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ABSTRACT

Anodic films formed on Pt(100) in 0.3M HF using a quasi thin-layer electrochemical cell within a vacuum envelope were transferred to ultra-high vacuum for study by AES and TDS. Films generated at potentials above 1.1V (RHE) survived emersion and pumpdown in a hydrated state. As the emersion potential increased, the integrated H₂O and O₂ thermal desorption signals increased in parallel, indicating a constant stoichiometry consistent with the formation of a platinum hydroxide layer. The oxygen TDS and AES signals after holding the electrode at constant potentials above 1.9V(RHE) for several minutes saturated with formation of a surface phase containing 2.3 O/Pt (desorbing as O₂) and 2 H₂O/Pt. Much thicker films could be grown by AC polarization. XPS analysis combined with TDS indicated the most likely chemical state of the saturation layer to be Pt(OH)₄. Water evolved from all films at 400K and higher, temperatures much higher than that reported for surface adsorbed hydroxyl groups produced by low-temperature gas-phase coadsorption of O₂ and H₂O [1]. The higher temperature desorption is ascribed to the incorporation of hydroxyls into a surface phase involving place-exchange between Pt and OH.

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1. Introduction

The electrochemical interactions of oxygen and water with platinum are central to the operation of metal-air batteries, fuel cells, and electrolyzers, in which Pt-group metals or their alloys have proven to be the best electrocatalysts. Anodic oxides on platinum have been studied extensively by electrochemical and optical techniques and to a lesser extent by UHV surface analytical methods, but the composition and hydration of the films remain subjects of controversy. Much discussion has centered upon the distinction between adsorbed oxygen and phase oxides, the latter being defined as involving disruption of the Pt metal lattice [2]. Biegler and Woods [3] explained electrochemical stripping data with an adsorbed oxygen state which reached a limiting coverage of 2.66 O/Pt at 2.2V(RHE). Thacker and Hoare [4], also using stripping studies, concluded that, after surface adsorption started at 0.8V, dermasorption (sorption into the first few layers of the metal) commenced at 1.0V. Dermal sorption and surface adsorption continued together up to 1.6V, where a monolayer of PtO was thought to be present. At higher potentials some of the PtO was further oxidized. Vetter and Schultze [5] also analyzed charging and stripping curves and concluded that the coverage of adsorbed oxygen did not exceed a few percent, with a rate-determining, field-dependent place exchange leading to a phase oxide that represented most of the anodic charge. Fleischmann et al. [6] proposed the formation of four different "oxides" on Pt anodes. Angerstein-Kozłowska et al. [7] have given the most detailed interpretation of voltammetric and ellipsometric data to date. They have proposed a series of oxidation steps which occur as a polycrystalline Pt electrode is swept to

progressively higher potentials in acidic electrolyte. The initial oxidation, in the potential region 0.8–0.93V(RHE), was ascribed to reversible hydroxylation of the surface. Above 0.93V place exchange between adsorbed hydroxyl species and Pt occurs, and electrochemical irreversibility sets in. The place exchange is a rather slow process, and leads to complex aging behavior. In the potential range of ca. 1.0 to 1.2V (depending upon time factors) the peak potential of the subsequent reduction wave is independent of the total oxidation charge. This invariance was ascribed to constant Pt–O geometry, and the charge passed in this region was considered due to oxidative deprotonation of the hydroxyls previously incorporated into the surface. The above conclusions were based upon analysis of details of cyclic voltammetry curves. Optical studies showed that for oxidation up to a charge of $0.6e^-/\text{Pt}$ the same value of the ellipsometric parameter Δ was observed for a given surface charge on both the anodic-going and cathodic-going sweeps. For more complex oxidations the Δ/Q curves for the anodic and cathodic sweeps diverged, suggesting that the oxidized species first formed was also the first reduced. This species was suggested to be the reversible hydroxyl groups residing at the surface. A change in the Δ/Q slope at $0.5e^-/\text{Pt}$ (anodic direction) was ascribed to the onset of formation of the deprotonated oxide. At $1.0 e^-/\text{Pt}$ (1.13V) a further change was seen in the Δ/Q slope, which then continued unchanged out to at least $2 e^-/\text{Pt}$. The identification of the individual chemical species in this complex scheme was indirect and has awaited confirmation by direct spectroscopic and structural studies.

Attempts to identify the anodically formed surface species on Pt electrodes directly by spectroscopy have met with little success. Ellip-

sometry has been used in a number of studies [8-12] and while changes in the optical properties of the anodic film were observed at certain potentials and/or coverage, the interpretation of these changes was problematic, and the results were limited to estimation of layer thicknesses of "oxides" of indeterminate chemistry. Ex-situ analysis of anodic layers by XPS has been used in attempts to identify the oxidation state of Pt surface atoms.

