Anion Effects in the UPD of Copper on Pd/Pt(111) Bimetallic Electrodes

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The underpotential deposition (UPD) of copper has been used to characterize the structure of palladium films supported on Pt(111). Depending upon the nature of the anions in solution (HSO₄⁻, Cl⁻, Br⁻), a variety of adsorption behaviors are revealed. In pure sulfuric acid, palladium islands give rise to copper stripping peaks some 100-150 mV negative of the copper desorption states associated with Pt(111). As already deduced from hydrogen electrosorption measurements, palladium islands form at coverages of palladium <1 monolayer (mL), and long-range (111) order is preserved within regions of the surface free of palladium, even at coverages close to the completion of the first monolayer. The palladium films themselves are stable up to 0.6 V ($Cu^{2+/}$) Cu), but desorption is facilitated at 0.8 V (Cu^{2+}/Cu), leaving behind a somewhat disordered Pt/Pd phase. In contrast, copper UPD in the presence of strongly adsorbing anions (Cl⁻, Br⁻) leads to a much narrower range of stability [0.3 V (Cu²⁺/Cu)] for the palladium film although, from inspection of copper UPD data, island growth of palladium for $\theta_{Pd} < 1$ mL is again implied with significant preservation of long-range Pt(111) order. It is reported that desorption of multilayer palladium films may be catalyzed by Cl⁻ and Br⁻ anions, resulting ultimately in a highly ordered palladium monolayer. Further oxidative desorption of the ordered palladium monolayer produces new copper adsorption states associated with place exchange between the halide and the palladium monolayer and also copper UPD onto the resulting Cu-Pd surface alloy. Repetitive potential cycles between 0.1 and 0.8 V (Cu^{2+}/Cu) transform all palladium islands into a Cu-Pd surface alloy. Further oxidative desorption beyond this stage generates a disordered copper-rich Cu-Pd alloy phase and palladium-free regions of Pt(111). After complete desorption of palladium, the UPD voltammogram of Pt(111)-copper is fully restored with no evidence of surface perturbation having occurred. The relevance of these findings in the context of halide-catalyzed dissolution of palladium surfaces is discussed.

Introduction

The underpotential deposition (UPD) of metals (the deposition of foreign metal ions onto a metallic substrate at potentials positive of the Nernst potential) is one of the most extensively studied processes in surface electrochemistry.¹ Recently, a variety of in situ and ex situ spectroscopic,² surface imaging,³ surface diffraction,⁴ radiochemical,⁵ and thermodynamic⁶ methodologies have been utilized in order to gain insight into the nature of this apparently "simple" redox reaction. It has been found that coadsorption of cations and anions within the interphasial region constituting the UPD layer is a general phenomenon with the relative strength of interaction between anion-substrate, cation-substrate, and anion-cation governing the overall structure of the coadsorbate film. Questions as to the exact location of the charge transferred to the interface as a consequence of metal deposition and the precise concentration of each surface component have also been addressed.⁶ In the present study, the UPD of copper will be used as a structural probe of well-defined palladium films on Pt(111) produced as a consequence of "forced deposition".⁷ Palladium adsorption on platinum is an attractive system for study since, on the basis of thermodynamic and lattice strain considerations, high-quality films should form.⁸ Experimentally, this prediction has been borne out in several studies.⁷⁻¹⁰

The UPD of copper on Pt(111) proceeds via a two-stage adsorption process.^{4a} In pure sulfuric acid, the initial adsorption of copper has been shown to generate a mixed, almost coplanar, honeycomb structure of copper/sulfate corresponding to ap-

proximately ²/₃ mL of copper and ¹/₃ mL of sulfate.^{3b,11} An overpotential for the second stage of adsorption is associated with the place exchange of the sulfate anions within the coadsorbed copper-sulfate layer by $\frac{1}{3}$ mL of copper. In the presence of Cl⁻-containing acidic aqueous electrolytes, again a two-stage copper adsorption process is observed on Pt(111), but from recent RRDE, XRD, and STM data,^{3d,12,13} it is clear that, in this case, the first stage of adsorption corresponds to the formation of a copper-chloride bilayer, although residual chloride adsorbed on Pt(111) still remains adjacent to copperchloride bilayer islands.¹⁴ Presumably, the second stage of copper adsorption to complete the copper monolayer¹³ is associated with place exchange with copper of these residual chloride ions bonded to Pt(111). The deposition of copper in the presence of Br^- on Pt(111) follows a similar course to that of Cl^{-,15} Copper UPD onto single crystalline palladium electrodes has also been extensively investigated¹⁶ as has copper UPD onto thick (>5 mL) palladium films supported on Pt(100) and Au(111).^{17,18} Interestingly, the CV of copper UPD on massive palladium films mimics exactly the response of welldefined, bulk, single-crystal palladium electrodes.^{16b} This is not unexpected considering the high quality of palladium films formed on Pt single crystals reported by the present authors and others.7-10,18

