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LONG-RANGE STRUCTURAL EFFECTS IN THE ANOMALOUS

VOLTAMMETRY ON ULTRA-HIGH VACUUM PREPARED Pt(111)

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ABSTRACT

The cyclic voltammetry of Pt(111) in three different structural states (well-ordered, restructured by electrochemical redox cycling, and restructured by Ar^+-sputtering) was studied in aqueous acidic and basic electrolytes using a UHV-electrochemical transfer system. The well-ordered surface gave distinctive voltammograms with anomalous features identical to those first reported by Clavilier using flame-annealed (111) surfaces transferred through the air while hot. Electrochemical cycling above the sharp oxidation peak removed the anomalous features and introduced randomly-spaced monatomic steps to the surface, as shown by low energy electron diffraction (LEED). Ar^+-sputtered surfaces, with a similar randomly-stepped structure, yielded on the first cycle the same voltammetry as the redox-cycled surfaces, clearly demonstrating that the loss of the anomalous features upon cycling is due to a disruption of the long-range (>5 atomic spacings) order of the surface, rather than to a simple irreversible oxidation of adventitious impurities. Cycling in basic electrolytes produced voltammetric and structural changes similar to those seen in acid. Possible origins of the anomalous features are discussed in light of collected electrochemical and surface science data. The extreme sensitivity of these systems to disruption of long-range surface order is ascribed to the ability of hydrogen-bonded aqueous networks to transmit structural phase information over greater-than-molecular distances.

1. INTRODUCTION

Cyclic voltammetry on Pt single crystal surfaces, though extensively studied, remains a subject of considerable controversy. Early studies of hydrogen and oxygen electrosorption on UHV cleaned and annealed single crystals [1-4] produced few surprises relative to prior experience with electrochemically-cleaned polycrystalline and single-crystal Pt electrodes [5]. In many of these studies impurities picked up during transfer required the use of electrochemical cleaning before voltammetry was recorded [1,3], use of a non-inert backfill gas [4] and/or Ar^{+}-sputtering of the surface to allow post-electrochemical surface analysis [3]. While the polycrystalline electrode results could not be completely reproduced as simple linear combinations of (111), (100), and (110) surfaces, no new peaks totally outside the envelope of states on polycrystalline electrodes appeared. The major "strongly" and "weakly" bound hydrogen states on polycrystalline platinum coincided in potential with the largest peaks observed on Pt(100) and (111) (or (110)) respectively. The satisfying structural picture which had emerged by 1980 was upset when more recent work by Clavilier et al. [6-8] employing flame-annealed beads did produce new, highly reversible, pseudocapacitative peaks for the Pt(111) surface which had no precedence in polycrystalline work. The unusual preparative technique and the simplicity of the equipment employed precluded the use of non-electrochemical surface spectroscopic techniques to determine the elemental composition and the atomic-scale structure of the surfaces so produced without through-air transfer. The unusual voltammetric features were removed by several cycles into the oxidation region. Since such potential excursions are known to both remove impurities and alter the surface structure [9-11], impurity and structure-related effects cannot be unambiguously separated. Only flame-annealed beads had produced the unusual peak, and there existed the

possibility that unique structures possibly induced by rapid cooling caused the unusual new electrochemistry [12]. LEED and AES were later performed on flame-annealed surfaces in separate experiments [13], but these analyzed surfaces were not subjected to through-air transfer or electrochemistry.

In the present work, relatively large (1 cm dia.) Pt single-crystal surfaces were prepared by standard UHV surface science methods, and voltammetry was performed after room-temperature transfer through highly purified argon. The use of UHV equipment allowed the atomic-scale structure and composition of the surfaces to be determined independently of any interpretation of electrochemical results. Preliminary results have been reported previously [9]. Our electrochemical results on Pt(111) largely agree with those reported by Clavilier et al. and show that their results were not artifacts unique to their flame annealing technique or through-air transfer. Low energy electron diffraction (LEED) was used to monitor the restructing of the surface induced by potentiodynamic cycling. Similar restructuring could be introduced independently by Ar^+-sputtering the surface without changing the types and levels of impurities either in solution or picked up during transfer of the crystal. Comparison of the voltammetry in different electrolytes of well-ordered surfaces, electrochemically restructured surfaces, and/or UHV-restructured surfaces allowed unambiguous discrimination between structural and chemical effects accompanying electrochemical cycling. While the identity of the chemical species responsible for the unusual voltammetric features on well-ordered Pt(111) remains uncertain, comparison of the present data with other electrochemical and surface science results narrows the range of possibilities.

2. EXPERIMENTAL

The ultra-high vacuum/electrochemical transfer system has been described in detail elsewhere [11]. Clean Pt surfaces were produced by standard Ar^+-sputtering/thermal annealing cycling. After confirmation of cleanliness and surface order by Auger electron spectroscopy (AES) and LEED, the crystal was transferred through purified argon to a quasi-thin layer electrochemical cell containing 100 ml electrolyte, a Pt counterelectrode, and a Pd-H reference electrode. Electrolytes were prepared from a commercial ultra-pure water (Harleco Chemicals # 64112) and Ultrex or Puratronic-grade reagents, and were further purified by 24 h of Pt pre-electrolysis. All potentials are reported versus the reversible hydrogen electrode in the same electrolyte (RHE).

3. RESULTS

3.1 Acid Electrolytes

Figure 1 shows a window-opening experiment for well-ordered Pt(111) in 0.3 M HF (pH=2). Contact was made with the crystal potentiostated at 480 mV; a slight anodic current pulse was observed on contact. The electrode was first swept to lower potentials. The smallest window shown is the third sweep to 580 mV, which was identical to the first, showing a reversible region at 0-320 mV and a small reversible peak at 530 mV. The first sweeps up to 680 and 780 mV showed anodic charge which did not appear in later sweeps; this corresponds to the oxidation of a small amount of CO picked up during transfer as proven by intentional dosing in UHV of the surface with larger amounts of CO before transfer. A slight sharpening of the reversible peak at 230 mV accompanied this oxidation. At 580-830 mV two highly reversible peaks appeared at 660 mV and 760 mV which constitute the most significant deviation from the behavior of polycrystalline Pt. As noted by previous workers, the

sum of the pseudocapacity in this region and that in the normal hydrogen region approximated the $240\mu C/cm^2$ expected for a 1:1 H:Pt stoichiometry on Pt(111).

From 800–1000 mV the window-opening showed a lack of any pseudocapacity above the capacity also observed in the flat "double-layer" region, while polycrystalline surfaces are oxidized over this potential range. At 1080 mV a sharp anodic peak was observed. The charge corresponding to this peak appeared in the reduction wave at potentials between 1080 and 450 mV. Auger spectroscopy of electrodes emersed below 1000 mV showed no significant oxygen, while emersion at higher potentials produced measurable Auger oxygen. This data indicates that the anodic peak at 1080 mV corresponds to an electrochemically irreversible oxidation of the surface. However, the electrode could be cycled through this peak many times with no discernible change in the voltammetry. The lack of oxygen at lower potentials does not show that the 730 mV peak is not due to electrosorption of oxygen, since work on Pt(100) has shown that low coverages of electrosorbed oxygen do not survive emersion, evacuation, and transfer [14].

Although cycling repeatedly through the sharp peak at 1080 mV had no discernible effect on the voltammetry, cycling to higher potentials did. Figures 2a, b, c show the voltammetry after 1, 4 and 10 cycles to 1.28 V and Fig. 2d that after 10 cycles to 1.58 V. After four cycles to 1.28 V the major features of the initial voltammetry, such as the small couple at 520 mV, the two anodic peaks at 650 and 730 mV, and the oxidation peak at 1080 mV, remained, though the latter is reduced in intensity. After ten cycles to 1.28 V major changes were more evident, such as the growth of the reversible peak at 100 mV and the growth of anodic charge around 900 mV (in the region where the initial surface showed little capacity beyond that of the double layer). The

sharp features at 760 mV and 1080 mV were partially suppressed. LEED patterns taken after ten cycles to 0.83 V showed little if any beam-energy dependent LEED spot broadening, suggesting that the mean diameter of flat regions at this stage was at least 30 Å. After ten cycles to 1.28 V (Fig. 2c) the LEED spots for out-of-phase beam energies consisted of bright central spots surrounded by diffuse halos. This spot profile is indicative of a randomly-stepped surface with residual flat areas [10]. After ten cycles to 1.58 V (Fig. 2d) a number of features of the initial voltammetry were gone. The former sharp anodic peak at 1080 mV was completely buried in a featureless region of anodic film formation, replaced by a broad anodic peak at 900 mV. The reversible peak at 630 mV was gone, and the sharp peak at 720 mV was reduced to a small shoulder. In addition, the reversible peak at 100 mV grew and broadened. This increase in pseudocapacity in the hydrogen region roughly equaled the decrease in pseudocapacity in the peaks at 630 and 720 mV. Overall, the cycled-surface voltammetry of Fig. 2d reproduces that previously reported for Pt(111) by numerous workers [1-5]. The LEED pattern corresponding to this surface showed [10] a strong dependence of spot size on beam energy with no central sharp spots, indicating a randomly-stepped surface with a mean terrace width of about 12 Å (4-5 atoms) and no significant residual flat areas. Aberdam et al. [15] later observed similar LEED patterns. Using simplified analysis, which assumes that mixing of different terrace widths within the LEED coherence length has no effect on spot profiles, they derived terrace widths somewhat larger than those reported by us in Ref. [10]. Correlation of LEED and voltammetric data shows that Fig. 2a is the voltammogram of a well-ordered surface and Fig. 2d is that of a randomly-stepped surface. Figures 2b and 2c show intermediate voltammograms which correlate with an intermediate structure as determined by LEED. The voltammetry thus appears to

depend upon the long-range order of the surface. However, at this point it was not clear that the changes in voltammetry upon repetitive cycling could not arise from oxidation of surface impurities or from subsurface oxidation of the Pt rather than from restructuring of the surface. We, therefore, investigated the voltammetry of surfaces which were roughened by a process which did not entail the possible simultaneous chemical cleaning or oxidation induced by cycling above 1200 mV.