Hammond and Winograd [13] used glove-box transfer and ESCA to characterize Pt foils oxidized potentiostatically at 1.92-2.54V (RHE). Their deconvolution of the data for the limiting oxide yielded a Pt 4f 7/2 line at 73.6eV (shifted 2.6eV from metallic Pt), ascribed to Pt in the (+II) state based upon a reference PtO material whose composition is controversial [14,15]. After anodization at 2.54V they reported indications of an additional peak at 74.4eV ascribed to Pt (+IV). Brandt [16] found the predominant oxidized Pt 4f 7/2 line for foils anodized at 1.25-3.25V (RHE) to lie at 73.8eV, a binding energy which did not allow certain discrimination between Pt (+II) and Pt (+IV). Long polarization at 3.25V led to a major peak at 74.1eV.

The interactions of gas-phase water and oxygen with single-crystal Pt surfaces have been extensively studied under UHV conditions, but the extent to which conclusions drawn from such studies are applicable to electrochemical conditions have not been adequately tested. Fisher and Gland [18] reported that sub-monolayer quantities of water adsorbed on Pt (111) at low temperature desorbed completely around 180K with a reaction order suggestive of a rate-limiting step at the edges of water patches. Vibrational spectroscopy of this system also showed that hydrogen bonding and clustering occurred even at submonolayer coverages [19]. Ibach and Lehwald [20] observed similar clustering and desorption at 170K on Pt (100). In the

presence of oxygen preadsorbed on Pt (111), water adsorption led to the formation of surface hydroxyl groups [1]. Water desorbed upon heating the hydroxylated surface to 215K. A number of studies [21-23] have shown that anhydrous oxygen adsorbs dissociatively on Pt (111) at room temperature to give an ordered 2x2 structure, saturating at 0.25 oxygen atoms per surface Pt atom, which desorbs at 700-850K. On Pt(100) substantial adsorption of oxygen requires dosing at elevated temperatures. Barteau et al. [24] and Derry and Ross [23] both reported unusually sharp desorption features around 660K. The latter work, using variable take-off angle XPS, showed that the oxygen in the high coverage state ($\theta/\text{Pt}=0.75-1.0$) resided on, not under, the surface. Little if any chemical shift from the metal was observed in the Pt 4f lines. However, formation in UHV of phase oxides of Pt from which oxygen desorbs at 1200K or higher has been reported by a number of groups [25-27]. In at least some cases these oxides have been related to the presence of impurities such as Si and Ca [28], but controversy remains on this subject [25].

The present work was undertaken to provide a bridge between the electrochemical and UHV studies of water and oxygen on Pt. Electrochemically grown films were cleanly transferred to vacuum and subjected to the same analytical techniques as were used in the cited low-pressure UHV studies of oxygen and water adsorption on Pt. This paper deals with the determination of the composition of anodic films by AES and TDS analysis. The atomic-scale structural consequences of anodic film formation as determined by LEED are the topic of a second paper [29]. The results show some parallels between the surfaces formed electrochemically and the surfaces

formed by low-pressure interaction with gases, but sufficient differences were also observed that suggest the need for caution in the use of conclusions drawn from low-pressure UHV experiments in developing a picture of the solid-liquid interface.

2. Experimental

The directly coupled electrochemical-UHV surface analysis system used in these studies has been described in detail elsewhere [30,31]. Clean, ordered, well-characterized Pt (100) surfaces prepared by standard UHV techniques were moved to a turbomolecularly-pumped transfer chamber by means of a long-throw magnetically coupled manipulator. This chamber was then back-filled to near atmospheric pressure with electronic-grade argon further purified by passage through high purity Ti sponge at 1200K. This improved treatment of the backfill gas has led to a 3 to 4-fold reduction in the carbon contamination of the surface reported previously [30], leaving the Auger equivalent of 0.1 graphite layers on the surface after exposure to backfill gases plus electrolyte vapor and pumpdown as shown in Fig. 1. No additional contamination as seen by Auger was picked up upon contact with the liquid electrolyte itself. An electrochemical cell, featuring an α -Pd hydride reference electrode and a Pt ring counterelectrode to which a ca. 100 μ l droplet of 0.3M HF had been previously admitted, was lowered to make contact with the crystal under potentiostatic control. The electrolyte was prepared from Ultrex-grade 40% HF and Harleco ultra-pure water and was further purified by Pt pre-electrolysis in the external reservoir. In most

of the experiments reported here the crystal was held at a given potential for about 2 minutes, after which time the transfer chamber was slightly overpressurized with Ar to drive the electrolyte cleanly out from the gap between the crystal and the counter-reference electrode assembly into a capillary leading to an external electrolyte reservoir. This emersion technique leaves an electrolyte film ca. 4000Å thick adhering to the crystal face [32]. The electrochemical cell was then pulled up and valved off, the transfer chamber was evacuated, and the crystal was returned to UHV for post-electrochemical analysis.

AES was performed with a single-pass cylindrical mirror analyzer equipped with an on-axis electron gun. The electron beam could be rastered and an image obtained in either the absorbed current or the secondary emission mode. This imaging capability allowed determination of the fraction of the crystal surface which had been in contact with the electrolyte, allowing normalization of coulometry and thermal desorption intensities to the actual anodized area.