Recent investigations have also concentrated on the iodinecatalyzed dissolution of palladium single-crystal electrodes¹⁹ in which ostensibly "disordered" surfaces have been transformed into highly crystalline two-dimensional lattices. This finding has implications for ongoing research into electropolishing technologies. The ability to monitor electrochemically the dissolution of well-defined thicknesses of palladium supported

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Figure 1. UPD of copper on Pt(111) in 10^{-3} M Cu²⁺_(aq) + 0.1 M H₂SO₄. Sweep rate = 10 mV/s. Insert: cyclic voltammogram of Pt(111) in 0.1 M H₂SO₄. Sweep rate = 50 mV/s.

on Pt(111) appeared to the present authors a suitable strategy for further investigating this interesting phenomenon.

Experimental Section

The experimental apparatus used in the present investigation and glassware/solution preparation has been fully described elsewhere.²⁰ Briefly, the electrochemical hardware consisted of a homemade potentiostat/computer interface/voltage ramp generator connected to a three-electrode cell (Pd/H reference electrode in pure sulfuric acid, copper wire reference electrode for UPD, Pt counter electrode) containing a variety of O2-free electrolytes (0.1 M H₂SO₄, 0.1 M H₂SO₄ + 10^{-3} M CuSO₄, $0.1 \text{ M H}_2\text{SO}_4 + 10^{-3} \text{ M CuSO}_4 + 10^{-3} \text{ M NaCl}, 0.1 \text{ M H}_2\text{SO}_4$ $+ 10^{-3}$ M CuSO₄ $+ 10^{-3}$ M NaBr), depending upon the type of experiment to be performed. All solutions were prepared from ultrapure reagents (BDH Aristar grade) and Millipore 18.2 $M\Omega$ cm⁻¹ water. The Pt(111) bead electrode, approximately 2 mm in diameter, was manufactured using the method developed by Clavilier.²¹ After flame annealing and cooling in H₂/H₂O, the electrode surface was protected by a droplet of ultrapure water and transferred to the electrochemical cell where it could be brought into electrical union with the test solution via a meniscus contact under potential control. Palladium deposition was carried out by placing a droplet of aqueous palladium nitrate solution onto the surface of a freshly flamed Pt(111) electrode. By passing hydrogen gas over the droplet of palladium nitrate for a set period of time, a well-defined coverage of palladium could be obtained:

$$Pd^{2+}(aq) + H_2(g) \rightarrow Pd(adsorbed) + 2H^+(aq)$$
 (1)

This so-called "forced deposition" of palladium has been fully described previously.⁷

All voltammetric data involving copper-free electrolytes are referenced to a saturated palladium—hydrogen electrode in contact with the electrolyte. UPD measurements were referenced to a copper wire (Goodfellow Metals Ltd.) also in contact with the electrolyte, and 1 mL is defined as 1.5×10^{15} atoms/ cm², the density of Pt atoms in the surface of Pt(111).

Results and Discussion

Copper UPD in 0.1 M H₂SO₄. As signified by the intensity and sharpness of the "spike" at 0.42 V, the Pt(111) electrode used in the present study appears to be well-ordered and essentially free of surface defects (insert of Figure 1).²² Figure 1 also shows the same electrode in a copper UPD experiment in order to assess the degree of surface perfection using an alternative procedure to that of hydrogen adsorption and to estimate the surface coverage of copper formed prior to bulk deposition. The two adsorption states of copper depicted in Figure 1 are in excellent agreement with previous findings for this adsorption system.¹¹ The total Coulometric charge deduced



Figure 2. Insert: cyclic voltammogram of irreversibly adsorbed palladium on Pt(111) in 0.1 M H₂SO₄. Sweep rate = 50 mV/s. $\theta_{Pd} = 0.33$ mL. UPD of copper on the same electrode in 10^{-3} M Cu₂₄²⁺ + 0.1 M H₂SO₄. Sweep rate = 10 mV/s.