Figure 3 shows initial window-opening for a Pt(111) surface which had been given the standard Ar^+-sputtering treatment (1.5 keV, 20 mA emission, 10 min at 10^{-5} torr) but had not been thermally annealed to remove the structural damage induced by sputtering. From the start the voltammetry was strongly suggestive of that for the well-annealed surface after cycling above 1.28 V. A single peak at 90 mV predominated in the "normal" hydrogen adsorption region, though a smaller second peak grew in at 200 mV when the small amount of CO picked up during transfer was anodically oxidized. The oxidation peak at 900 mV, characteristic of the cycled surface, was pronounced on the first sweep of the sputtered surface, and the peak at 1080 mV was very weak. This sputtered surface would have picked up whatever impurities the annealed surface had picked up during transfer; the voltammetric differences are therefore structure-related. The LEED pattern of the sputtered surface showed the alternation of spot width with beam energy characteristic of monatomic steps also observed for annealed Pt(111) cycled above 1280 mV. While the gross LEED characteristics of the sputtered and electrochemically cycled surfaces were similar, they differed in detail. While cycling produced rotationally symmetric "halo"-type spots with a shallow minimum of intensity in the spot center [10], sputtering yielded spot profiles with no local minima, but with greater breadth parallel to the direction of incidence of the ion beam than

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perpendicular to it. This difference in spot profile shapes suggests that the sputtered surface has a somewhat broader distribution of terrace widths than that produced by electrochemical cycling, and that the mean distance between steps is smaller along the azimuth of the argon ion beam than perpendicular to it. The electrochemically significant result, however, is that disruption of the long-range in-plane order of the surface through introduction of predominantly monatomic steps removes the unusual voltammetric features, producing voltammograms consistent with, though distinct from, work on polycrystalline surfaces and with earlier work on Pt(111) in which the surface was cleaned by electrochemical cycling [1-3].

Aberdam et al. have presented results of a somewhat similar experiment, in which a Pt(111) crystal sputtered at 590 K was removed from a vacuum system and carried through air over to an electrochemical cell [16]. They also observed a first-cycle voltammogram for the hot-sputtered surface similar to that produced by extensive redox cycling of the well-ordered surface. The LEED spot shape for their hot-sputtered surface suggested preferential orientation of step edges along [110] directions, while our room-temperature sputtered surfaces and electrochemically cycled surfaces showed no such preferential crystallographic orientation of the steps. Since both random and oriented steps disrupt the anomalous features of the voltammetry of well-ordered Pt(111), it would appear that the width of the flat (111)-type terraces, not the presence or absence of a particular step configuration, determines whether or not the anomalous couple at 580–830 mV will appear.

While the results for sputtered surfaces unambiguously show that the transition from anomalous to "normal" voltammetric behavior is related to a breakdown in long-range order of the surface, the adsorbed species involved in the unusual pseudocapacitative peaks has not been identified unambiguously, i.e.,

not been identified by spectroscopy. Further, the possibility of participation of impurity species other than Pt, H_2O and HF, cannot be absolutely excluded since trace quantities of impurity elements like carbon and chlorine were usually observed by Auger spectroscopy of emersed electrodes in our experiments. However, as discussed later in the text, the reproducibility of the voltammetric features, both within our work and in Clavilier's work which used a drastically different sample preparation technique, argue against an impurity explanation.

3.2 Other Electrolytes

The initial window opening voltammetry for well-ordered Pt(111) in 3 mM H_2SO_4 is shown in Fig. 4. In agreement with Clavilier's results [7], we found that in H_2SO_4 the anomalous features occur at lower potentials than in HF (or $HClO_4$) and the capacitance in the "oxide" potential region (0.8-1.1 V) is dramatically reduced. Clavilier reported a similarly reduced capacitance in the "oxide" potential region, and attributed this reduction to the specific adsorption of HSO_4^- anions which inhibits oxygen adsorption. Increasing the anodic potential limit above 1.2 V so as to produce a significant quantity (>500 $\mu C/cm^2$) of anodic charge had a more pronounced effect on the capacitance in the "oxide" formation potential region than in the "normal" hydrogen potential, as clearly seen by the window-opening voltammetry in Fig. 4. LEED analysis of the surface after a single anodization to 500-550 $\mu C/cm^2$ showed a slight broadening of LEED spots, probably indicative of some loss of long-range order in the surface. The change in structure was, however, at the limit of resolution of our LEED optics and was not quantifiable. The balance of anodic charge at 0.4-1.4 V and cathodic charge at 0.4-1.1 V was within 5% (Clavilier claimed 1%) so there is little evidence that the anodic process

involves irreversible oxidation, e.g., oxidation of an impurity species. There is, therefore, some evidence from LEED analysis in support of Clavilier's "conclusion" that the anodization to 500-550 $\mu C/cm^2$ produces a structural alteration of the surface that transforms the voltammetry. That a barely detectable (by LEED) change in long-range order in the surface has such a dramatic effect on the surface chemistry is, to our knowledge, unprecedented.

The electrochemical oxidation in H_2SO_4 of Pt(111) pre-dosed with CO in the UHV chamber to saturation is shown in Fig. 5. The CO reduces the inner-layer capacitance by about an order of magnitude, and completely blocks the species causing the anomalous voltammetry. The CO oxidation peak is at the same potential in H_2SO_4 as in HF and the peak also occurs at the same potential at high CO coverages as at low CO coverages. On the cathodic sweep after complete oxidation of the CO the cathodic process of the anomalous feature is observed. Clearly, the species causing the anomalous feature in H_2SO_4 is not as strongly adsorbed as CO, and does not participate in CO oxidation.

Results in basic electrolytes are shown in Figs. 6-8 (a single voltammogram to 1.4 V in NaOH has been previously published without comment in ref. [17]). In both bicarbonate/carbonate buffer (5 x 10^{-3} M $NaHCO_3$ + 2 x 10^{-3} M Na_2CO_3, pH=10) and hydroxide (7 x 10^{-3} M NaOH, pH=12) solutions apparently pseudocapacitive peaks were seen in the region 600-800 mV, as in HF or $HClO_4$. However, while the HF results showed a sharp peak at 760 mV with a shoulder around 660 mV, in base a single broad peak was observed at 700 mV (NaOH) or at 640 mV ($NaHCO_3/Na_2CO_3$). The single peak seen in base appears equivalent to the low-potential shoulder in HF, not to the sharp main peak. While in acid the area of the anomalous peak is roughly one-half that in the normal hydrogen region, in base the anomalous area was 10-20% larger than the normal hydrogen area. The results in basic solutions also showed less than half of the

current (seen in HF) in the potential region between the anomalous couple and "normal" hydrogen, e.g., a "double-layer" capacitance of about 30 $\mu F/cm^2$. Also, a small reversible peak was seen at 330 mV which grew upon cycling to 1200 mV or above (Fig. 6), becoming the second-largest hydrogen peak on the extensively cycled (111) surface (Fig. 8). The largest hydrogen peak on the cycled surface in basic solutions grew in at 200 mV RHE as opposed to the 100 mV peak seen in acid, although the broad hydrogen region for the well-ordered surface showed a similar envelope in basic as in hydrofluoric or per-chloric acid electrolytes. Thus the results in base show a different struc-ture in the anomalous peak region on the well-ordered surface and a different evolution of the classical hydrogen adsorption region upon cycling from those seen in acid.

4. DISCUSSION

Previous sections of this paper have shown that the anomalous voltammetric behavior of Pt(111) is dependent upon the long-range order of the surface. Auger spectroscopy analysis showed the sharp anodic peak at 1080 mV in HF to be due to oxidation of the surface, but the surface species corresponding to the unusual, highly reversible peaks around 760 mV could not be identified by ex-situ spectroscopy. To our knowledge, there has been no spectroscopic iden-tification (neither ex-situ nor in-situ) of the species involved in the anom-alous voltammetric features. Until such evidence is obtained, the identity of the species involved and the nature of electrochemical processes giving rise to these features will remain the subject of speculation and argument. In the ensuing discussion, we use the observations made in this work and in other recent work known to us to construct plausible arguments in an attempt to narrow the range of possible species/processes as a guide to future studies.

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Clearly, the narrowing of possibilities is argumentative, and others using the same data base may arrive at a different ranking of possibilities. We have organized the arguments in terms of four general classes of surface species: (a) derived from impurities in the electrolyte, transfer gases, or bulk Pt; (b) hydrogen-like species (i.e. reduced with respect to water); (c) oxygen-like species (oxidized with respect to water); (d) majority anions; and (e) strongly adsorbed water.