Thermal desorption data were obtained with a Spectramass 1000M residual gas analyzer controlled by an LSI-11/23-based minicomputer to allow several mass peaks to be monitored. The ionizer of the gas analyzer was mounted within a conical Ta nozzle tube [33] with a 6.4 mm aperture next to which the crystal face could be placed. The nozzle increased the signal due to molecules desorbing from the crystal face while discriminating against molecules from the support structures. Identical oxygen desorption peak shapes were obtained with and without the nozzle in place, indicating that in both cases the effective pumping speed was sufficiently rapid to keep the

signal proportional to the desorption rate. The crystal was gold-brazed to a Ta cup, which was held in a stainless-steel transfer frame. This frame positioned the cup in front on the Ta filament used for radiant heating of the sample. Time-temperature curves for a given heating current were obtained with a Pt-Pt/10% Rh thermocouple spot-welded to the crystal and used to calibrate an infrared pyrometer. Use of the pyrometer allowed confirmation of the reproducibility of the time-temperature function when the thermocouple was removed to permit the crystal to be transferred to the electrochemical cell. A heating rate of 11 K s^{-1} was used in all experiments unless otherwise noted.

Thermal desorption data were quantified by comparison of integrated TDS signals with those obtained from the saturation coverage of CO on Pt(100). The latter coverage has been calibrated at 0.77 CO/surface Pt by Davies and Norton [34] using nuclear reaction methods. The sensitivity of the gas analyzer to CO, O₂, and H₂O was experimentally determined for comparable ion-gauge pressures of the pure gases, and published sensitivity factors for the ion gauge [35] were then mixed in to give correct relative sensitivity factors for the RGA.

3. Results

In this work three techniques, Auger electron spectroscopy, thermal desorption spectroscopy, and coulometry, were used to study the composition of thin anodic films. These methods differ in their sensitivity to the oxidation and hydration of the surfaces; some consideration should be given

to these differences so that the detailed results below can be understood in their proper contexts.

Coulometry is the classical electrochemical technique whereby the extent of anodic film growth has been followed. The reference oxidation states for the anodic film-free Pt surfaces in these studies are Pt(0) in metallic Pt, O(-II) in H_2O , OH^- , and H_3O^+ , and F(-I) in F^- . For Pt(100) 1x1 the passage of $209\mu\text{C}/\text{cm}^2$ of anodic charge corresponds to $1e^-$ oxidation per surface Pt atom. While coulometry provides a sensitive in-situ measure of the oxidation state of a surface, it gives no indication of the hydration state since the water of hydration remains in the reference oxidation state.

Thermal desorption spectroscopy measures both the oxidation and hydration states of anodic films on Pt after their emersion and evacuation. Upon heating, the anodic films evolved molecular H_2O and molecular O_2 . Since water is in the reference oxidation state, its desorption constituted a dehydration, but not a reduction, of the films. On the other hand, each O atom desorbing as O_2 represented a $2e^-$ oxidation from the reference O(-II) state during film formation. Since no desorption of other oxidized species such as O_2 , $\text{OH}^\cdot$, $\text{F}^\cdot$, or F_2 was observed, and since heating the films to 820K completely reduced them to metallic Pt, the integrated O_2 thermal desorption measured the total level of oxidation of the emersed and evacuated films.

The O/Pt Auger peak ratio, in the absence of beam effects, should measure all oxygen atoms on the surface, both those destined to desorb as O_2 and those desorbing in H_2O . However, the Auger beam rapidly dehydrated the surface, as will be shown in section 3.3. The Auger-determined oxygen

thus corresponded to an oxidation above the reference state of about $2e^-$ per O atom, rather than to the combined hydration and oxidation.

3.1. Anodic film composition as a function of potential

Anodization of UHV-prepared Pt(100) for ca. 2 min. at potentials above 1.1V(RHE)[†] produced films which survived emersion and evacuation with at least some of the hydration water intact. Figures 2, 3, and 4 show the O/Pt Auger signal ratio, the integrated O₂ thermal desorption signal (M/e=32), and the integrated H₂O thermal desorption signal (M/e=18) as functions of emersion potential. All three signals showed a similar increase in intensity with increasing potential over the region 1.1-1.9V. The parallel increases in the oxygen and water desorption signals indicate the growth of a hydrated film of nearly constant stoichiometry (approximately PtO_x·xH₂O) rather than the growth of an anhydrous oxide under a constant hydration sheath as suggested by the tritium data of Schultze [17]. Above 1.9V the leveling out of the Auger and O₂ thermal desorption signals indicate the formation of a passive layer which prevents further oxidation on the ca. 2 min. time scale of these experiments. According to thermal desorption data the saturated passive film contained 2.3 O atoms (desorbing as O₂) and 2 water molecules per surface Pt atom on the 1x1 Pt(100) surface. Stripping coulometry following transfer to UHV and return gave good agreement with the O₂ TDS measurements, yielding 1040 μ C/cm² (equivalent to 2.5 O atoms/surface

[†]All potentials given in this paper are referenced to the reversible hydrogen electrode in the same electrolyte (RHE).

Pt atom) for a film formed at 2.2V. This level of agreement indicates the validity of the calibration of the thermal desorption data based on the saturated layer of adsorbed CO.

