CONF-960502--19 ANL/MSD/CP--90769

PLACE-EXCHANGE MECHANISM OF PT (111) OXIDATION/REDUCTION AS OBSERVED BY SYNCHROTRON X-RAY SCATTERING*

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July 1996

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Submitted to the Proceedings of the 6th International Symposium on Electrode Processes (presented at the 189th ECS Meeting, May 5-10, 1996, Los Angeles, CA)

This work is supported by the Division of Materials Sciences, Office of Basic Energy Sciences of DOE, under contract No. W-31-109-ENG-38.

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To be submitted to the
Proceedings of the 6th International Symposium on Electrode Processes
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ABSTRACT

Structural changes in the Pt(111) single crystal surface associated with incipient electrochemical oxidation/reduction were studied by *in situ* synchrotron x–ray reflectivity. It was shown that lifting of Pt atoms of the surface layer occurs, substantiating the long–standing hypothesis of a *place–exchange* mechanism for solution/metal interface oxidation. It was also shown that, for a charge transfer of $\lesssim 1.7\ e^-$/Pt atom, the initially flat surface structure could be recovered by electrochemical reduction. In contrast, the surface was irreversibly roughened for amounts of charge transfer exceeding $\sim 1.7\ e^-$/Pt, but the roughening involved only the atoms in the top layer of the original flat surface. A detailed mechanism is proposed for the place–exchange mechanism and the subsequent roughening of the electrode surface.

INTRODUCTION

The alteration of the surface of platinum by the electrochemical formation and reduction of an oxide layer is of importance in the operation of several electrochemical systems ranging from fuel cells and metal–air batteries to electrochemical syntheses. Many important reactions, such as hydrogen, oxygen, chlorine, persulfate and percarbonate production, Kolbe reactions, and electrocatalytic oxidation of organic fuels, among others, proceed on surfaces either formed by oxida-

tion/reduction or covered by oxide. It is not surprising therefore that much work was done to characterize these surfaces. The early work was carried out, almost invariably, on polycrystalline platinum electrodes using electrochemical techniques. Numerous reviews of this research have been written (1–5).

Anodic oxidation of noble metals has received considerable attention also in recent years, and the behavior of platinum has been of particular interest. Recent results in this area are described, for example, in (6–8) and references therein. Despite the numerous studies, lack of direct, *in situ* experimental probes has left microscopic details of the oxidation phenomena unproven and controversial, especially at the incipient stages of oxidation involving submonolayer coverages. Nevertheless, a certain amount of indirect evidence has accumulated indicating the involvement of a place–exchange step during the oxidation/reduction process. The conditions favoring place exchange (potential, solution composition, etc.) and the conditions under which it leads to surface roughening have not been clarified. Furthermore, the exact nature of the oxygenated species taking part in the place exchange has not been determined. The most suggestive evidence for place exchange came from low energy electron diffraction studies in a UHV–electrochemical transfer system (7,9), which indicated increased diffuse scattering around the Pt(10) spots after oxidation/reduction cycles covering a charge transfer $\gtrsim 1$ e^-/Pt. It was suggested that the diffuse scattering is due to increased step density on the reduced surface resulting from the PtOH–to–HOPt place exchange during oxidation. However, because the oxidized surface structure was not observed, this result could be explained without necessarily postulating place exchange.

From the electrochemical irreversibility of platinum oxide reduction on polycrystalline platinum, a mechanism has been proposed (10–11) in which platinum and oxygen undergo a place exchange during oxidation. Upon reduction of the place–exchanged oxide, the displaced platinum atoms do not return to their original positions in the surface mesh thereby causing roughening of the platinum surface. Oxidation/reduction cycles cause an irreversible change in the well–known Pt(111) voltammetric signature, causing disappearance of the "butterfly" and reversible oxide peaks and an increase in the low energy hydrogen adsorption peak. Evolution of the platinum surface order with oxidation and reduction has been studied by voltammetry, low energy electron diffraction, scanning tunneling microscopy and, preliminarily, by x–ray crystal truncation rod studies.