a. Impurities

In order to understand the physical processes related to the anomalous voltammetry it is extremely important to know whether or not impurity species are involved. It, however, is very difficult to obtain definitive evidence of the absence of impurity species, i.e., that the only species present are H_2O, the acid molecule and solvated ions of the acid and Pt. Nonetheless, all the evidence known to us, from our own experiments and those known to us, suggest that the anomalous features are not associated with impurity species. We have concluded this on the basis of the following plausibility arguments. Clavilier's voltammetry with the flame-annealed bead through-air transfer method has been reported in several laboratories [18-21], and our results with UHV prepared (111) crystals have been reproduced by Hanson [22] and by Aberdam, et al. [15]. Since the voltammetry is highly reproducible using both UHV techniques and the flame-annealed bead through-air transfer method, only saturation coverages of phases due to adventitious impurities seem possible since low coverages would not be so reproducible between laboratories. While small coverages (~1% of a monolayer) of impurities could escape detection by AES, this is improbable for saturation coverages. Despite the precautions taken in these experiments, electrolyte impurities were present, as they most probably

are in all electrochemical experiments. One would expect trace chloride in any HF electrolyte, and a few percent (~5%) of a monolayer of Cl was seen by AES in some of these experiments. Our voltammetry in HF was identical to that reported by Marcovic et al. [21] in which the Cl^- concentration was known to be less than 10^{-7} M, so it seems likely our Cl^- level was less 10^{-7} M as well. The persistence of the anomalous features to very high (>20 V/s) sweep rates militates against specific adsorption of Cl^- to 70–90 $\mu C/cm^2$ of charge as there is an insufficient quantity of Cl^- in the diffusion layer at 10^{-7} M to produce this much charge. The only other spectroscopic indications of electrolyte impurities were highly localized Na, Ca, and O Auger signals, seen when failure of the usual emersion technique left a large droplet of electrolyte on the surface (these signals were seen at the point where the last liquid evaporated away). Basic electrolytes always left behind measurable Na and O signals as expected for the non-volatile solutes in these solutions. Carbon, at the level of about one carbon atom per ten surface Pt atoms, was always seen after transfer of non-oxidized Pt surfaces. While some experiments suggest that this was picked up primarily during pumpdown after the electrochemical experiments [11], this was not rigorously proven. The Auger carbon was not due to CO, which is distinctive both in its appearance in voltammetry in the fine structure of the Auger emission from the carbon in CO. The equivalence of results between our UHV methods and Clavilier's hydrogen-oxygen flame annealing followed by transfer of the still hot Pt bead through air again suggests that carbon is not a decisive impurity. While our transfer through ultra-pure argon (in reality slightly contaminated with vacuum-system background gases such as CO and H_2), involved slightly reducing conditions amenable to carbon deposition, Clavilier's hot through-air transfer involved oxidizing conditions which would burn off carbonaceous materials. Yet, nearly identical voltammetric results were obtained.

Impurities segregating to the surface from the bulk of even high-purity zone-refined crystals have produced some anomalous results in the experimental surface chemistry of Pt. In particular, surface segregation of Si and Ca (as oxides) have been associated with the formation of an unusual type of platinum oxide on Pt crystals dosed with oxygen at high temperature [23]. However, these effects have not been found to be as reproducible as the voltammetric features under discussion here, i.e., the saturation coverage argument holds in this case as well. The bulk impurities known to be both present and hard to detect in Pt, e.g., Si and Ca, do not have plausible redox chemistry in the relevant potential region. Segregated bulk impurities thus also seem an unlikely explanation for the unusual voltammetry on Pt(111).

b. Hydrogen-Like Species

Clavilier, et al. [6-8] have proposed that the unusual reversible peaks are due to strongly bound states of hydrogen, based primarily upon the extreme reversibility of the couple, its shift to lower potentials in the presence of specifically-adsorbed anions, and the near-constant 240 $\mu C/cm^2$ sum of the pseudocapacities in the normal hydrogen and the anomalous regions in different electrolytes. The binding free energy ($H_2(g) = 2 H_{ads}$) of ca.160 kJ/mole implicit in such an interpretation is in marked contrast to the 42 kJ/mole zero-coverage heat of adsorption of hydrogen on clean Pt(111) observed in UHV [24]. From an electrostatic point of view, the known Pt-H dipole direction (in UHV) and the direction of the electric field in the most prevalent theory of the double-layer would interact to destabilize adsorbed hydrogen at the Pt-electrolyte interface vs. the Pt-vacuum interface. Thus, if the species is a form of stabilized adsorbed hydrogen, it is most likely stabilized by specific covalent or hydrogen-bonding interactions rather than by purely electrostatic

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effects. Thermal desorption results for H_2 + H_2O coadsorption on Pt(111) in UHV indicate no significant thermal stabilization of water on the surface by hydrogen [25-26]. Since during the upwards temperature ramp H_2 desorbs long after H_2O leaves the surface, stabilization of H_{ads} by water could not be checked directly. However, if H_{ads} were stabilized by water as strongly as indicated by the Clavilier interpretation of the voltammetry, the stabilization of H and H_2O would have to be mutual, and water would desorb from Pt(111) at a much higher temperature with coadsorbed hydrogen than without. To the still-unknown extent that UHV results are relevant to electrochemistry, the lack of stabilization upon H_2/H_2O coadsorption casts doubt on the Clavilier interpretation.

Direct experimental evidence against a hydrogen-alone interpretation has been given by the pH-dependence work of the Kolb group [19]. They observed that the potential of the anomalous couple versus a pH-independent reference (SCE), did not vary with pH (as would a couple due to hydrogen adsorption) when the sulfate concentration was held constant.

c. Oxygen-Like Species

The potential range of the anomalous reversible couple on Pt(111) partially overlaps the onset of the surface oxidation of either Pt(100) or polycrystalline Pt electrodes [14]. It is thus useful to consider whether the charge passed in this region is due to some form of highly reversible electrosorbed oxygen related to O_{ads} or OH_{ads} in some way. Such a reversible oxygen species could have exciting implications for electrocatalysis. Although no oxygen was seen by Auger or thermal desorption on surfaces emersed at potentials just above this couple, this does not necessarily militate against an oxygen-type

species since highly reversible species can spontaneously discharge in the electrolyte layer which remains on the surface upon emersion [14].

It is possible to construct an argument in support of the oxygen-like species interpretation from the observations of anion effects on peak positions of the anomalous couple and from thermodynamic arguments. The recent report by Marcovic et al. [21] showed that the addition of small amounts (less than 0.1 mV) of Cl^- ion to $HClO_4$ caused the anomalous features to shift anodically and the coverage (charge under the features) to be decreased in magnitude, indicating adsorptive displacement of the species in the anomalous peak by Cl^- anion. The anodic shift is consistent with the destabilization of an oxygen-type species, i.e., a shift closer to the $O2/H_2O$ equilibrium potential for an electrode process of the type

$$OH_{ads} + H^+ + e^- = H_2O$$
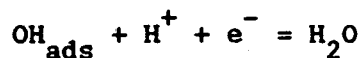
On the other hand, Kolb and co-workers [19] reported a cathodic displacement of the anomalous features upon the addition of sulphate anion, but with approximately constant charge in the feature. However, the anomalous couple need not represent the same species in all electrolytes, and the Kolb group interpreted their results as indicating that in electrolyte containing significant (>1 mM) quantities of sulfate ion the anomalous feature is due to the process of specific adsorption of sulphate anion and due to another process (probably oxygen-like) in $HClO_4$. Their interpretation indicates the species in the anomalous couple is displaced from the surface by sulphate when the anion concentration is high enough, suggesting an adsorption energy either equal to or somewhat lower than that of sulphate anion.

In a similar manner, the CO oxidation results might be interpreted as consistent with an oxygen-like species for the anomalous couple in HF electro-

lyte, but suggesting a chemically different state for H_2SO_4 electrolyte. In HF the electrooxidation of CO pre-adsorbed (in UHV) onto Pt(111) occurs in the same potential region (literally on-top-of) the anomalous feature, suggesting that the species in the anomalous feature might be an oxygen-like species that participates in CO oxidation. In H_2SO_4, the electro-oxidation (Fig. 5) of CO does not occur at the same potential as the anomalous features, even for low CO coverages. Rather, CO oxidation occurs at the same potential as in HF, with the anomalous features occurring ca. 300 mV cathodic of the CO oxidation potential. In H_2SO_4, if the anomalous feature were an oxygen-like species, it would be an oxygen-like species not capable of oxidizing CO, and thus chemically different from the species in HF (or $HClO_4$). However, the equality of the CO oxidation potential in H_2SO_4 and HF suggests that the superposition of CO oxidation and the anomalous couple in HF may be fortuitous; even in HF the anomalous species may not be directly involved in CO oxidation.

The principal difficulty with the oxygen-type species interpretation is in distinguishing how or why it is different from the oxygen-type species that form on the other Pt surfaces (having different surface structure, either long-range or short-range), or that forms at more anodic potentials on this same surface. Recent studies by electron spectroscopy and thermal desorption spectroscopy [14,27] have established that the oxygen-type species forming at more anodic potentials (>1 V RHE) is place-exchanged OH, and that the change that occurs with increasing potential of formation is the coordination of the OH group(s) around the Pt surface atoms. In this potential range, ex-situ spectroscopic analyses have not indicated that the oxygen-type species forming on the Pt(111) surface is any different in molecular configuration from that forming at the Pt(100) (or polycrystalline Pt) surface. Rather, the same disordered (to LEED) hydroxide phase is formed on all surfaces. How then does

the anomalous oxygen-type species differ from place-exchanged OH in molecular configuration/structure and why is that structure so sensitive to long-range order in the metal surface? The anomalous features are clearly due to a surface-adsorbed species, rather than to a place-exchanged amorphous phase since repeated cycling through the couple does not reconstruct the surface. Though one would expect the properties of a surface-adsorbed species to be more sensitive to surface order than those of an overlayer of an amorphous phase, the origin of the extreme structure sensitivity remains to be defined. Proposals in this regard will be made in section e.

d. Anion Adsorption

It is observed that the anomalous reversible peaks appear at widely-varying potentials in electrolytes with specifically adsorbing anions (Cl^-, HSO_4^-), but in electrolytes with "non-specifically" adsorbed ions (F^-, ClO_4^-, OH^-) the peaks all appear within a narrow potential range (vs. RHE) independent of pH and with total capacitance no smaller than those seen with specifically-adsorbed electrolytes. Both charge transfer processes involving the ionic constituents of the electrolyte and purely capacitive processes involving these constituents should be considered in the interpretation of these observations. Scherson and Kolb [28] have discussed sharp, reversible spikes seen in the voltammetry of Au(111) in acid media containing specifically-adsorbed ions in this light. They interpreted these sharp voltammetric features as involving adsorption and phase transitions between states of specifically adsorbed ions such as the heavier halides and bisulfate. Charge transfer accompanying the specific adsorption of halide ions on Au(111) [29] produced integral charges as large as 70-90 $\mu C/cm^2$, in the range required for the