3.2 Structure of anodic films

Low energy electron diffraction from anodic films formed above 1.5V on well-ordered Pt(100) or (111) surfaces gave only a general diffuse background with no defined spots, indicating the lack of order in the films. LEED patterns for films formed at lower potentials showed only diffuse background and partially attenuated substrate spots. The films remained disordered after being dehydrated by heating to 450K. Electrochemical reduction of the anodic films removed the oxygen and restored the substrate LEED spots. Repetitive oxidation/reduction cycling produced LEED patterns with spot sizes modulated by changes in the beam energy in a manner suggestive of the introduction of predominantly monatomic steps [30]. Since thermal reduction of the film required temperatures sufficiently high to anneal out most of the electrochemically induced defects, direct comparison of the atomic-scale structural effects of thermal and electrochemical reduction is impossible. Detailed description and analysis of the structural changes induced by repeated redox cycling are given in another paper [29]. Here it is sufficient to note that formation and reduction of the thin films discussed in this paper left the local order of the surface largely intact through quasiepitaxial reduction of the amorphous films, but the introduction of steps indicates that place exchange of Pt and O atoms during anodization at 100mV/s starts at 1.0V and becomes more pronounced above 1.2V.

The general properties of the anodic films have been outlined in the preceeding two sections. Each of the techniques used in these studies has a subtly different response to nonidealities inherent in surface science experiments performed on surfaces prepared in a medium 10^{15} -fold more dense than the UHV environment. These nonidealities include such effects as vacuum dehydration, gas-phase cleanoff reactions, electrochemical self-discharge, and electron beam damage. The results of each technique will now be considered in detail.

3.3. Auger electron spectroscopy

The AES O(513eV)/Pt(238eV) peak ratio increased with anodization potential as shown in Fig. 2. The ratios in Figure 2 are steady-state values obtained with a static electron beam focused to ca. 100 μ m. Under these conditions no significant changes in the peak ratio were seen for beam exposure times of 5s to 1 hr. A representative Auger spectrum for Pt(100) emersed at 1.9V is given in Figure 5. The O(513eV)/Pt(238eV) peak ratio of 4.6 is about ten-fold larger than the maximum value reported for low-index Pt dosed with oxygen from the gas phase (22). The O KVV/KLV peak ratio of 2.5 is smaller than that for most oxides but is similar to that previously reported for O adsorbed on Pt (36). This low peak ratio is a fingerprint for the Pt-O system. N(E) spectra obtained by beam-blanking showed that the low N'(E) peak ratio was due to an unusually broad KVV peak. When the electron beam was rastered over the maximum area consistent with good spectrum resolution (ca. 3x3mm), larger O signals with more typical oxide peak shapes were observed for the first few tens of seconds of

beam exposure. Rastering the beam for extended times over most of the electrolyte contact area significantly decreased the water thermal desorption signal, as shown by the point marked by the triangle in figure 4. The initial rapid decrease in the oxygen Auger signal thus corresponded to a beam-induced dehydration of the surface; once dehydrated the surface was stable to the beam. The steady-state Auger signal obtained with the static electron beam arose from the anhydrous oxide produced locally from the original hydrous film. Since the Auger analysis area was much smaller than both the electrolyte contact area and the aperture of the gas analyzer nozzle, normal Auger analysis had no significant effect on the results of subsequent thermal desorption experiments. Under conditions of maximum beam raster (ca. 15x15mm) at low beam energies, beam damage was sufficiently slow that an adsorbed current image could be taken to identify the electrolyte contact area without significantly dehydrating the surface.

Auger analysis with both static and rastered beams showed no incorporation of the fluoride anions from the 0.3M HF electrolyte into the anodic films. In the same apparatus fluoride was readily detected in anodic films formed in 0.3M HF on Ta, a material for which anion incorporation has been previously demonstrated by other means [37]. Although no traces of the major anion, fluoride, were found in the anodic films, small levels of chlorine, a common impurity in HF as chloride, were seen by Auger. This observation is in concert with electrochemical results which have indicated that Cl^- interacts much more strongly with Pt than does F^- [38]. Over the emersion potential range of 0.0–1.1V the Cl Auger signal was almost constant, corresponding to a Cl/Pt surface atomic ratio of 0.01 (based upon a monolayer HCl on Pt Auger spectrum published by Garwood and Hubbard [39]). In

anodic films a larger chlorine signal was seen which decreased at higher potentials from a surface atomic ratio of ca. 0.08 at 1.2V to ca. 0.02 at 1.95V.

As monitored by oxygen AES, the hydrated anodic films were stable to UHV conditions. Overnight exposure to background gases (10^{-10} torr range) caused no significant diminution of the oxygen Auger signal. However, the oxygen signal from a film dehydrated by partial thermal desorption disappeared after extended exposure to background gases. The oxygen signal for a hydrous film was completely removed by brief exposure to 1 torr H_2 . This reactivity, plus the lack of Auger signals at 296eV (Ca), and 1606eV (SiO_2) show that the observed oxygen signals were not due to the oxidation of impurities often found in Pt crystals as may have been the case for some "Pt oxides" grown from the gas phase [28].