Motoo and Furuya (12) used the height of the "butterfly" spike in the voltammetric profile as a measure of surface damage by oxidation. They oxidized the Pt(111) surface by potentiostatting at an anodic potential for 10 s or by pulsing

to the oxidizing potential. They found that the surface exhibited damage when the potentiostatted potential exceeded 1.2 V, however a pulsed potential of 1.4 V (RHE) was necessary to induce damage. It was found that a given amount of "butterfly" peak decrease occurs with a smaller amount of oxygen when pulsing as compared to potentiostatting. The voltammetric profile observed after these oxidations was identical to that seen when adsorbing oxygen from the gas phase. They concluded that the place exchange of oxygen and platinum and subsequent removal of the oxygen results in holes in the surface mesh. These holes destroy the sites responsible for "very strong hydrogen" adsorption which is the source of the voltammetric "butterfly" spike.

Aberdam et al. (13) and Wagner and Ross (7,9,14) have studied the oxidation of platinum single crystal faces using ex situ ultra–high vacuum techniques. Aberdam et al. found that cycling to 1.15 V (RHE) adsorbs a quarter of a monolayer of oxygen and causes no LEED–detectable change in the surface structure. However, cycling the potential up to 1.37 V causes the formation of monoatomic steps. These point defects are nearly randomly distributed and are separated by at least eleven to twelve compact rows. These defects tend to cluster into steps with repeated cycling to lower the excess surface energy. Wagner and Ross found that cycling to 0.83 V (RHE) causes no LEED–detectable change in the surface structure, cycling to 1.28 V causes random steps with residual flat areas and cycling up to 1.58 V yields a randomly stepped surface with a mean terrace width of 4 to 5 atoms with no residual flat areas. They concluded that oxidation below 1.0 V occurs through surface adsorption of oxygen, whereas oxidation above 1.0 V occurs by adsorption into a new surface phase. They state that the driving force for place exchange between oxygen and platinum is the electrical potential gradient across the metal/solution interface. The critical coverage necessary to induce surface disorder was one monolayer of a one electron species (OH^-) or half a monolayer of a two electron species (O^{2-}).

Sashikata et al. (15) studied the effects of oxidation/reduction cycles on Pt(111) using in situ scanning–tunneling microscopy. They found smooth terrace–step structures with monatomic steps as long as the electrode potential was held in the 0.3 to 1.0 V region. One cycle to 1.5 V caused the formation of small islands with diameters of 5 to 20 Å and monatomic height. A steady–state structure was reached after 5–10 potential cycles. This structure contains a three–fold symmetry array of islands with an island diameter of 20 to 30 Å. Both diatomic and monatomic step heights were seen with the most probable step height being diatomic. The islands of this highly roughened surface are hexagonal or trigonal instead of circular, indicating preferential orientation. This preferential orientation may explain the evolution of the low energy hydrogen adsorption peak in the

cyclic voltammograms with repeated oxidation/reduction cycles. The low energy hydrogen adsorption peak has been attributed to adsorption on Pt(110) island edge sites (16,17).

The results of a preliminary study of electrochemically induced roughening of a Pt(111) surface using the crystal truncation rod technique have been reported by Bommarito et al. (18). The platinum surface was roughened by applying a potential of 1.0 V (Ag/AgCl) for 15 minutes to a single crystal immersed in pH 7.0 phosphate buffer containing 0.1 M sodium sulfate. Prior to this oxidation treatment the surface roughness was 3.3 ± 0.3 Å and was attributed to displaced atoms occupying lattice positions. Oxidation caused the surface roughness to increase to 225 Å. Based on these results, they suggested a roughening mechanism where the outermost layers amorphize and the subsequent layers largely retain the structural features of the original surface.