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anomalous pseudocapacity on Pt(111). In a follow-up study [19], the Kolb group reported the pH and the anion concentration dependence of the anomalous couple on Pt(111) prepared by the Clavilier method. The anomalous couple shifted in potential versus SCE with total sulfate concentration at constant pH, but did not shift in potential versus SCE with changing pH at constant total sulfate concentration. On the other hand, in ClO_4^- electrolytes they observed a potential shift versus SCE of 59 mV/pH with changing pH at constant total perchlorate concentration. They concluded that for total sulfate concentrations above ca. 1 mM the anomalous couple is due to specific adsorption of sulfate or bisulfate and proposed that chloride specific adsorption accounts for the low-potential anomalous couple seen in electrolytes containing significant (>1 μM) chloride [7,21]. The extent of charge transfer in such interactions remains unclear, and charge-transfer adsorption of other species (such as hydrogen) in competition with anion adsorption could yield the observed concentration dependencies. Although the anion adsorption appears consistent with the observations in electrolytes containing strongly-adsorbing (HSO_4^-, Cl^-) anions, it requires a different adsorption phenomenon (having the same potential dependence as the RHE) in electrolytes in which the majority anions are F^-, ClO_4^- or OH^-. This requirement is problematic in terms of current concepts for ion adsorption at metal surfaces. In particular, it is problematic to propose F^- and ClO_4^- as the anions specifically adsorbing in these acids (with a 59 mV/pH potential dependence vs. SCE as well). In the basic electrolytes, it is not unreasonable to suggest OH^- specific adsorption for the anomalous couple, but the concentration of OH^- in HF and $HClO_4$ at pH of 1-2 seems too low to be a reasonable candidate (an enhancement of 7-8 orders of magnitude in ionic concentration in the inner layer relative to the bulk electrolyte is required for the rapid adsorption of 10^{13} – 10^{14} ions/cm^2). Furthermore, the shape of the anomalous features changed

significantly when the pH was increased from 2 to 9 or 10 as indicated by the comparison of Fig. 1 with 6. Note also the dramatic decrease in capacitance around 0.4 V at pH 9-10 relative to pH=2, i.e., from 100 $\mu F/cm^2$ to 30 $\mu F/cm^2$, the latter being the smallest capacitance we have ever observed on any Pt electrode. Therefore, it does not seem probable that the same anion could adsorb in the pH = 9-10 electrolytes as in the pH = 1-2 electrolytes.

Another difficulty inherent in a simple anion adsorption explanation of the anomalous features lies in the small magnitude of the pseudocapacity in the normal hydrogen region seen on well-ordered (111) surfaces. If the cathodic part of the anomalous couple is due to the desorption of anions there is nothing left on the surface at lower potentials to block "normal" hydrogen adsorption to account for the ~1/3 lower hydrogen pseudocapacity seen on well-ordered (111) versus other surfaces. While UHV investigations of H_2 adsorption have reported low (0.73 H/Pt) saturation coverages on Pt(111) [30], H/Pt ratios very close to 1 have been seen for the higher H_2 pressures analogous to electrochemistry near the RHE potential [31]. The apparent reduction in coverage by adsorbed hydrogen below the desorption potential of the anion and the similar characteristics of the anomalous couple in both weakly and strongly adsorbing electrolytes lead one to consider the possibility (necessity?) of unique interactions between Pt(111) and water itself.

(e). Water Adsorption

A correct interpretation of the anomalous voltammetry must account for the remarkable effects of long-range (>10 Å) structure on the processes involved. These effects have a longer range than those commonly seen for small molecules at gas-solid interfaces. A unique aspect of aqueous interfaces which could maintain structural correlation over many molecular diameters is the strong,

directional hydrogen bonding possible when water is present. In situ characterization of water structure at electrochemical interfaces is in its infancy, but the UHV literature on water adsorption at cryogenic temperatures (100–200 K), recently reviewed by Thiel and Madey [32], can illustrate the structural consequences of hydrogen bonding which may survive, in clusters of as-yet-undetermined size, on aqueous interfaces at room temperature. It is now well established that adsorption of water onto surfaces at temperatures above ~30 K yields not isolated water molecules, but extensively hydrogen-bonded clusters, even at low coverages. On a number of metal surfaces having hexagonal symmetry, i.e., fcc (111) and hcp (0001), including Pt(111) [33,34], ordered superlattices are formed, having the $(\sqrt{3} \times \sqrt{3})R-30°$ symmetry (as deduced from LEED) expected for ice-like lattices. The most detailed and convincing study of the structure of these water superlattices was by Doering and Madey [35] for water on Ru(0001). They supplemented their LEED analysis with ESDIAD (electron stimulated ion angular distribution), which provided information about the orientation of the water molecules on the surface, and applied the Bernal-Fowler-Pauling symmetry rules for the·hydrogen-bonded structure shown in Figure 9. In the first water bilayer, which, considering connectivity, could also be termed a puckered monolayer, every other water molecule forms (1) a bond to the surface via the oxygen lone pair and (2) two hydrogen bonds to oxygen lone pairs of two water molecules in the outer part of the bilayer (the out-puckered positions). The observed structure is highly ordered only in the first bilayer. On some surfaces more highly corrugated than fcc(111) or hcp(0001) other water structures have been observed, at least at low coverages. Thiel and Madey argue that the non-ice-like structures on these surfaces are due less to the lack of appropriate epitaxial relations for ice-layer formation than to the greater magnitude of the bond energy of water on

the more corrugated sites in relation to the strength of the water-water hydrogen bond. On numerous fcc(111) surfaces, the metal-water bond energy is roughly equal to twice the OH^--O hydrogen bond energy (21 kJ per mole of hydrogen bonds), so that the breaking of ice symmetry to form an additional metal-water bond (e.g. lowering water molecules from hydrogen-bonded sites to chemisorption sites) does not result in a net lowering of the surface energy. On the more open surfaces such as fcc (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 optimally hydrogen bonded symmetry is not always favored over a structure having a greater number of water molecules bonded to strong chemisorption sites on the metal surface. These UHV studies of water on metal surfaces at cryogenic temperatures clearly illustrate that the stable configuration of water on a metal surface <u>at any temperature</u> depends on the interplay of forces acting both parallel (adsorbate-adsorbate) and perpendicular (metal-adsorbate) to the surface. While it is doubtful that perfect ice-like structures would be maintained at a real electrochemical interface at room temperature, clusters with diameters at least the size of three water rings (consistent with the size of the atomically flat regions required for anomalous behavior) might be expected to flicker in and out of existence. We postulate that such clusters with well-defined phase relations to the surface would tend to block the surface against adsorption of other species more effectively than would a disordered collection of water molecules. In the random water case, adsorption of a foreign species would completely displace one water molecule, but need not have major effects on neighboring water molecules. In the case of ice-like clusters adsorption requires disruption and reorganization of the entire cluster (adsorbate-adsorbate and adsorbate-metal bonds), exacting an enthalpic penalty which, though small per water molecule, could be quite large

per foreign adsorbate molecule. If steps spaced more closely than the cluster size were introduced to the flat surface, the phase relations (particularly vertical) between the water clusters and the metal atoms would be destroyed, destabilizing the clusters and decreasing the tendency of water to block the adsorption of other species.

The hypothesis of blocking water clusters can explain the voltammetric features observed on well-ordered Pt(111) and the extreme surface structure dependence of these features. First, the decreased pseudocapacity in the "normal" hydrogen region can be understood as being due to partial blocking of the surface by water clusters which are stable down through the hydrogen evolution potential. During the anodic sweep these clusters can also block the anionic adsorption which has been shown to start on polycrystalline Pt within the normal hydrogen region [36]. If strongly adsorbing anions are present in solution they can, above a concentration-dependent critical potential, abruptly displace the water clusters, yielding the anodic wave of the anomalous couple. This anionic layer, also hydrogen-bonded and sensitive to surface structure, blocks access of non-solvating waters to the surface, thereby suppressing oxidation of the surface, as seen in the H_2SO_4 voltammograms of Fig. 4. Cycling to still higher potentials (i.e., above 1200 mV) allows the surface to abstract oxygen from either the ionic layer or the waters above it, finally yielding above 1300 mV the place-exchanged hydroxide layer formed on other surfaces at much lower potentials. In the absence of strongly adsorbing anions the blocking water clusters remain on the surface to a higher potential (than in electrolytes with strongly adsorbing anions). In these electrolytes, the anodic wave of the anomalous couple is due to partial oxidation of the clusters to form a hydrated surface OH layer which is sufficiently stable to resist further oxidation over the potential range of 800-1000 mV. We suggest

that this hydrogen-bonded OH+water layer also has well-defined phase relation-
ships to the well-ordered Pt(111) surface. At ~1050 mV RHE the sharp oxida-
tion peak corresponds to the conversion of this OH layer to another, non-
place-exchanged surface species, possibly through oxidative deprotonation of
the previous mixed OH-H_2O layer. This anhydrous OH layer is sufficiently
similar in free energy to the place-exchanged OH phase that the place-exchange
process can start upon cycling to slightly higher potentials [10].

Certain complications in the data, for example the slightly different
voltammetry in NaOH and in bicarbonate buffer, indicate that the above picture
is still incomplete. Some adsorption of even weakly-bound ions probably oc-
curs, and specific interactions between ions and particular binding sites
probably play a role in determining the detailed structure of the voltammo-
grams within the envelopes for hydrogen, anion, surface hydroxyl, and place-
exchanged hydroxyl adsorption proposed above. Some competitive adsorption of
at least two species, in addition to water, probably occurs within each of the
potential envelopes. In all cases the extreme sensitivity of the voltammetric
features to long-range order probably arise from hydrogen-bonded networks
which extend beyond the dimensions of individual molecules.