from integration of the copper stripping peaks amounted to 480 μ C cm⁻², a value consistent with the formation of an epitaxial monolayer of neutral copper adatoms on Pt(111). However, that this charge is the net sum of several adsorption/desorption processes has been recognized for some time.⁶ Making no assumptions as to the nature of the distribution of charge within the adlayer, underpotential deposition of 1 mL of copper in the presence of bisulfate may be represented formally as

$$Cu^{2+}(aq) + [\theta_1 HSO_4^{(1-\delta)^-}/Pt^x] + (\lambda + (\theta_2 - \theta_1) + (\theta_1 \delta - \theta_2 \gamma) + x - y)e = [\theta_2 HSO_4^{(1-\gamma)^-}/Cu^{(2-\lambda)^+}/Pt^y]$$
(2)

where

$$\begin{split} 0 \leq \delta \leq 1, \quad 0 < \theta_1 < 1, \quad 0 \leq \gamma \leq 1, \quad 0 < \theta_2 < 1, \\ 0 \leq \lambda \leq 2 \end{split}$$

depending upon the precise distribution of charge within the region comprising the adsorbed overlayer before and after copper adsorption. *x* and *y* are the screening charges associated with the substrate in response to electrosorption, and θ_1 and θ_2 are the fractional coverages of adsorbed anions before and after copper adsorption, respectively. Even within this very generalized form, the possible contribution of coadsorbed hydroxonium ions to the total charge,²³ particularly on the left-hand side of

eq 2, has been ignored. What is actually measured upon integration of the copper stripping peaks is $(\lambda + (\theta_2 - \theta_1) +$ $(\theta_1 \delta - \theta_2 \gamma) + x - \gamma$ electrons per adsorbed copper cation. That this quantity should correspond precisely to $480 \,\mu C \, cm^{-2}$ (equivalent to exactly two electrons transferred to the interface per surface platinum atom) should be seen as fortuitous since it will be shown later that an even greater amount of charge is generated from the stripping of copper from Pt(111) in the presence of chloride anions. Furthermore, in a future publication by Wieckowski and co-workers,²⁴ it will be demonstrated using AES that 1 mL of copper adatoms is formed in the UPD potential range. Nonetheless, the stripping charge for the copper monolayer was found by these workers to be a sensitive function of bisulfate concentration-the more concentrated the solution, the greater was found to be the stripping charge. Therefore, the present voltammetric data appear to be consistent with the presently accepted model of a two-stage adsorption process for copper UPD on Pt(111)^{13,14} in which 1 mL of copper is formed prior to bulk deposition.

Irreversible adsorption^{7,25} of increasing submonolayer amounts of palladium on Pt(111) and its subsequent electrochemical characterization are shown in Figures 2 and 3. In 0.1 M H₂-SO₄, the presence of adsorbed palladium manifests itself in two ways. First, a new adsorption state is observed between 0.16 and 0.17 V (Pd/H) which is very narrow and intense. This state



Figure 3. Insert: cyclic voltammogram of irreversibly adsorbed palladium on Pt(111) in 0.1 M H₂SO₄. Sweep rate = 50 mV/s. $\theta_{Pd} = 0.66$ mL. UPD of copper on the same electrode in 10^{-3} M Cu²⁺_(aq) + 0.1 M H₂SO₄. Sweep rate = 10 mV/s.

has been ascribed to coupled adsorption/desorption of anions and hydrogen.^{7,8,25} It grows in intensity up to a maximum of exactly 1 mL of palladium.^{7,8} The second consequence of palladium growth on Pt(111) is the decrease in the intensity of the "anomalous" region.^{7,8} The presence of this state for θ_{Pd} < 1 mL implies island growth of the palladium deposit in which significant long-range order is preserved within Pt(111) domains free of palladium.^{7,8} Previous AES/LEED/XPS investigations of palladium growth on Pt(111) in UHV^{8,9} have also concluded that epitaxial palladium islands form at submonolayer coverages followed by Frank-Van der Merwe growth at higher coverages. Factors favoring island growth would include negligible lattice mismatch between palladium and platinum (atomic diameters of 2.76 and 2.77 Å, respectively²⁶), the greater surface energy of platinum compared to that of palladium²⁷ and attractive lateral interactions exhibited by transition metal adatoms adsorbed on close-packed transition metal surfaces.8