3.4. TDS of thin anodic films

Upon heating, anodic films formed in 0.3M HF evolved H_2O and O_2 at widely separated temperatures (Fig. 6). Interruption of the thermal ramp after the water peak appeared had no effect on the temperature, shape, or size of the subsequent O_2 desorption peak, showing that dehydration and thermal reduction were separate processes. The integrated O_2 and H_2O TDS signals increased in parallel, indicating a constant film stoichiometry of $PtO_x \cdot xH_2O$. At the highest O/Pt ratios observed, a small evolution of oxygen accompanied the start of dehydration, but this never amounted to a large proportion of the total oxygen desorbed from the anodic films.

3.4.1. Water thermal desorption

Water was evolved in a single broad peak at 400K, a much higher temperature than the 170K reported for low-pressure, low-temperature dosed clean Pt (100) [19] or the 215K reported for low pressure, low temperature water co-adsorption with oxygen on Pt (111) [1]. The peak temperature and shape were invariant with coverage as would be expected for a dehydration process first-order in the water-containing species. Application of the Redhead correlation of peak temperature with activation energy (assuming a pre-exponential of 10^{13}s^{-1}) [40] yielded an activation energy of 24 kcal/mole, twice the heat of sublimation of water. Since the peak shape showed asymmetry opposite to that expected for a simple first-order process, it is unlikely that this simple model accurately describes the desorption process. However, even without an accurate model, the high desorption temperature shows a stronger binding of water on the electrochemically anodized surfaces than has been seen in gas-phase water dosing experiments on either clean or oxygen pre-dosed surfaces.

Some water desorbed at 400K from surfaces emersed at all potentials, including potentials below the point of zero charge. Less than 0.5 water molecules per surface Pt atom desorbed from surfaces which showed no Auger or TDS oxygen. Once water was removed by partial desorption (to ca. 450K), it could not be replaced on the room temperature crystal by a 100L dose of water vapor at 10^{-7} torr, showing that this water was not bound to trace alkali impurities from the electrolyte. Such impurities could at times be detected at the spot where the capillary which removed the electrolyte from

the cell had touched the crystal. These small patches of alkali oxides/hydroxides remained on the surface after partial desorption experiments; had they or other thermally resistant impurities (such as the small amounts of C, S, and sometimes Cl picked up during transfer) contributed significantly to the initial water desorption signal a similar signal should have been seen after dosing with water vapor. Comparison of experiments run with and without the nozzle tube around the ionizer of the gas analyzer showed that, while the broad water desorption background seen in Figure 6 did arise from support structures, the peak at 400K evolved from the crystal face. Measurable CO_2 ($M/e=44$) desorbed from the crystal face in the same temperature range as water. Avery [41] has reported CO_2 evolution from decomposition of carboxylate species at similar temperatures on Pt (111) and it seems most likely that the water observed desorbing from nonoxidized Pt electrodes (i.e. potentials below 1.2V) was associated with carboxylic impurities. However, at emersion potentials above 1.2V the water and oxygen thermal desorption signals both increased with increasing potential, maintaining a roughly constant ratio of one water molecule desorbed per oxygen atom desorbing as O_2 . The increase in water desorption signal with increasing oxidation of the surface was too large to be accounted for by impurities; it corresponded to the presence of a hydrated phase oxide or hydroxide.

3.4.2. Oxygen thermal desorption.

O_2 ($M/e=32$) desorbed from Pt(100) anodized in acidic electrolytes in a sharp primary peak at 570–630 K with smaller features at higher temperatures. The same complex structure was seen in O_2 desorption from two

different Pt(100) crystals anodized in HF and also from Pt(100) anodized at 1.58V in $5 \times 10^{-3} \text{M H}_2\text{SO}_4$. As shown in Fig. 7, the temperature at which the maximum desorption rate occurred, T_p , increased with increasing coverage. The leading edges of the desorption curves for different coverages did not align as would be expected for a simple zeroth-order process governed by a constant activation energy [42]. Rather, the leading edges and peaks for lower coverages occurred at lower temperatures than were observed for the same desorption rates from more heavily oxidized surfaces. The shift in T_p showed a continuity of behavior over an emersion potential region of at least 1.35–2.1V(RHE). The O_2 desorption curves from Pt(100) displayed a shoulder at ca. 640K which showed a lesser shift in temperature for different coverages. At the limiting coverage the low temperature main peak overlapped this higher temperature shoulder. At the lowest transferable coverages only the 'shoulder' was seen. The main peak and shoulder could not be separated by interruption of the heating ramp; i.e. once desorption started it continued until all of the oxygen in both the main peak and the shoulder had left the surface.

At 725 K another small peak was seen which became larger but shifted slightly, if at all, to higher temperature at higher coverages, suggesting a zero to first-order desorption process. This peak could be at least partially isolated by stopping heating at 650 K. When the crystal was then cooled and reheated, the remaining oxygen desorbed at 725 K, showing that the oxygen in this peak is kinetically distinct from that in the lower temperature features. The area under this peak was a relatively constant 10–15% of the total O_2 desorption area. As will be seen in section 3.5,

this peak was similar in temperature to that observed for a thick anodic film, suggesting that the peak corresponds to islands of thicker film on the otherwise uniform anodic layer. The fact that the anodic film saturated at $Q/Pt=2.3$ rather than 2 (by TDS) also suggests ca. 15% of the anodic charge went into "multilayer" islands while the rest of the surface was covered by a uniform "monolayer" of anodic film. The uniform "monolayer" is actually several atomic layers thick when oxygen, hydrogen, and displaced Pt atoms are taken into account.