SUMMARY

The use of Pt(111) single crystals with varying degrees of ordering of the
surface, as determined independently by LEED, has shown that the anomalous
voltammetry on Pt(111) first reported by Clavilier [7] is unique to a (111)
surface constituted from structurally perfect domains containing at least
50 Pt atoms (i.e., minimum characteristic diameter of 5-8 atoms or approxi-
mately 12 Å to 25 Å). There is a critical nature in the relation between the

range of perfection in the structure and the anomalous features in the voltam-metry, i.e,. with the introduction of a critical number of defects the features disappear entirely. To our knowledge, such criticality in a structure-property relation is unprecendented in electrochemistry, or even in surface chemistry in general.

The anomalous features are observed on well-ordered Pt(111) electrode 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 curves change considerably. Specifically, the potential region (versus RHE) in which the features appear changes with anion concentration in sulfate and chloride electrolytes, but not in fluoride, perchlorate, bicarbonate or hydroxide elec-trolyte. In sulfate electrolyte, at constant anion concentration the region shifts (versus RHE) with varying pH, while in fluoride, perchlorate, bicarbon-ate and hydroxide electrolyte it does not. The use of UHV methods and surface analytical techniques has established to a reasonable (but not definitive) extent that adventitious impurities are not involved in the process, i.e., the only species participating are protons, water and the anions of the solute. On the basis of the pH and anion concentration dependencies, we agree with the suggestion put forth by the Kolb group [19] that the anomalous features on Pt(111) in sulfate and chloride acid solutions are associated with the process of specific adsorption of these anions. We offer further a rationalization of the extreme structure sensitivity of the specific adsorption process based on the concept of stably-adsorbed hydrogen-bonded clusters of a size on the order of the critical terrace width (>5 atomic spacings).

The identity of the species and processes involved in the anomalous fea-tures observed in perchlorate, fluoride, bicarbonate and hydroxide electro-lytes remains more uncertain than in the cases of the sulfate and chloride

electrolytes. Primarily by process of elimination, i.e., hydrogen adsorption and specific adsorption of F^- and ClO_4^- appear highly unlikely, the process in acidic F^- and ClO_4^- electrolytes is most probably related to water anodization, and the species are most probably surface intermediates of this process, i.e., oxygen-like. In basic electrolytes, we have suggested, by a direct analogy with the process in sulfate electrolytes, that specific adsorption of OH^- is the process there. The specifically adsorbed OH^- (pH >9) and the oxygen-like states formed by water dissociation (pH <5) may have similar final state molecular configuration on the surface even though they derive from different initial states. However, the molecular configuration of these oxygen-like intermediates is unknown and there remain difficulties even with this very unspecific identification. Identification of the exact mix of processes corresponding to each voltammetric peak, and determination of the structural relationships between terraces, steps, and hydrogen-bonded adsorbate clusters remain topics ripe for continued research.

ACKNOWLEDGMENTS

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Fig. 1   Window-opening experiment on well-ordered Pt(111). Starts with third

cycle to 550 mV (RHE), with subsequent sweeps to higher anodic

limits. dE/dt = 100 mV/s.

Fig. 2   Voltammetry of Pt(111) showing effects of repetitive cycle:

(a) 1 x 1.28 V (after window-opening), (b) 4 x 1.28 V;

(c) 10 x 1.58 V. dE/dt = 100 mV/s.

Fig. 3   Window-opening experiment on Ar^+-sputtered Pt(111). Starts with

contact at 500 mV, cathodic sweep, then successive sweeps to higher

anodic limits. dE/dt = 100 mV/s.

Fig. 4   Window-opening experiment on well-ordered Pt(111) in 5×10^{-3} M

H_2SO_4. Starts with third sweep to 1000 mV (RHE), with subsequent

sweeps to higher upper limits. Anodic peak at 530 mV and large

anodic current between 900 and 1200 mV occur on second sweep to 1380

mV. dE/dt=100 mV/s.

Fig. 5   Voltammetry of well-ordered Pt(111) in 5×10^{-3} M H_2SO_4 after

100 Langmuir exposure to CO in UHV. Solid line: first sweep. Dotted

line: second sweep. dE/dt = 100 mV/s.

Fig. 6   Voltammetry of well-ordered Pt(111) in 7×10^{-3} M NaOH (solid line)

and in 5×10^{-3} M $NaHCO_3$ + 2×10^{-3} M Na_2CO_3 (dotted line).

dE/dt = 25 mV/s.

Fig. 7   Window-opening experiment on well-ordered Pt(111) in 7 x 10^{-3} M NaOH.
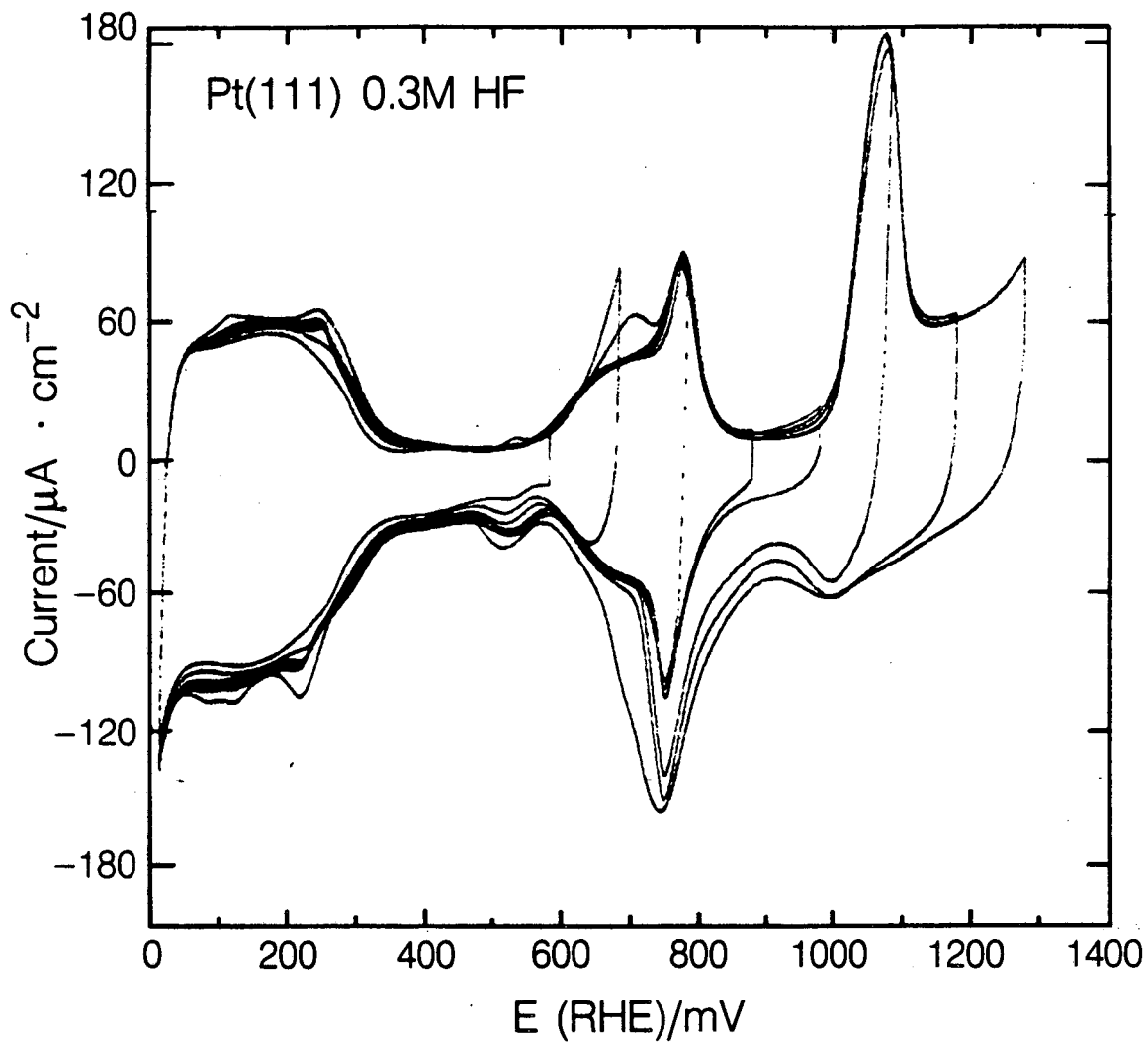dE/dt = 100 mV/s.