To estimate the coverage of palladium, the area under the clean surface "anomalous" peak was utilized. Since, for island growth of palladium, the charge associated with the anomalous peak bears a simple relationship to the number of platinum sites free of palladium (80 μ C cm⁻² \equiv 1 mL, 40 μ C cm⁻² \equiv 0.5 mL, etc.⁷), the coverage of palladium in the insert of Figure 2 is deduced to be 0.33 mL. Independent confirmation of this estimate comes from Figure 2 itself, showing the corresponding

copper UPD CV from the same sample. The sharp, wellresolved peaks of copper UPD on Pt(111) between 0.30 and 0.35 V (Cu²⁺/Cu) give rise to 327 μ C cm⁻² of charge. Since 480 μ C cm⁻² is required to strip 1 mL of copper from Pt(111), it is estimated that the palladium coverage in this case is (1 – 327/480) = 0.32 mL, in good agreement with the coverage deduced in aqueous sulfuric acid. Since long-range Pt(111) order appears to be a prerequisite to observe the two copper stripping peaks,²² island growth of palladium is strongly suggested, in agreement with findings obtained in copper-free electrolytes.^{7,8} In a similar fashion, taking into account copper stripping and "anomalous" region charges leads to a palladium coverage of 0.66 mL for Figure 3.

The presence of palladium in Figure 2 is signified by the broad multiplet just negative of the clean surface peaks between 0.1 and 0.3 V (0.2–0.32 V for copper stripping and 0.1–0.20 V for copper adsorption). It is seen that these multiplet peaks increase in magnitude as the palladium coverage is increased in parallel with a decrease in the size of the copper peaks derived from the clean surface. Charge integration over the entire potential range of UPD, including both platinum and palladium sites, always produced a total charge of 480 μ C cm⁻². This implies that, by taking the charge under the multiplet peaks, it is also possible to estimate the palladium coverage. For example, in Figure 3, the charge derived from stripping of



Figure 4. UPD of copper on bulk palladium film irreversibly adsorbed on Pt(111) in 10^{-3} M Cu²⁺_(aa) + 0.1 M H₂SO₄. Sweep rate = 10 mV/s.

copper from palladium is 313 μ C cm⁻². Therefore, if 480 μ C $\rm cm^{-2}$ is the charge produced by desorption of copper from an epitaxial monolayer of palladium, the coverage of palladium is 313/480 = 0.65 mL, in good agreement with estimates made from hydrogen and copper adsorption on domains of clean platinum. The upper potential limit of stability of palladium films in the presence of aqueous copper sulfate was found to be 0.6 V (Cu^{2+}/Cu). Potential excursions to 0.8 V and above always led to stripping of palladium, and in the case of bulk films, significant roughening of the surface was observed as signified by peak broadening and increased irreversibility. It is necessary, at this juncture, to point out also that the "multiplet" state only appeared at submonolayer coverages of palladium and that, for coverages of palladium in excess of approximately 1 mL, only one peak was observed. This is exemplified in Figure 4 in which copper UPD onto palladium multilayers on Pt(111) gave rise to a single UPD peak. It should be noted that the copper stripping charge in Figure 4 amounts to only 452 μ C cm⁻², again emphasizing the "conditionality" of the stripping charge (see eq 1) and also the significant differences between the adsorption characteristics of bulk palladium films and their monolayer counterparts.

Interestingly, the stripping peak in Figure 4 is very similar to that reported for UPD of copper onto massive Pd(111) electrodes^{16b} and also multilayers of palladium on Au(111).¹⁷ For multilayers of palladium adsorbed on Pt(100), it has also been shown that an almost identical voltammetric response to electrosorption of copper onto bulk Pd(100) is obtained.¹⁸ Thus, we conclude that high-quality Pd(111) films may be produced by irreversible adsorption of palladium on Pt(111) as also deduced from LEED.^{8,9} Speculations as to the origin of the splitting of the copper UPD peak on submonolayer palladium sites await further work using STM and stepped single crystals.²⁹

Copper UPD in 0.1 M H₂SO₄ in the Presence of 10^{-3} M Chloride. In Figure 5a is shown the CV resulting from copper UPD on Pt(111) in the presence of chloride. Agreement between the present study and earlier work is good.^{4a,b,11,13} A two-step adsorption process for copper is once again signified by the presence of two adsorption states as found for copper UPD in pure sulfuric acid although, for chloride, the potential separation (130 mV) between each state is somewhat greater



Figure 5. (a) UPD of copper on Pt(111) in 10^{-3} M Cu²⁺_(aq) + 0.1 M H₂SO₄ + 10^{-3} M NaCl. Sweep rate = 10 mV/s. (b) UPD of copper on bulk palladium film irreversibly adsorbed on Pt(111) in 10^{-3} M Cu²⁺_(aq) + 0.1 M H₂SO₄ + 10^{-3} M NaCl. Sweep rate = 10 mV/s. Insert: corresponding CV of hydrogen electrosorption.