The inability to separate the 640K shoulder from the main thermal desorption peak by interruption of the heating ramp suggests that this shoulder, unlike the 725K peak, is kinetically associated with the main peak at 570-630K. Even without the added complication of this shoulder, the behavior of the main TDS peak suggests a complex desorption mechanism. Considering first simple n -th order desorption with constant activation energy, the increase in T_p with coverage suggests that $n < 1$. The leading edges of the lower coverage peaks lie outside those for higher coverages, contrary to the expectations for $1/2$ or 0 order for which the low coverage leading edges should lie, respectively, inside or on top of the high coverage leading edges. The data thus indicate a process with an effectively negative reaction order in surface coverage. This effective negative order at high coverages could be simulated by at least three processes: (1) Fig. 8a, desorption rate proportional to the perimeter between covered and uncovered patches, (2) Fig. 8b, explicit positive-order dependence on both covered and uncovered sites, and (3) Fig. 8c, increasing E_a for desorption with increasing coverage. Brief details of each of the models are given in Appendix 1. All of the models gave best fit with the coverage dependence of T_p and the peak widths using activation energies of

20-26kcal/mole. Only the first model produced the low-temperature shoulder growing to become the main peak as shown by the data.

3.5. Thick anodic films

Although the formation of a thin passivating anodic film on Pt has been indicated by the present Auger and thermal desorption work on single crystals and by some previous electrochemical work on foils [2,3,44], other investigators have reported the formation of thick (on the order of 100 nm) films during prolonged direct-current anodization [45]. At least in some cases the thick film formation was enhanced by mechanical introduction of defects [46]. Burke, et al, [47] have employed a technique of rapid potentiodynamic cycling between the double-layer and oxide regions which reliably produces thick anodic films on Pt without recourse to mechanical roughening. Figure 9 shows thermal decomposition results for a polycrystalline foil oxidized in 0.3M HF by cycling at 0.3Hz between 0.5 and 2.4V for ten minutes. This treatment produced a compact-appearing layer with a gold interference color which graded to purple and blue around the edges. The appearance of the film was unaltered by drying and evacuation. As in the case of the thin films, water came off upon heating in a single broad peak at 400K (Fig. 9). The major O₂ evolution occurred in a single peak at 715K, with minor oxygen loss accompanying dehydration. No higher temperature structure was seen in the O₂ TDS. One water molecule was evolved for every oxygen atom which came off at O₂, again indicating a stoichiometry of PtO_x·xH₂O. The thick film was quite stable to exposure to ambient atmosphere, allowing anodized foils to be carried through the air and mounted in a second vacuum system equipped with a double-pass

cylindrical mirror analyzer and x-ray source for XPS analysis. This technique yielded a broad Pt 4f 7/2 line at 74.2eV indicative of Pt in the (+IV) oxidation state. This result, combined with the 2:1 $\text{H}_2\text{O}:\text{O}_2$ ratio from TDS, identifies the stoichiometry of the thick film as $\text{PtO}_2 \cdot 2\text{H}_2\text{O}$. A single broad oxygen 1s line was seen at 530.7eV binding energy indicating, per discussion in the next section, that the films have the composition $\text{Pt}(\text{OH})_4$ with a single type of oxygen species.

4. Discussion

The parallel increase in O_2 and H_2O thermal desorption signals with increasing emersion potential shows that the emersed and evacuated films formed at 1.2V and above have a constant hydration stoichiometry of $\text{PtO}_x \cdot x\text{H}_2\text{O}$. Since emersion and evacuation would tend to dehydrate films generated in aqueous solutions, it can be concluded that the films as formed in the electrolyte are hydrated to at least this extent. XPS results provide insight into the type of hydration in the thick films grown by AC cycling, for which a single O 1s peak was observed at 530.7eV. Fisher and Sexton [1] have reported that oxygen and water adsorbed separately on Pt yielded O 1s peaks at 529.8 and 532.3eV, respectively. They assigned a peak near 531eV to a surface-bound hydroxyl group formed after adsorption of both oxygen and water. On the basis of this assignment the thick anodic film appears to be best described as $\text{Pt}(\text{OH})_4$ (with a single type of oxygen rather than $\text{PtO}_2 \cdot 2\text{H}_2\text{O}$ (with two types of oxygen). Other workers, applying XPS to oxygen species on a variety of metals, have observed O 1s levels over different ranges of binding energies. For example, Brundle [48] has generalized that an adsorbed oxygen peak appears at $530 \pm$