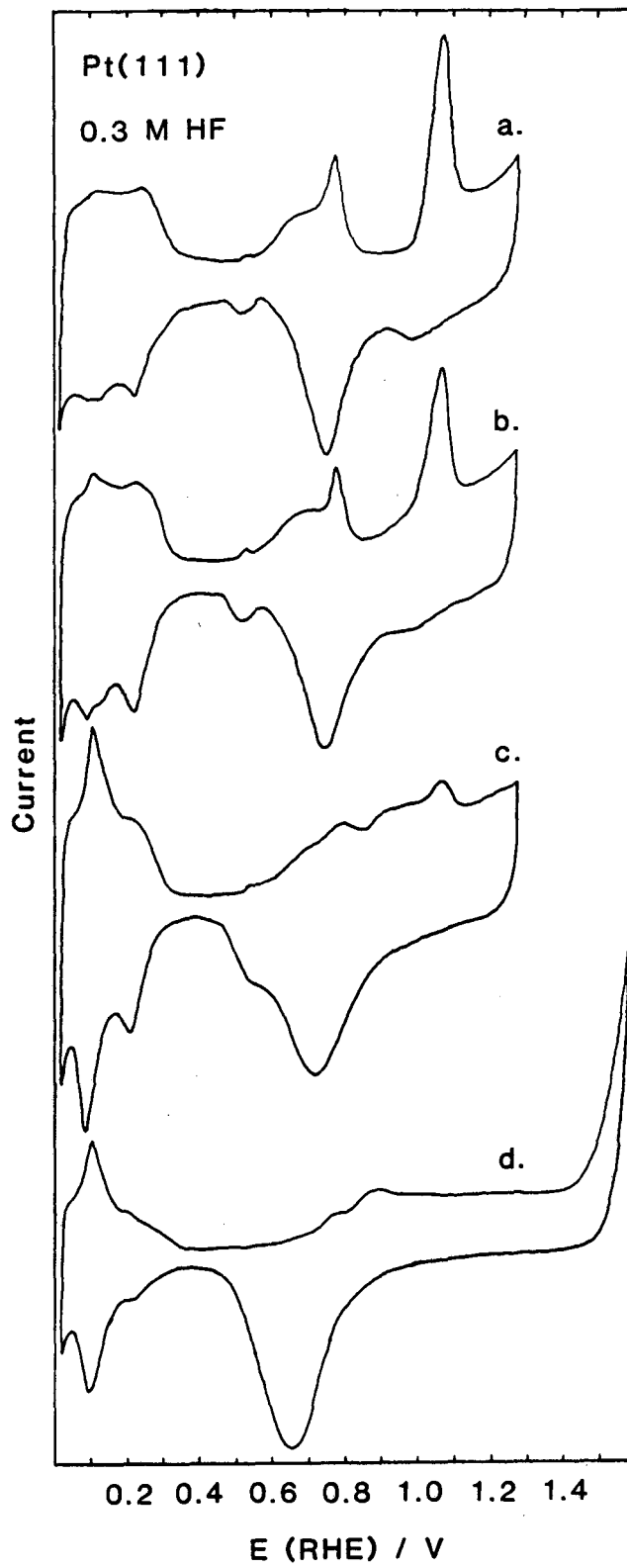Fig. 8   Tenth cycle to 1.5 V of Pt(111) in 7 x 10^{-3} M NaOH.
dE/dt = 100 mV/s.

Fig. 9   Schematic diagrams of a perfect, infinite, adsorbed water bilayer on
an fcc(111) or an hcp(001) metal surface.   (a) side view;
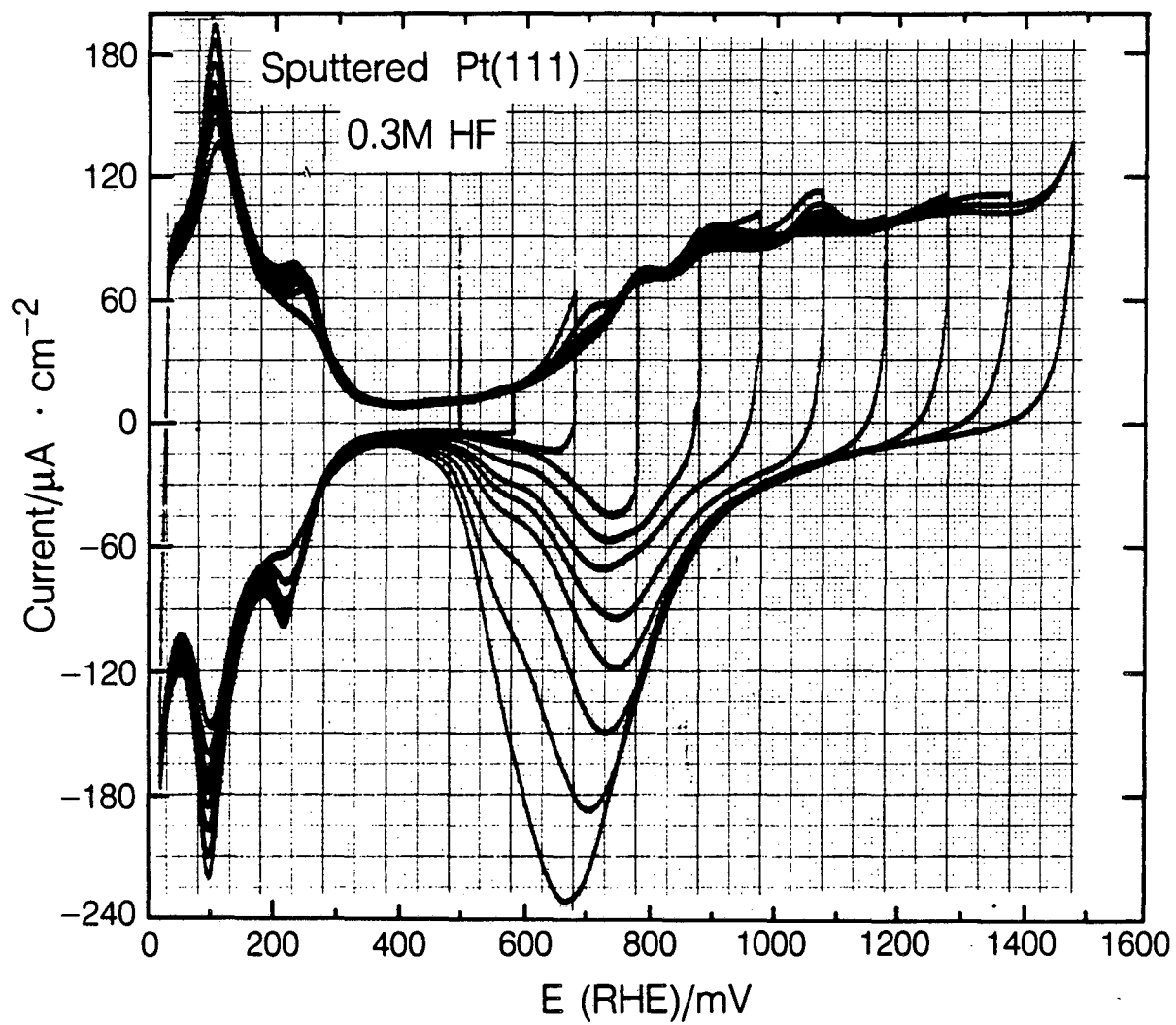(b) top view.

Figure 1

XBL 838-11243
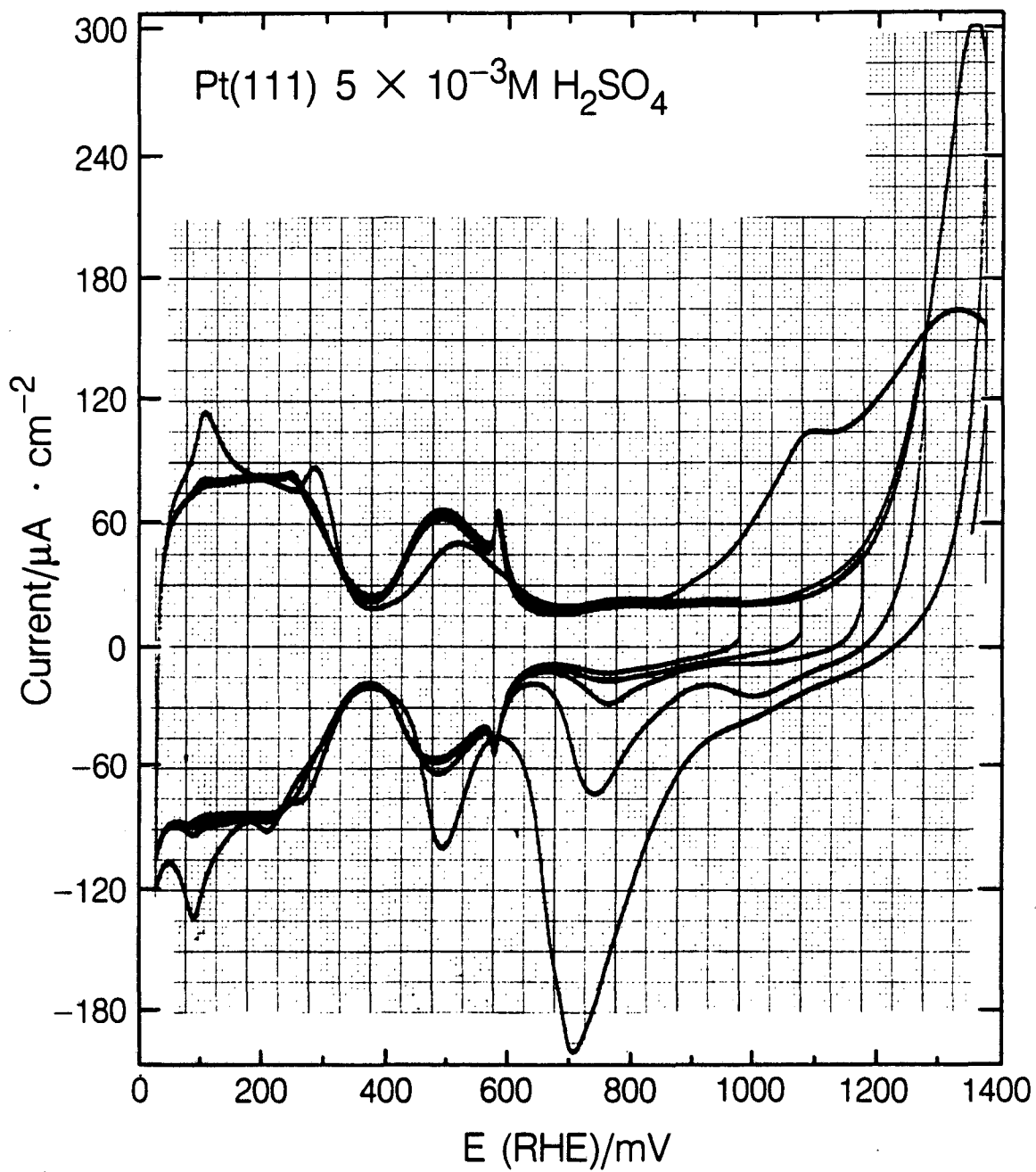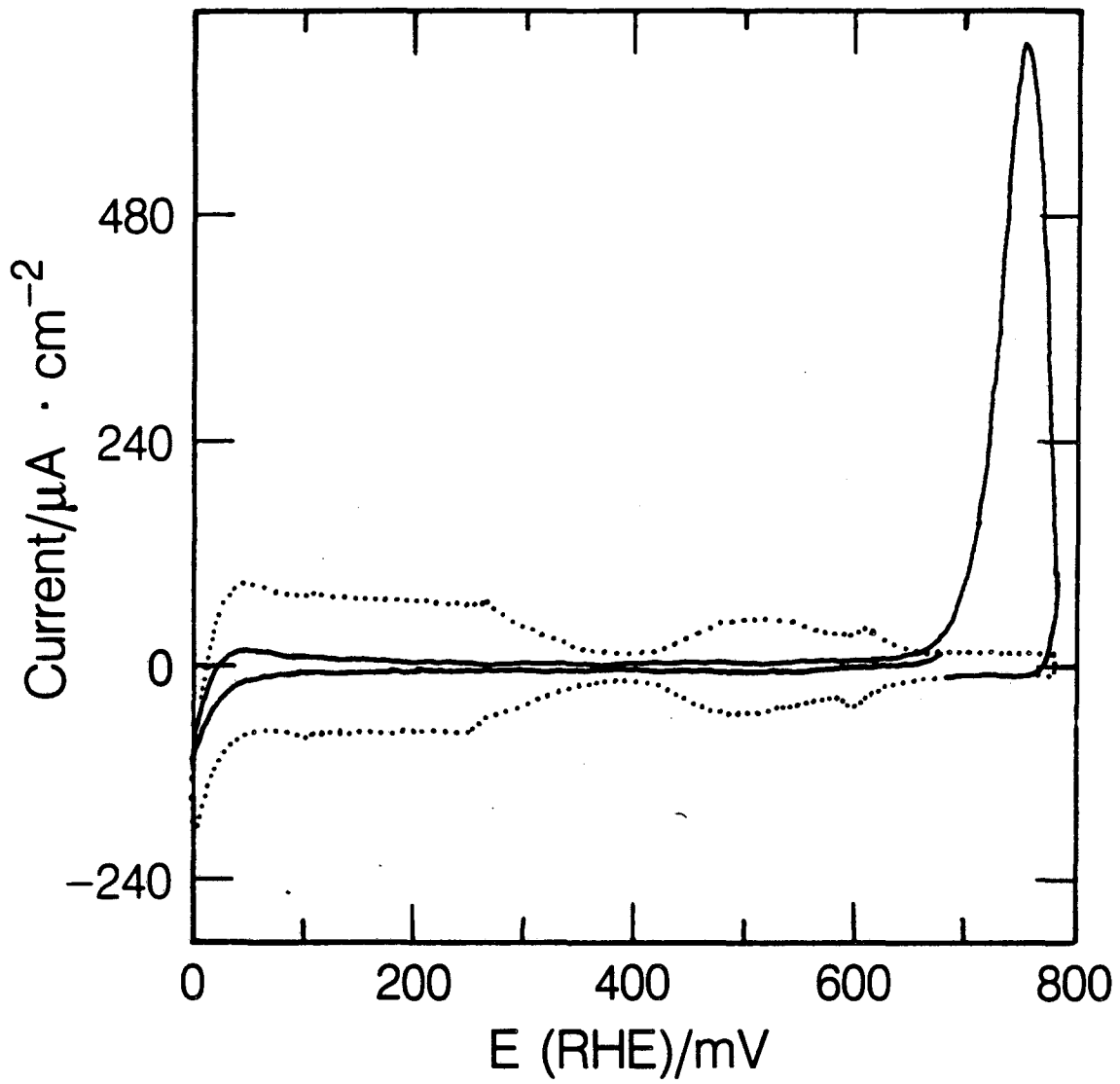
32