It is fair to state that a reasonable consensus opinion is that the mechanism of platinum oxidation is one of the following:

$$Pt + H_2O \longrightarrow PtOH + H^+ + e^- \quad (1)$$

$$PtOH \longrightarrow HOPt \quad (2)$$

$$HOPt \longrightarrow OPt + H^+ + e^- \quad (3)$$

or

$$Pt + H_2O \longrightarrow PtOH + H^+ + e^- \quad (4)$$

$$PtOH \longrightarrow PtO + H^+ + e^- \quad (5)$$

$$PtO \longrightarrow OPt \quad (6)$$

where the second and sixth steps are place exchanges. There is no clear evidence that would permit a selection between the two mechanisms, and most of the evidence for either mechanism is largely indirect and circumstantial.

Our work was carried out to explore the feasibility of the *in situ* examination of the incipient oxidation/reduction process of platinum using synchrotron x–ray reflectivity techniques. In recent years, this technique has been proven to be a useful tool for the *in situ* study of single–crystal/solution interfaces under electrochemical control (19). In this communication, we will focus on the question of place–exchange mechanism and on the extent of roughening after oxidation/reduction of a Pt(111) surface. Some of the experimental results we rely on for our conclusions have been published before (20,21),[1] and other aspects of this study, including details of the experimental techniques and data analysis, will be given elsewhere together with the results of a similar study on the Pt(110) surface (22).

[1]Figures 2 and 4 of reference (20) were inadvertently interchanged.

EXPERIMENTAL

X–ray reflectivity measurements were carried out in a transmission geometry (23) at the X10B bending magnet beamline of the National Synchrotron Light Source (NSLS) with $\lambda = 0.9682$, and at the F2 24–pole wiggler beamline of the Cornell High Energy Synchrotron Source (CHESS) with $\lambda = 0.9611$. The longitudinal instrumental resolution was $\sim 3 \times 10^{-3}$ Å^{-1}. Single crystals of Pt were precut to expose a rectangular Pt(111) surface with an area of 3 mm by 10 mm, mechanically polished, and annealed in a high–vacuum furnace at ~1900 K. The measured mosaic width of the two crystals used in this study was ~0.1 degree and the surface miscuts were smaller than 0.05 degree. At the time of the experiments, the Pt crystals were further prepared by annealing in hydrogen flame (~1300 K), followed by slow cooling in an inert atmosphere containing I_2 vapor. The adsorbed iodine served to protect the surface from contamination during transfer of the crystal and assembly of the x–ray/electrochemical cell (24). The iodine was subsequently removed from the surface by electrochemical reduction in 0.1 mol/liter NaOH solution. This procedure has been shown to generate a surface equivalent to that produced by UHV techniques (25). The measurements were performed in 0.1 mol/liter $HClO_4$ solution or in 0.1 mol/liter CsF solution. The results were essentially the same in either solution. The electrochemical potentials are referred to the potential of hydrogen evolution in the test solution. The uncertainty of the potential values is generally about ± 25 mV, but maybe even as high as ± 50 mV because of slow drifting of the reference potential in our synchrotron setup.

RESULTS AND DISCUSSION

In the early stages of our investigation of platinum oxidation (20), we found that the surface was not roughened by oxidation/reduction for charge transfers $\lesssim 1.7\ e^-$/Pt, while the surface irreversibly roughened for charge transfers $\gtrsim 1.7\ e^-$/Pt. The irreversible roughening of the surface above the critical charge transfer level implies surface diffusion of Pt atoms or a Pt compound during oxidation/reduction. Hence, a series of measurements was made to explore whether place exchange occurs before the surface diffusion step.

We performed a series of specular and off-specular reflectivity scans at various potentials to understand the nature of the surface modification during oxidation. The potential was changed to four consecutively more oxidizing potentials between 1.025 V and 1.175 V. The x–ray reflectivity was considerably distorted from that of

the original smooth surface, indicating a structural change of the oxidized surface. Finally, the surface was reduced, and the final x–ray measurements indicated that the original smooth surface was recovered.