0.5eV, with the upper limit being dangerously near the 530.7 ascribed here to a hydroxyl species. XPS of bulk hydroxides has produced O 1s binding energies as high as 531.7eV [49]. This range of energies indicates the need for caution in determining the nature of oxygen-containing species from XPS data alone and shows the utility of the complementary thermal desorption data. The work in ref. 1 used here for comparison combined data from XPS, UPS, and HREELS to identify the adsorbed species and was carried out on Pt itself. Adsorbed oxygen, dehydrated thin anodic films, and dehydrated thick anodic films all share the low KVV/KLV oxygen Auger peak ratio of 2.5 not seen on baser metals. This unusual ratio indicates that oxygen on Pt or in Pt oxides is in a significantly different electronic environment than on less noble metals, so that comparison of O 1s binding energies is best restricted to known O species on Pt. Restricting such comparisons to Pt and considering the data from other techniques leads to the conclusion that the thick films are $\text{Pt}(\text{OH})_4$. Although no XPS data was obtainable for thin films due to the necessity of through-air transfer, they gave the same integrated $\text{H}_2\text{O}/\text{O}_2$ TDS ratio and the same H_2O peak temperature and shape, suggesting that they too consisted of a platinum hydroxide.

The transferable hydroxide layers are chemically distinct from any species previously produced in UHV by adsorption of water and/or oxygen from the gas phase. Water desorbed from both thick and thin anodic films at temperatures 185K higher than those reported for the water-producing decomposition of surface-adsorbed hydroxyl species produced by sequential dosing with oxygen and water in UHV [1]. This temperature difference is a consequence of the Pt/OH place exchange which occurs during anodic film formation, stabilizing the hydroxyls within a three-dimensional (albeit very thin) phase. Anodic films

formed below 1V did not survive transfer, despite coulometric indications that the surface was oxidized up to $0.5e^-/\text{Pt}$. LEED results have shown [29] that these electrochemically-reversible low-potential films are surface-adsorbed rather than place-exchanged, and are likely to be analogous to the unstable UHV-grown hydroxyl species.

O_2 thermal desorption data for thin anodic films, thick anodic films, and gas-phase dosed Pt(100) (from ref. 23) are shown together for comparison in Fig. 10. Since thermal dehydration of anodic films preceded thermal reduction, comparison with an anhydrous oxygen layer is valid. While water evolved from the anodic films at temperatures substantially above those reported for hydroxides formed from the gas phase, O_2 evolved from thin anodic films at lower temperatures than those reported for Pt surfaces exposed to oxygen in UHV. Thermal desorption of anodic oxygen gave a very sharp peak which qualitatively resembles the unusually sharp features observed for high coverages of O_{ads} on Pt(100) by Barteau, et al. [24] and Derry and Ross [23], but differences in temperature, peak separation, and absolute coverage dependence attest to the distinct chemical natures of the two types of oxygen. No very broad bulk diffusion-limited O_2 desorption peaks such as might be expected for subsurface or dermasorbed [4] oxygen were observed, indicating that all anodically formed oxygen resided very near the surface. While the complex nature of O_2 desorption peaks from anodic films precluded accurate determination of the desorption activation energy, the lower desorption temperatures for anodic oxygen relative to gas-adsorbed oxygen are actually consistent with the observation that the heat of adsorption of surface oxygen on Pt exceeds the heat of formation of bulk Pt oxides [50] (if we assume that the anodic oxygen has the thermochemical properties of bulk oxide). As pointed

out in the comprehensive review of Fromm and Mayer [51], this type of relationship between surface and bulk phase thermochemistry is unusual for metal/oxygen systems, and is more common in metal/carbon and metal/nitrogen systems. Following the arguments of Fromm and Mayer, we suggest that this unusual thermochemistry of Pt is responsible for the unique catalytic properties of Pt as a catalyst in oxygen reactions. The stronger bonding of oxygen atoms on the surface than in the bulk causes an activation barrier for penetration of oxygen below the surface [51], preventing loss of catalytically active (dissociated) oxygen to the bulk even at high oxygen partial pressures. Most metals, having the opposite thermochemistry [51], become deactivated at high oxygen partial pressure due to bulk oxidation.

5. Conclusions

Anodic films formed on Pt(100) above 1.1V (RHE) and thick layers formed by AC cycling survived emersion and evacuation in a hydrated state with the stoichiometry $\text{PtO}_x \cdot x\text{H}_2\text{O}$. The films formed at constant potential saturated at 2.3 O atoms and ca. 2 water molecules per surface Pt, with about 15% of the oxygen desorbing in a kinetically separable higher temperature peak suggestive of a small multilayer component. XPS analysis of the saturation layer and the AC formed film indicated that both are chemically identical, with the most likely chemical state being $\text{Pt}(\text{OH})_4$. The continuity of the water thermal desorption behavior with applied potential suggests that the films formed at all potentials above 1.1V (RHE) are hydroxides as well. Kinetic analysis of the thermal desorption data indicated that the hydroxyl groups are place-exchanged with Pt during anodization above 1.1V (RHE), a conclusion

consistent with LEED analysis of anodized surfaces reported previously [29-31].