(compare with Figure 1). The total copper stripping charge is 515 μ C cm⁻² with approximately twice as much charge appearing in the more positive stripping peak compared to the peak at more negative potentials. The result of dosing submonolayer amounts of palladium (0.27 mL) onto the Pt(111) substrate is shown in Figure 6a. A new peak is observed at 0.2 V associated with copper UPD onto islands of palladium and a second peak corresponding to the more negative of the two copper adsorption states characteristic of Pt(111). The need to limit the upper potential range to 0.3 V will be explained subsequently. Increasing the coverage of palladium up to 1 mL led to the attenuation of all voltammetric states pertaining to the Pt(111) substrate and a maximum in the intensity of the peak at 0.2 V. Thus, island growth of palladium is once again indicated. In contrast to copper UPD in pure sulfuric acid, however, palladium submonolayer islands may be assigned unambiguously to a single, sharp peak at $\simeq 0.2$ V. Also, in





Figure 6. (a) Copper UPD on 0.27 mL of palladium irreversibly adsorbed on Pt(111) in 10^{-3} M Cu²⁺_(aq) + 0.1 M H₂SO₄ + 10^{-3} M NaCl. Sweep rate = 10 mV/s. (b) Oxidative stripping of palladium irreversibly adsorbed on Pt(111) in 10^{-3} M Cu²⁺_(aq) + 0.1 M H₂SO₄ + 10^{-3} M NaCl. The gradual decrease in the magnitude of the copper adsorption state corresponding to second layer palladium and the simultaneous growth in the intensity of the first layer palladium peak are evident. Sweep rate = 10 mV/s.

contrast to findings in pure sulfuric acid, Figure 6b shows that, for coverages of palladium in excess of 1 mL, a second adsorption state of copper develops at more positive potentials, which may be attributed to copper UPD onto second layer palladium, as also reported in the case of hydrogen electrosorption.^{7,8} Oxidative desorption of palladium between 0.45 and 0.5 V gives rise to preferential desorption of second layer palladium (decrease in intensity of peak at 0.23 V) and an increase in the intensity of the peak at 0.2 V as more and more of the underlying palladium monolayer was exposed. At its

maximum intensity, the charge under the palladium monolayer peak corresponded to 428 μ C cm⁻². In Figure 5b is shown a voltammogram of the UPD of copper onto a thick palladium film (>4 mL) in the presence of chloride anions. The measured copper stripping charge in this case amounted to $420 \,\mu \text{C} \text{ cm}^{-2}$. Again, a remarkable similarity is observed between Figure 5b and previous data on palladium single crystals and (111) orientated supported films^{16b} whereby, in contrast to (111) surfaces of platinum and gold, a single copper adsorption state is observed. Interestingly, electrode surfaces such as Rh(111), Pd(111), and Ir(111) which display the strongest interactions with specifically adsorbed anions³⁰ also tend to produce a single copper UPD state.²⁴ Iodine on Pt(111) is also known to produce a single copper UPD peak,³¹ reflecting once again that strong anion-substrate interactions appear to preclude the possibility of a two-stage copper adsorption process. When further oxidative stripping of palladium from the well-ordered monolayer was carried out at potential excursions up to 0.6 V (Cu^{2+/} Cu), a remarkable change in the voltammogram was realized. It should be noted that these changes *only* occurred for $\theta_{Pd} \leq$ 1 mL at potentials in excess of 0.3 V (Cu²⁺/Cu). Figure 7a shows the effect of repetitive potential cycling of a palladium monolayer between 0.1 and 0.6 V (Cu²⁺/Cu). The adsorption state associated with the palladium monolayer is continuously transformed into two new states at $\simeq 0.4$ and 0.15 V. This behavior was not observed in $Cu_{(aq)}^{2+}/H_2SO_{4(aq)}$ solutions. A model in accordance with the present data would be as follows.