The specular reflectivities measured at these oxidized surfaces were compared to reflectivities calculated with a number of surface models, and good agreement was obtained only when we considered the rearrangement of Pt atoms by place exchange. In this case, the electron density in the original surface layer decreases by an amount corresponding to the number of Pt atoms lifted, resulting in two partially occupied layers. The fit to this model was excellent, and it also produced a measure of the fraction of the Pt monolayer lifted by the place exchange (20). It should be emphasized that only the positions of the Pt atoms can be considered in the modeling of the x–ray reflectivity because the electron densities of both the OH^- and O^{2-} species are negligible compared to that of Pt. Therefore, x–ray reflectivity cannot distinguish between OH^- and O^{2-}, nor can it be used to determine directly the position of these species.

We can now offer the following tentative explanation of our experimental observations. When surface oxidation occurs, either OH^- or O^{2-} is chemically adsorbed onto the surface. This process inevitably involves electron transfer from platinum atoms to OH^- or O^{2-}, therefore, molecular forms of Pt—OH or Pt—O should be present on the surface. Although the exact magnitude of the electric dipole moment of these species is not known, it is safe to assume that Pt—O has a larger dipole moment than Pt—OH because Pt—O formation involves two electron transfers while Pt—OH formation involves only a single electron transfer. On a Pt(111) surface, the platinum atoms available for chemisorption are on a triangular lattice. Because of the high repulsive dipole–dipole interaction energy, two parallel dipoles will not exist on nearest–neighbor sites; consequently, adsorption occurs in a "nearest–neighbor–avoiding" configuration, such as 2×2 or $(\sqrt{3} \times \sqrt{3})R30°$, depending on the details of the interactions (26). Although thermodynamic equilibrium and long range order cannot be achieved at room temperature with such super structures (no superlattice reflections were found experimentally in our x–ray studies), adsorption of OH^- and a subsequent oxidation process is expected to comply with the nearest–neighbor–avoiding scheme.

Within the framework of this scheme and based on our experimental results, a detailed model of surface oxidation can now be proposed. In Fig. 1 we present the voltammogram of our electrode, superimposed on the x–ray intensity scan as a function of the potential. In the cyclic voltammogram, we will consider only the features near 0.8 V and 1.1 V, to which we will refer hereafter as peak I through IV. Notice that no change in x–ray intensity is observed at 0.8 V (peak I),

but the x–ray intensity quickly drops at 1.025 V (peak II), where a sharp oxidation peak is observed. In the reduction cycle, the x–ray intensity quickly rises again at 1.025 V (peak III), where a relatively minor reduction peak appears, while there is no change in the x–ray intensity near 0.8 V (peak IV).

The fraction of a Pt monolayer place exchanged is plotted against the extent of charge transfer and electrode potential in Fig. 2, for the four potentials where full x–ray scans were made. At 1.025 V where the estimated total charge transfer is 0.7 e^-/Pt, we observe that an 0.20±.03 fraction of the top surface Pt atoms were place exchanged. That is, more than three electron transfers occurred for each place–exchanged atom. At this potential we are effectively sitting at a potential that is negative from the maximum potential of peak II and taking a long x–ray scan for approximately an hour or more. Therefore, we can assume that the structural change associated with peak II has not been completed, and the structure must be in an intermediate state. At 1.075 V (1.05 e^-/Pt transferred), the measured fraction of the place exchange is 0.24±.03, and the structural transformation associated with peak II should be completed or nearly completed. At 1.125 and 1.175 V (1.40 and 1.75 e^-/Pt), the place–exchanged fractions are 0.28±.03 and 0.32±.03, respectively. Note that at the highest potential about eight electron transfers occurred for every atom place exchanged in excess of the electrons transferred at 1.025 V where a 0.2 fraction of the monolayer was place exchanged. The highest fraction of atoms place exchanged in this series of experiments (0.32) occurred near to the potential of the critical charge transfer needed to cause permanent surface roughening, and transferring more charge at higher potentials resulted in roughening of the platinum surface as discussed earlier.