Pt(111)

0.3 M HF

a.

b.

c.

d.

Current

E (RHE) / V

XBL 871-290

Figure 2

33

Sputtered Pt(111)

0.3M HF

XBL 838-11250

Figure 3

34

Pt(111) 5×10^{-3}M H_2SO_4

XBL 838-11249

Figure 4

35

XBL 871-8913

Figure 5

y-axis: Current/$\mu A \cdot cm^{-2}$

x-axis: E (RHE)/mV
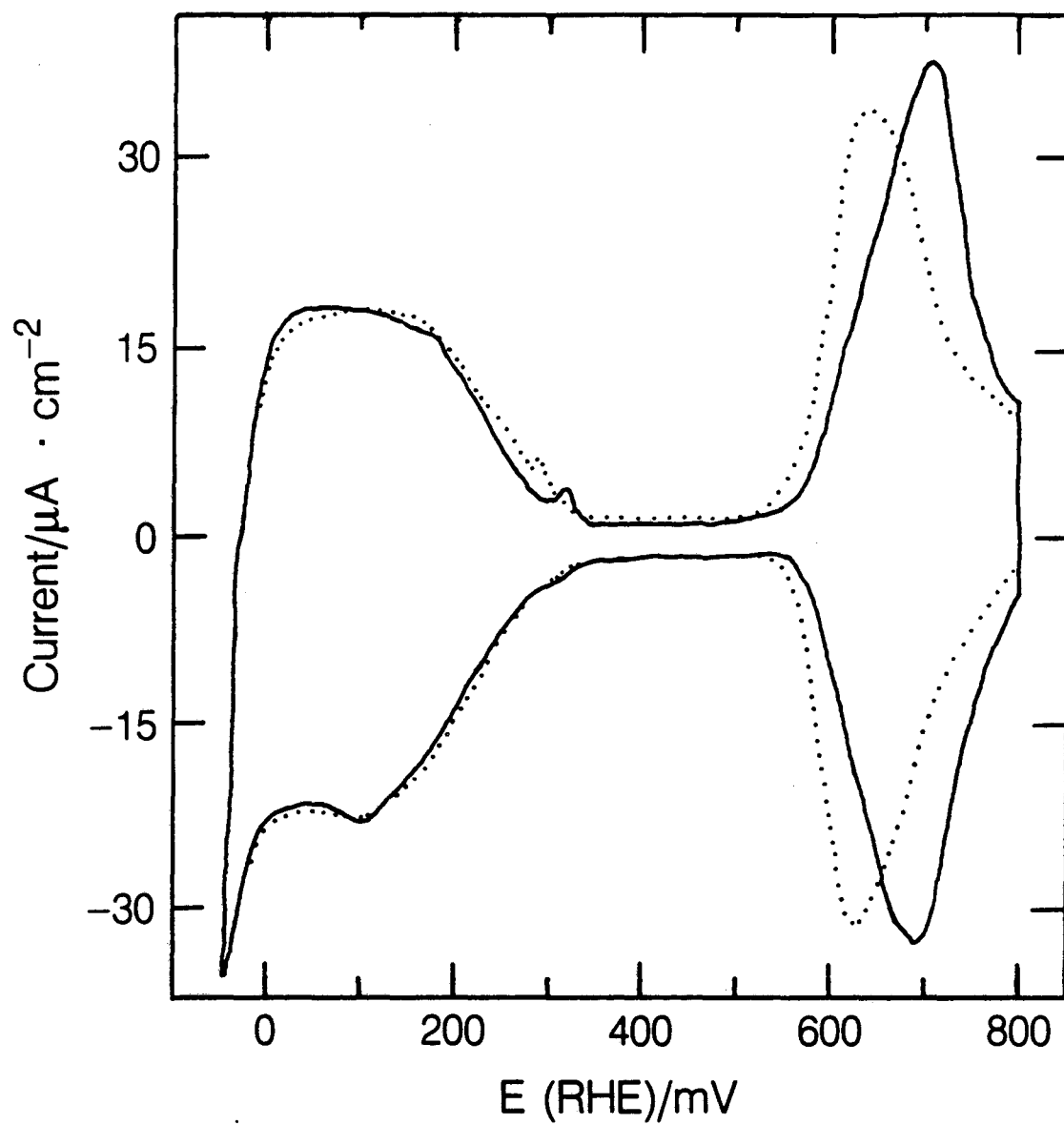
XBL 871-8912

Figure 6

37

Figure 7

XBL 838-11244

Figure 8

XBL 838-11241

first
layer

second
layer

a.

Side View Adsorbed Ice I$_h$

(001)

etc.