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Appendix: O_2 Thermal Desorption Models

Three models were tested which could produce the effective negative-order dependence on oxygen coverage displayed by the O_2 thermal desorption data from anodic films. Best-fit results are shown in Figs. 8a,b,c, derived from numerical integration of the following rate equations using parameters listed in the figure caption:

a.) Perimeter-controlled desorption

$$-d\theta/dt = p(\theta) (\nu/d) \exp (-E_a/RT)$$

where ν is the preexponential, d is the spacing between centers of open patches, E_a a constant activation energy, and $p(\theta)$ the perimeter around a given open patch at coverage θ . In this model, starting with a saturated surface, open patches are nucleated on a square grid with spacing d and grow outward as expanding circles until the point of tangency is reached. Beyond this point the circular fronts continue to advance, and the occupied patches resemble shrinking squares with concave sides. This model agrees in concept with electrochemical data indicating that electrochemical reduction of anodic films on Pt occurs at the edges of islands [5]. The model assumes that an initial coverage θ_0 has the same geometry as would result from desorption to θ_0 from saturation. Agreement between experiment and model thus implies that the emersed anodic films have an island structure, and that the islands fuse together at higher coverages. This is the only model tested which predicted the low temperature shoulder growing to become the major peak, as well as the

effective negative-order dependence on coverage, observed experimentally.

b.) Explicit autocatalytic process

$$-d\theta/dt = v\theta^m (1-\theta)^n \exp (-E_a/RT)$$

This model implies reaction between covered and uncovered centers to yield desorbed O_2 . Best match for peak sharpness and separation at different coverages was found for $m=1$ and $1 < n < 2$, with a disturbingly low pre-exponential ($5 \times 10^6 s^{-1}$). The model unrealistically implies high mobility for oxygen in a place-exchanged phase and produces peaks for very high coverages more strongly separated from those for lower coverages than indicated by experiment.

c.) Variable activation energy

$$-d\theta/dt = v\theta \exp \left[-(E_a + (\Delta E_a \cdot \theta)) \right]$$

The desorption activation energy is assumed to increase with increased coverage in accordance with a model for gas-phase O_2 on Pt(100) advanced by Barteau, et al. [23]. The fit with data suffers from a surprisingly low pre-exponential ($2 \times 10^7 s^{-1}$) and the inability to predict the two-peak structure.

All three models produced the observed effective negative-order desorption behavior. None gave excellent fit with secondary features in the data. Isothermal experiments which might further distinguish between the models proved impossible due to equipment design compromises necessary to carry out UHV-electrochemical transfer.

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Figure captions:

- Fig. 1. Unnormalized Auger spectra of Pt (100) after various stages of the transfer process.
- Fig. 2. Oxygen/platinum auger peak ratio as a function of anodization potential.
- Fig. 3. Integrated O_2 thermal desorption signal as a function of anodization potential. Signals were normalized to the overlap of the electrolyte contact area and the quadrupole nozzle aperture, then compared to the desorption signal for a saturation coverage of CO to allow O/Pt surface atomic ratios to be calculated (see text). O/Pt=1 corresponds to $2e^-$ /Pt of anodic charge.
- Fig. 4. Integrated H_2O thermal desorption signal as a function of electrode potential. Absolute coverage determined as in Fig. 3. Triangle gives datum for a surface exposed to rastered Auger beam.
- Fig. 5. Auger spectrum for anodic film formed at 1.9V (RHE) on Pt (100) in 0.3M HF.
- Fig. 6. O_2 and H_2O thermal desorption spectra for anodic film formed on Pt (100) at 1.8V (RHE).
- Fig. 7. O_2 thermal desorption spectra for films formed at different potentials.
- Fig. 8a. Perimeter desorption model. $E_a = 21$ kcal/mol, $\nu/d = 10^{14} \text{ cm}^{-1} \text{ s}^{-1}$. $\theta_0 = 0.99, 0.85, 0.75, 0.60, 0.50, 0.38, 0.21$.
- Fig. 8b. Explicit autocatalytic model (see Appendix): $E_a = 21$ kcal/mol, $m = 3/2$, $n = 1$, $\nu = 5 \times 10^6$. $\theta_0 = 0.99, 0.85, 0.75, 0.60, 0.50, 0.38, 0.21$.

- Fig. 8c. Linear increase in E_a with coverage (see Appendix): $E_a = 20$ kcal/mol, $\Delta E_a = 4$, $\nu = 2 \times 10^7$. $\theta_0 = 0.99, 0.85, 0.75, 0.60, 0.50, 0.38, 0.21$.
- Fig. 9. O_2 and H_2O thermal decomposition spectra for a thick film formed by AC anodization of polycrystalline Pt foil. $dT/dt = 19 K s^{-1}$.
- Fig. 10. Comparison of O_2 thermal desorption from: a,b,c, thin anodic films on Pt(100); d, thick anodic film; e, O_2 adsorbed from the gas phase on Pt(100) (ref. 21).

XBL 832-8234

Fig. 1.

XBL 832-8435A

Fig. 2

XBL 832-8428

Fig. 3

XBL 832-8433A

Fig. 4

XBL 832-8439

Fig. 5

XBL 832-8429

Fig. 6

XBL 832-8440

Fig. 7

XBL 846-8967

Fig. 8

XBL 832-8430

Fig. 9

XBL 832-8437

Fig. 10

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