In Fig. 3, six possible surface structures are shown schematically, and the estimated charge transfer for each structure is presented in Table I. The first structure is adsorption of OH^- forming a nearest–neighbor–avoiding structure with local $(\sqrt{3} \times \sqrt{3})R30°$ or 2×2 structures. This is the first step in either of the proposed three–step mechanisms. We calculate the charge transfer to be 0.33 e^-/Pt for the $(\sqrt{3} \times \sqrt{3})R30°$ structure and 0.25 e^-/Pt for the 2×2 structure. Since we cannot estimate the ratio of these two surface structures, as a first approximation, we take the average of the two charge transfer amounts, resulting in 0.29 e^-/Pt. The charge transfer amounts for the rest of the structures were calculated in the same way, assuming a 50–50 mixture of local $(\sqrt{3} \times \sqrt{3})R30°$ and 2×2 structures. The area under peak I of the voltammogram is approximately 0.3 e^-/Pt in agreement with the charge transfer calculated for structure 1, and no change in x–ray intensity (i.e., no rearrangement of platinum atoms) is observed. From these observations, peak I is consistent with step 1 or 4 of the proposed reaction sequences. On further increase of the potential, the OH^- coverage does not increase at first because it

would involve occupation of nearest–neighbor sites which is energetically unfavorable. Therefore, no current is flowing and no structural changes occur until peak II is approached at around 1 V.

Structures 2 and 3 show two possible intermediate stages between structures 1 and 4 (Fig. 3). Structure 2 represents the conversion of Pt—OH to Pt—O with the loss of H and an additional charge transfer of 0.3 e^-/Pt or a total of 0.59 e^-/Pt, and this corresponds to step 5 of the proposed mechanism. Structure 3 assumes that Pt—OH molecules are place exchanged (this is step 2 of the proposed reaction sequence), and subsequently more OH^- is attracted to the nearest–neighbor sites because of the favorable (antiparallel) dipole–dipole interaction. In structure 4, the Pt—O molecules are place exchanged and attract OH^- to the nearest–neighbor sites. For this structure, the total charge transfer is 1.17 e^-/Pt, which is 0.89 e^-/Pt more than that for structure 1.

The measured charge transfer under peak II is approximately three times that under peak I, which corresponds to the ratio of calculated charges for structure 1 being converted to structure 4, and we can conclude that at around 1.1 V (at the higher potential side of peak II), structure 4 must have been completely formed. At this point, the total charge transfer estimated from the measurements is 1.2 e^-/Pt consistent with the calculated charge transfer of structure 4 shown in Fig. 3. However, the mechanism of the transformation of structure 1 to structure 4 can not be determined experimentally. It can take place either via structure 2 or via structure 3. Nevertheless, the two reaction steps between structure 1 and structure 4 should occur practically simultaneously in either case because there is only a single peak (peak II) in the voltammogram. As the potential is increased beyond peak II, the nearest–neighbor OH^-s loose H and a fully oxidized Pt—O place–exchanged layer is formed as shown in structure 5. For this structure, the calculated charge transfer is 1.75 e^-/Pt. This is close to the critical charge transfer for the oxidation induced roughening and to the charge transfer measured at the potential of 1.175 V.

The energetics and dynamics of the place exchange can be considered as follows. In the case of a $(\sqrt{3} \times \sqrt{3})R30°$ structure, a triangular lattice of dipoles can have two degenerate configurations: (i) 2/3 sites up and 1/3 sites down and (ii) 1/3 sites up and 2/3 sites down. In other words, the majority dipoles can be up dipoles or down dipoles (26). This degeneracy stems from an assumption that an isolated dipole in zero external field (e.g., at the pzc) has no preferential direction. However, in our case, the dipoles are not isolated but are part of a solid lattice. Therefore, flipping an individual Pt—O (or Pt—OH) dipole requires a considerable energy because the six nearest–neighbor Pt—Pt bonds have to be broken for the

flip to occur. In other words, the nearest Pt—Pt bonds exert an "effective local field" on the individual Pt—O (or Pt—OH) dipoles. Consequently, to flip a single Pt—O (or Pt—OH) dipole, the external field first has to overcome the local field; that is, the total effective field that an individual dipole feels is the external field minus the effective local field. Therefore, we expect that zero effective field will occur at a considerably more positive potential than the pzc.