Sixth Layer
Fifth Layer } Third Bilayer

Fourth Layer
Third Layer } Second Bilayer

Second Layer
First Layer } First Bilayer
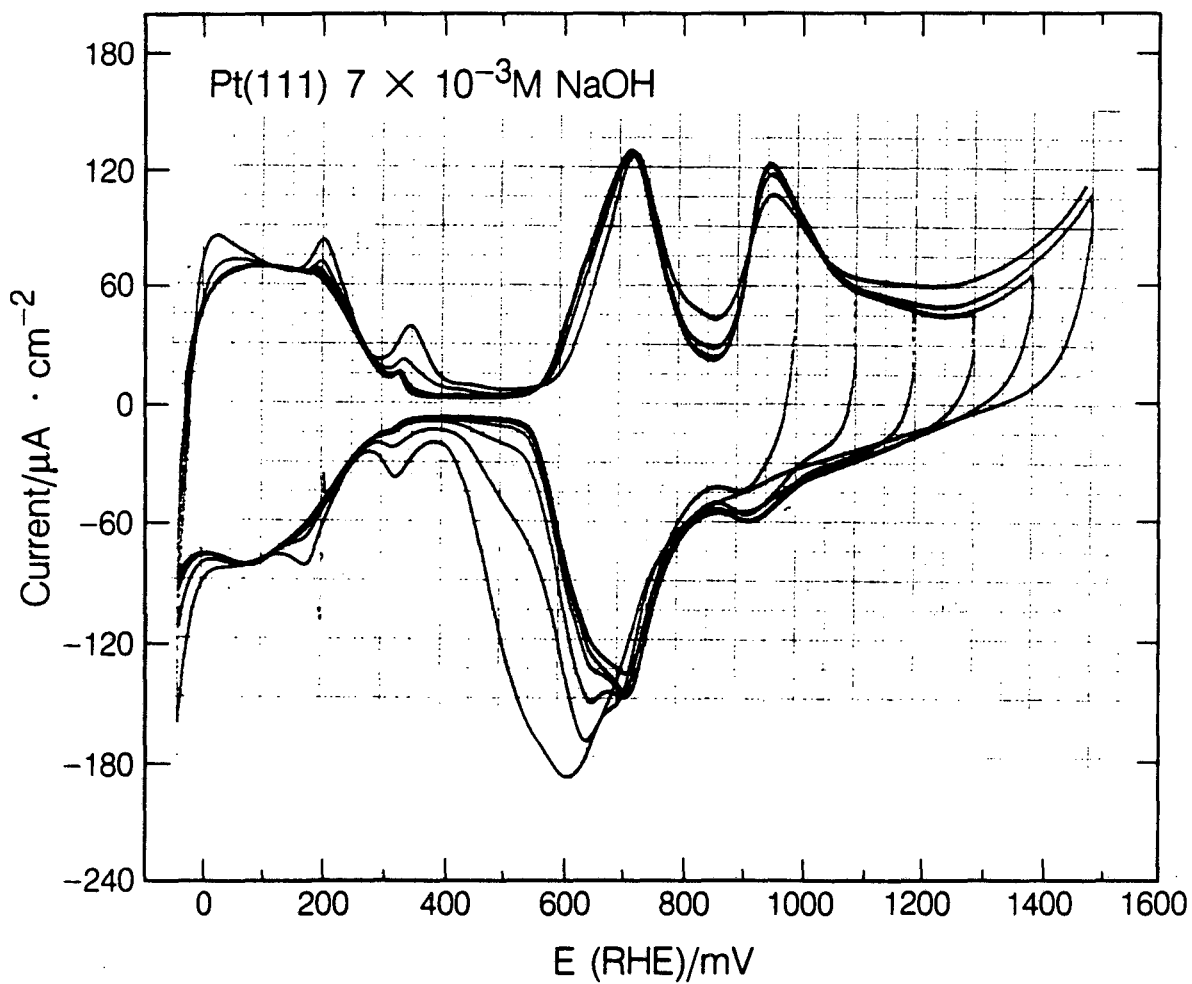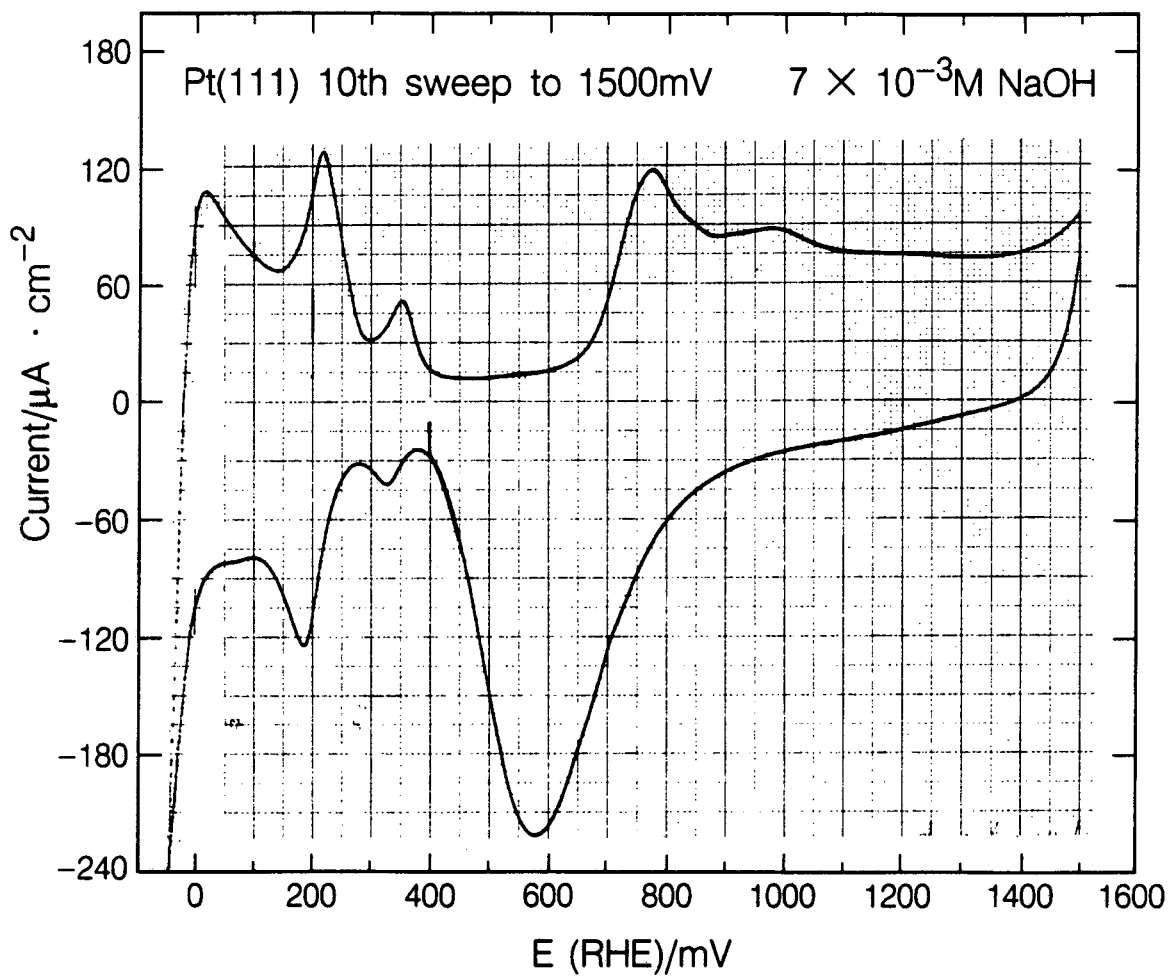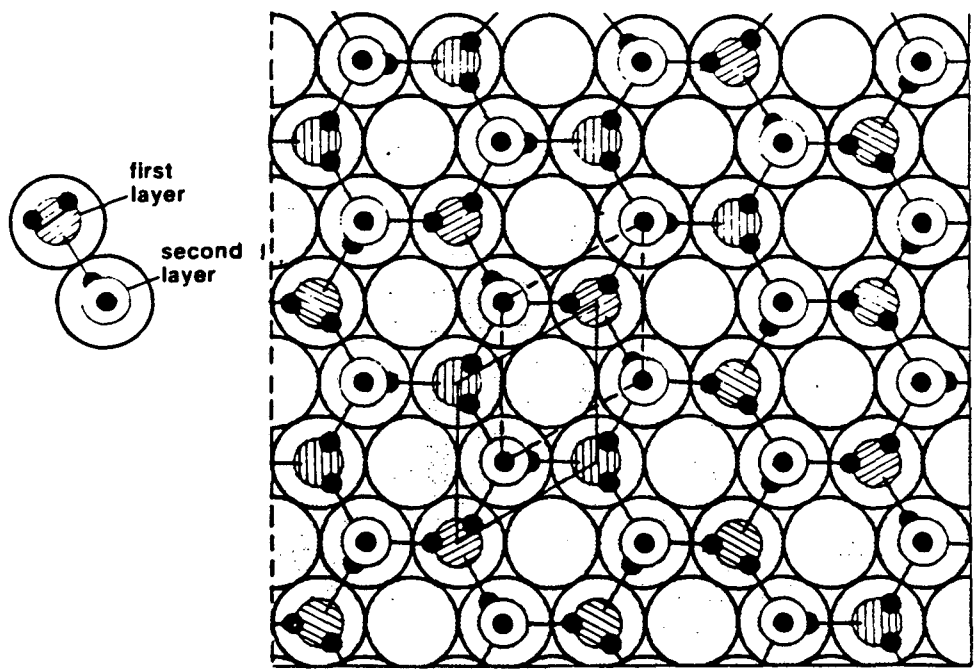
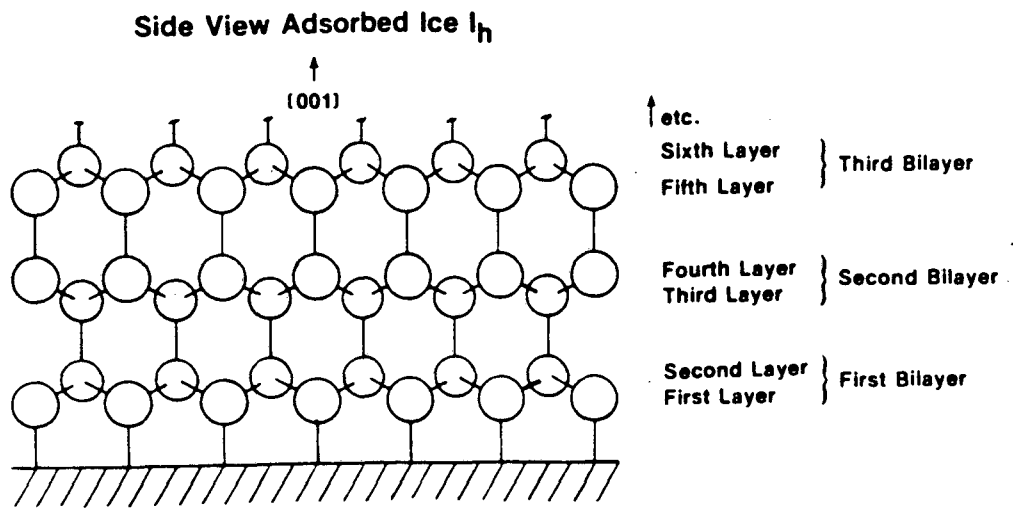b.

XBB 871-845

Figure 9

40

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