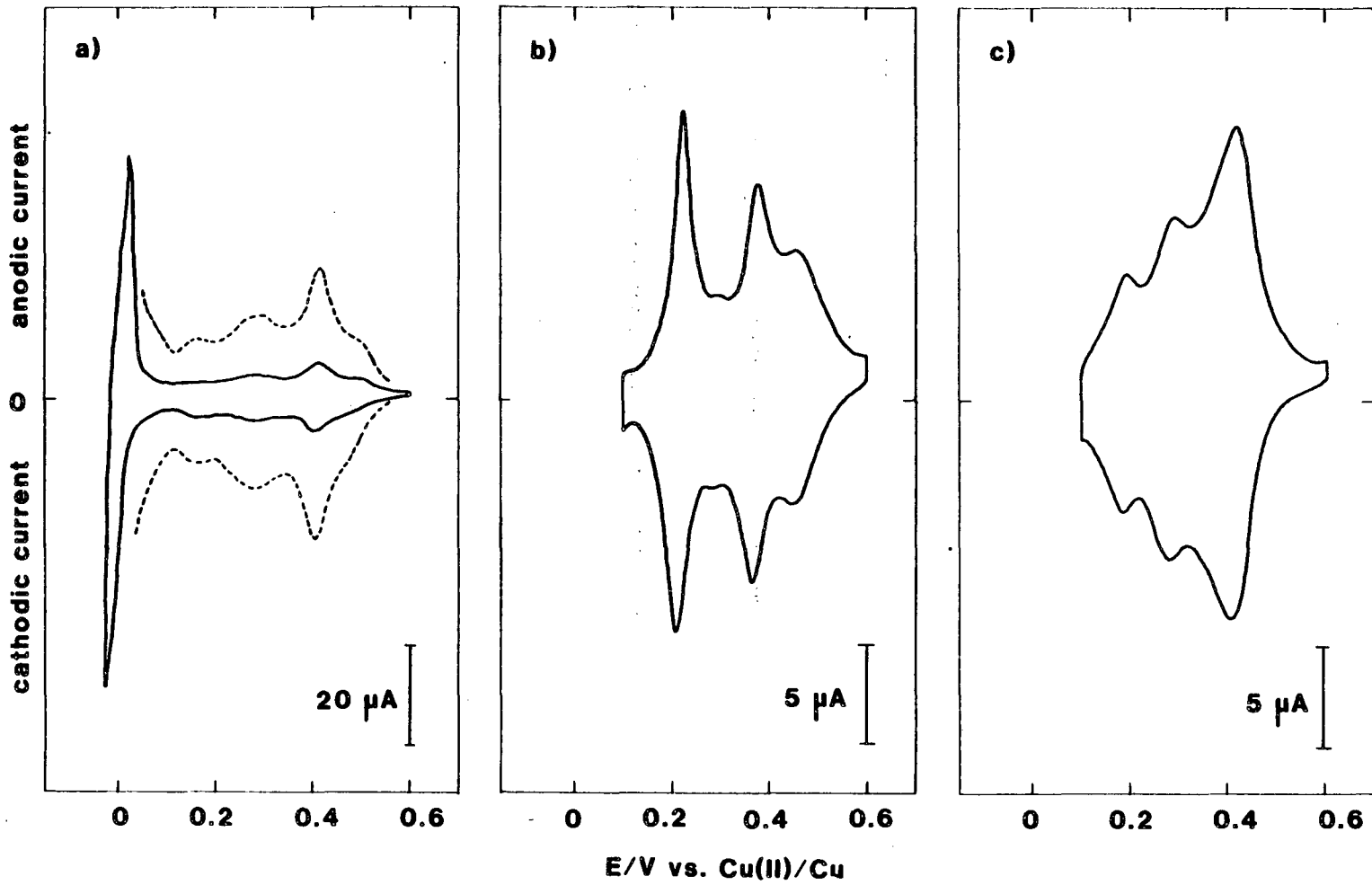


Fig. 3

XBL 841-269