As the potential approaches that of peak II, structure 1 of Fig. 3 prevails, while the external electric field strength increases on the Pt—OH molecules. Upon nearing the potential of peak II, two possibilities exists. (i) At the potential of the place exchange, the external field is strong enough to flip a Pt—O but not strong enough to flip a Pt—OH. In this case, protons have to be dissociated from Pt—OH before the actual place exchange occurs (reaction step 5 in the proposed mechanism). Because the dipole moment of the couple has now suddenly increased, its reaction to the external field forces the Pt—O to flip (step 6 of the proposed mechanism). Once a Pt—O flips, it can attract OH^-s to the nearest neighbors to form staggered dipole moments around it because the attractive (antiparallel) dipole–dipole interactions lower the total configurational energy. (ii) The external field may be strong enough to flip the Pt—OH dipole and to form an antiparallel structure as shown in structure 3 which lowers the energy. In either case, the place exchange occurs because it lowers the electrostatic energy of the place–exchanged molecules *and* also permits oxidation of the nearest neighbors. This explains the anomalously large charge transfer per place–exchanged Pt—O (5.3 e^-/ place–exchanged Pt) and the fact that the place exchange is accompanied by such the large charge transfer observed in voltammetry (peak II).

During the reduction cycle, the x–ray intensity recovers fully at peak III, which can be explained by a "reverse flip" of the place–exchanged Pt—O. Indeed, this peak is expected to appear in the voltammogram only when peak II exists (14). The fact that peak III is much smaller than peak II but their potentials are similar implies that the place exchange is driven by the total effective external field (therefore, the lowering of electrostatic energy) rather than the charge transfer itself. This is contrary to the oxidation reaction because oxidation of Pt—OH to Pt—O probably induces the entire place exchange sequence. In other words, oxidation can trigger the place exchange, but the reverse place exchange may not be necessarily triggered by reduction. It is probable that the small peak III is associated with the partial reduction of Pt—O to Pt—OH by readsorption of H. Finally, complete reduction occurs when the potential reaches peak IV, where the remaining OH^-s and O^{2-}s disassociate from the surface. The size of peak IV is experimentally found to be directly proportional to the total charge transfer amount, indicating that most reduction charge transfer occurs at peak IV without

structural modification of Pt atoms (14). The wide peak separation also implies that the oxidation/reduction reaction is electrochemically irreversible.

The following mechanism is suggested for the irreversible surface roughening occurring when the critical charge transfer amount is exceeded. When the conversion from structure 4 to structure 5 is completed, by further increase in potential beyond peak II, the fraction of place–exchanged Pt atoms is 0.29 for a random nearest–neighbor–avoiding structure (at a charge transfer of 1.75 e^-/Pt). Even for an ideal $(\sqrt{3} \times \sqrt{3})R30°$ arrangement of Pt—O dipoles, the fraction of place–exchanged atoms can not exceed 0.33. On further oxidation, structure 6 will be produced, and this provides an explanation of the irreversible surface roughening. Upon further oxidation, OH^- or O^{2-} reacts with the *place–exchanged* Pt atoms. Therefore, the formation of the Pt—O or Pt—OH (shown in the boxes) is accompanied by a decrease of the metal–oxygen bond strength in the second layer of platinum atoms. When this happens, the newly formed Pt—O or Pt—OH will easily move away from their original positions by surface diffusion, and reduction of the oxide will not recover the original Pt surface structure, resulting in irreversible roughening of the surface. This scenario of irreversible roughening is totally consistent with our experimental observations. The experimentally observed critical charge transfer is 1.70(5) e^-/Pt (20), compared to 1.75 e^-/Pt calculated for the complete nearest–neighbor–avoiding structure. The experimentally observed maximum fraction at the critical charge transfer is 0.32±.03 (20), compared to the calculated value of 0.29. It is also less than the maximum possible place–exchange fraction of 0.33.

ACKNOWLEDGEMENTS

This work was sponsored by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. W-31-109-ENG-38. We are grateful to R. M. Yonco for his help with many of the experimental details and to V. A. Maroni for a critical reading of the manuscript.

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Table I.

Amount of charge transferred for the structures shown in Fig. 3.

	Up	Down	Charge Transfer (e^-/Pt)		
			2×2	$(\sqrt{3}\times\sqrt{3})R30^\circ$	Average
Structure 1	OH	---	0.25	0.33	0.29
Structure 2	O	---	0.50	0.67	0.59
Structure 3	OH	OH	0.75	1.00	0.88
Structure 4	OH	O	1.00	1.33	1.17
Structure 5	O	O	1.50	2.00	1.75
Structure 6	O	---	---	---	>1.75

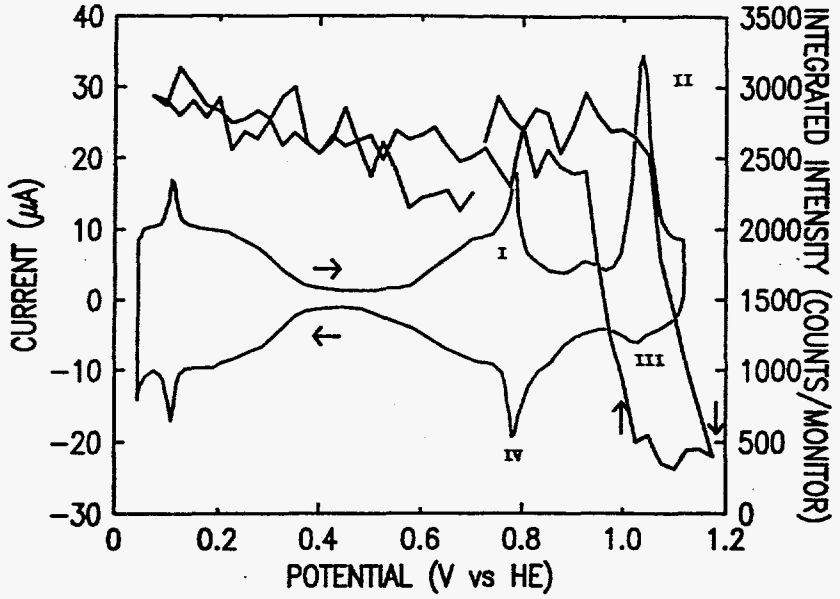

Fig. 1. Voltammogram of Pt(111) in 0.1 M $HClO_4$ solution (bottom curve) and the change of scattered x-ray intensity at (0,0,1.3) versus the potential (top curve).

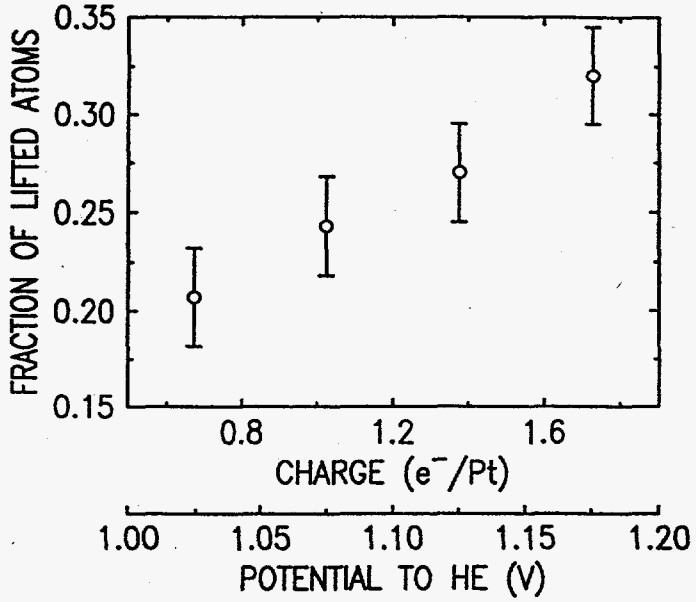

Fig. 2. Fraction of Pt monolayer place exchanged as a function of charge transferred and electrode potential.