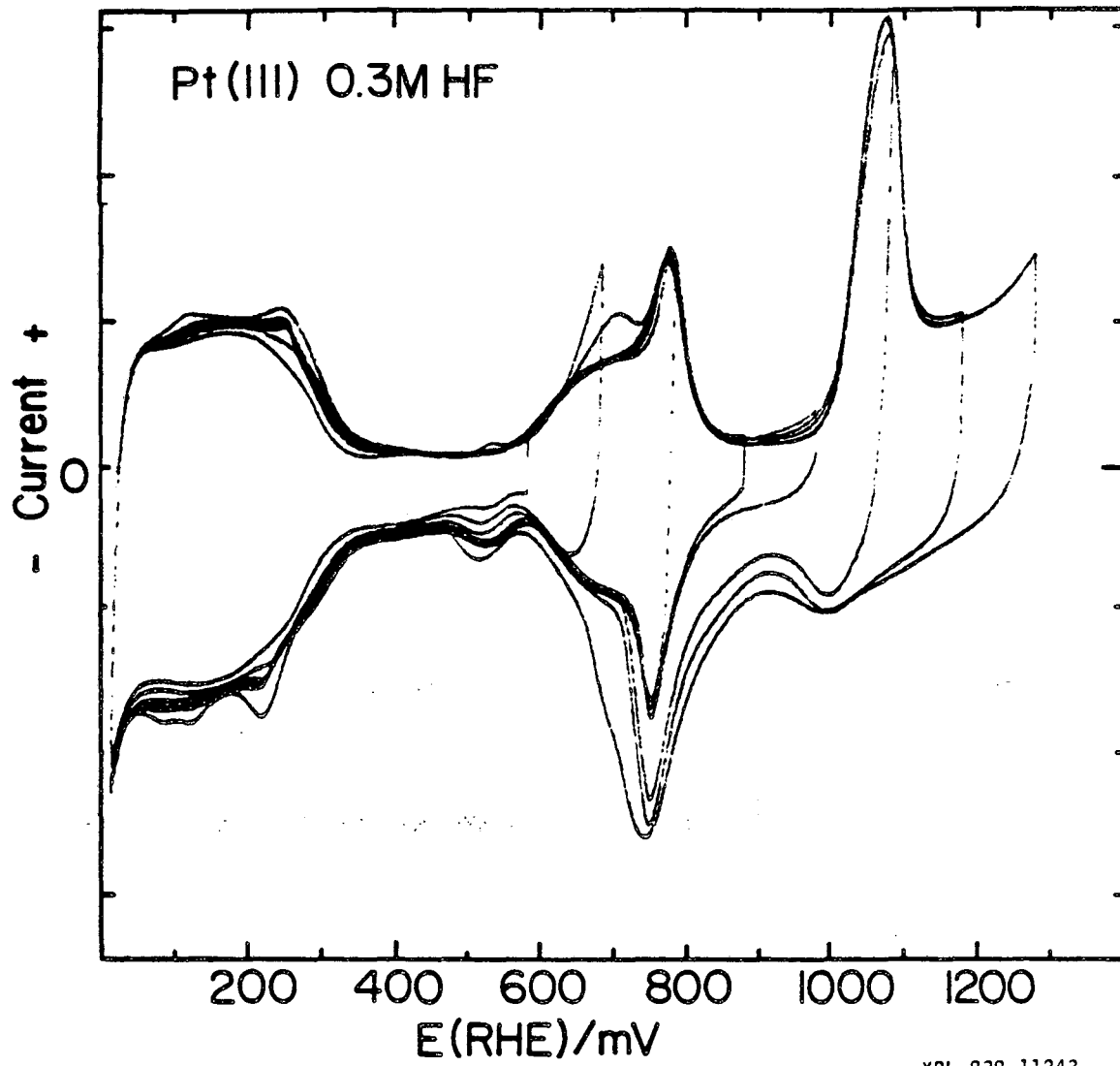


Fig. 4a

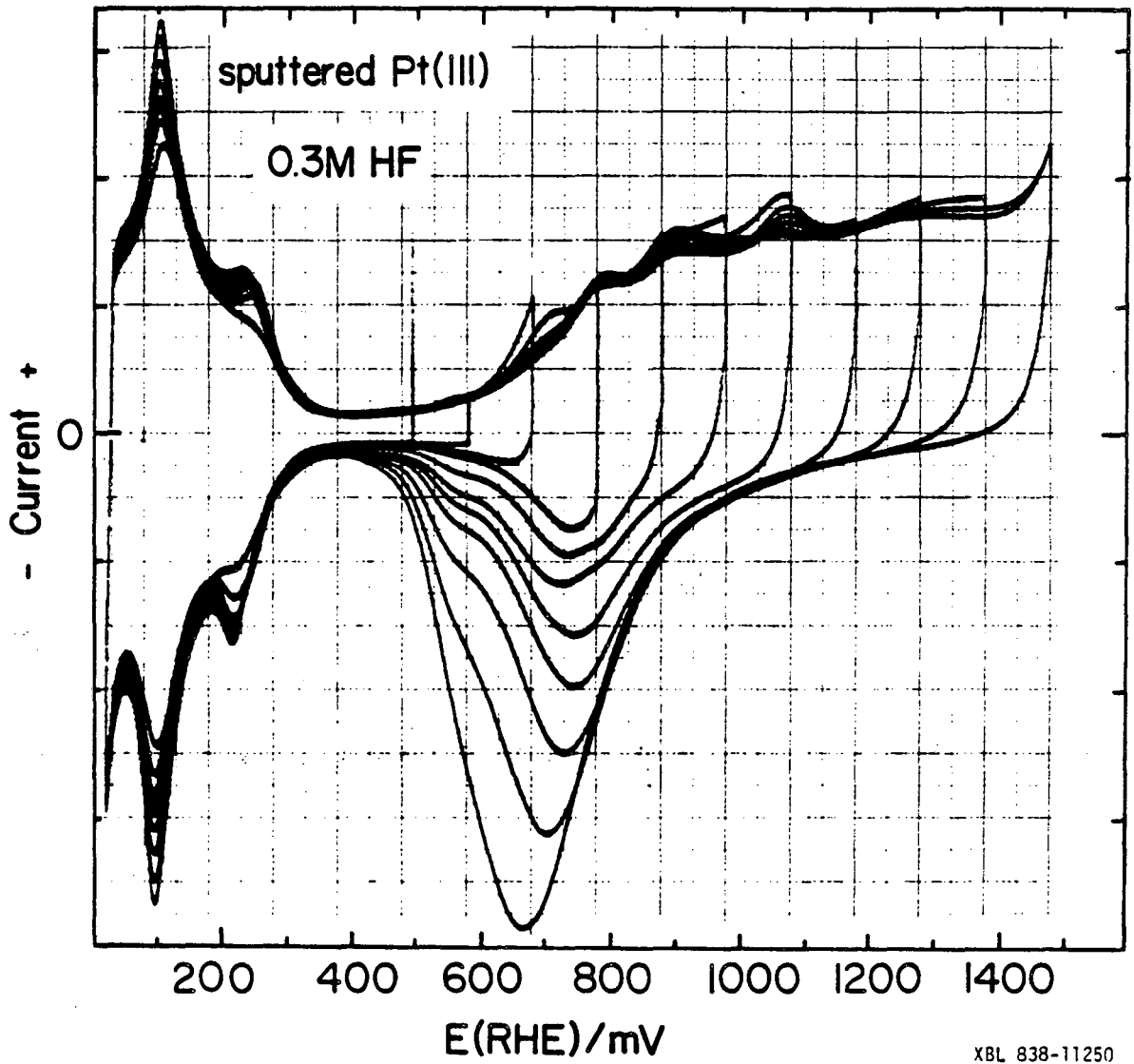


Fig. 4b

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