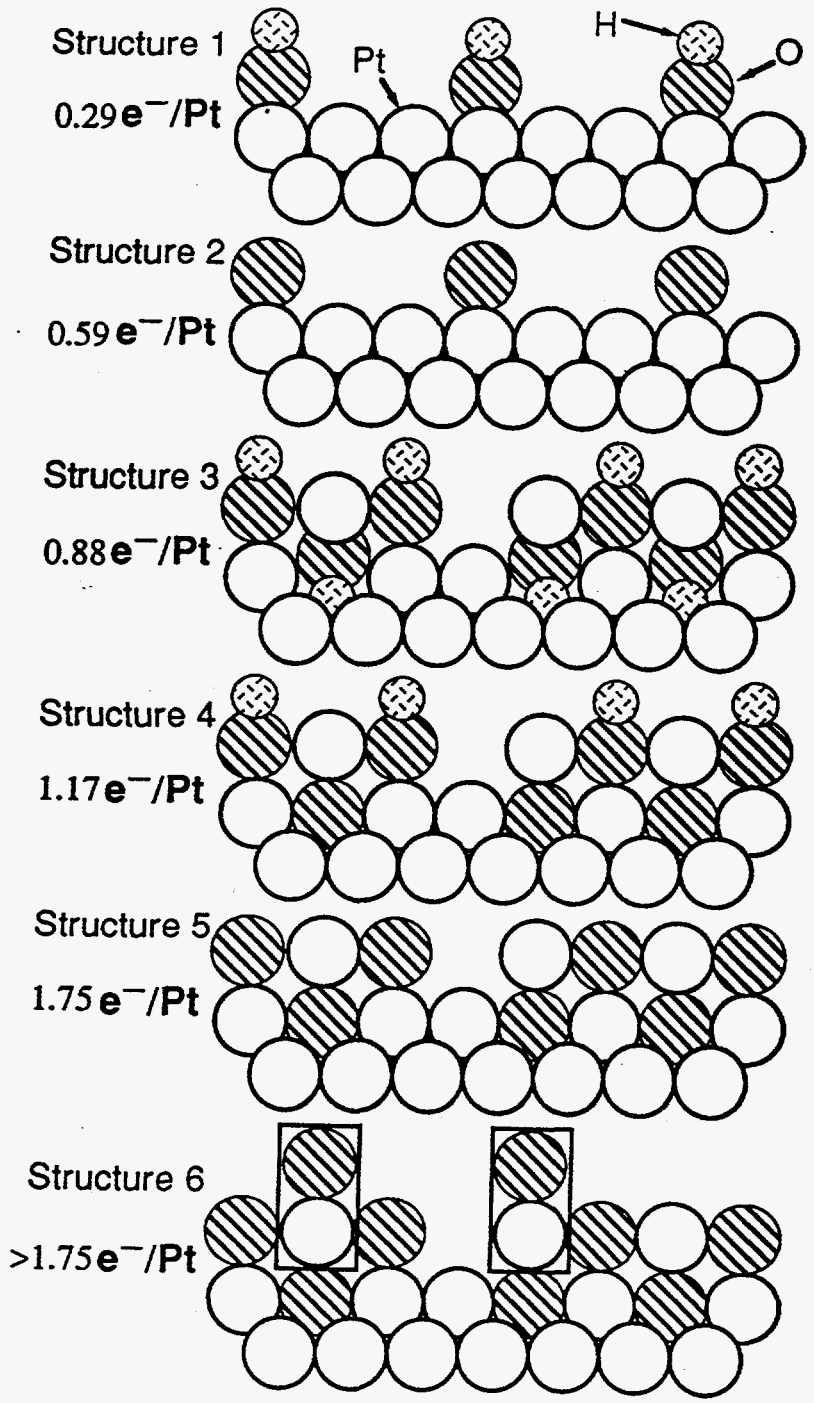

Fig. 3. Six possible structures of the oxidized surface.