At the edges of palladium monolayer islands, place exchange of strongly adsorbed chloride with palladium takes place. This would be consistent with the fact that chloride catalyzes the oxidative desorption of palladium relative to bisulfate (anioninduced weakening of Pt-Pd bonds), presumably via some complexation between Cl⁻ and adsorbed palladium. Since the new state at 0.4 V is slightly negative of the more intense of the copper UPD states found for copper adsorption on the wellordered Pt(111) surface, it would also be consistent with copper adsorption onto *platinum* sites. It should be remembered that the adsorption of copper onto palladium sites takes place some 200 mV more negative in potential. If the present assumptions holds and, following repetitive cycling, palladium is stripped off the surface to be replaced with strongly adsorbed chloride ions at the palladium island rim, the state at 0.4 V is simply copper UPD onto Pt sites originally occupied by placeexchanged chloride ions. However, the electronic structure of the Pd-Cu coplanar layer formed after place exchange of chloride with copper will obviously be different from that of the center of the palladium island which is still dominated by Pd-Pd interactions. Therefore, one would predict that copper UPD onto Pd-Cu sites would occur at a more negative potential than copper UPD on Pd-Pd regions. This is because (as has been noted by several workers^{32,33}) as a surface alloy becomes enriched with one component relative to another, UPD peaks tend to shift in potential away from the value associated with the initially more concentrated component to that of the majority component. Thus, since copper UPD on Cu-Pd alloys cannot take place at more positive potentials than on pure palladium or more negative potentials than on pure copper, one expects the potential of the copper UPD peak to lie between these two extremes, depending upon the precise surface composition of the alloy. Therefore, the new peak appearing at ≈ 0.15 V as a consequence of oxidative stripping of palladium in chloride would be wholly consistent with copper UPD onto a Pd-Cu alloy formed originally at potentials close to 0.4 V. The halfwidth of the 0.15 V peak is comparable with that of the 0.2 V UPD copper peak, indicating that the Cu-Pd alloy is welldefined. Progressive nucleation and growth of the place-



Figure 7. (a) Effect of potential cycles between 0.1 and 0.6 V ($Cu^{2+/}$ Cu) in 10^{-3} M $Cu^{2+}_{(aq)}$ + 0.1 M H₂SO₄ + 10^{-3} M NaCl on an irreversibly adsorbed palladium monolayer on Pt(111). Sweep rate = 10 mV/s. (b) Copper UPD on maximum surface coverage of copper–palladium surface alloy obtained from treatment outlined in (a). Sweep rate = 10 mV/s. (c) Changes in the voltammetric profile of (b) after repetitive cycles to 0.9 V, showing progressive desorption of palladium from Cu/Pd alloy phase and recovery of adsorption properties of Pt-(111). Sweep rate = 10 mV/s.

exchanged chloride sites toward the center of the palladium monolayer island would account for the quantitative decrease in the intensity of the 0.2 V peak and the correlated growth of the states at 0.15 and 0.4 V. A schematic of the processes thought to be occurring is presented in Figure 8. It should be noted also that the total stripping charge from all three states is fairly constant, indicating that the total number of sites for copper UPD remains the same-it is only the relative surface concentration of each type of copper adsorption site that is changing $[Cu^{2+} \text{ on } Cl-Pt (0.4 \text{ V}), Cu \text{ on } Pd-Pd (0.2 \text{ V}), and$ Cu^{2+} on Cu-Pd (0.15 V)]. Figure 7b shows the voltammogram of the palladium layer after extensive potential cycling in order to generate the maximum surface concentration of the Cu-Pd alloy. Although there is still a small amount of the 0.2 V palladium monolayer peak visible, it is clear that the majority of the surface has been converted to the Cu-Pd alloy phase. Integration of the stripping peaks at 0.15 and 0.4 V leads to values of 311 and 118 μ C cm⁻², respectively. Since, according to our model, this should reflect the number of palladium (0.15 V) and copper sites (0.4 V) within the alloy (ignoring differences due to anions as discussed in eq 2), it is possible to obtain an estimate of the stoichiometry of the alloy phase.

$$Cu:Pd = 118:311 = 0.38 \approx 1:3$$

Thus, if one asserts that, because of the narrowness of the two peaks at 0.15 and 0.4 V, the Cu-Pd alloy being generated as a result of potential cycling is uniform, its composition according to charge considerations is estimated to be Pd₃Cu. Further oxidative stripping of the Pd-Cu alloy beyond the point reached in Figure 7b is shown in Figure 7c (potential excursion to 0.9 V). It is evident from Figure 7c that the Pd₃Cu alloy phase is gradually changed into a more copper-rich alloy phase as oxidative stripping of palladium is continued. This is signified by the attenuation of the peak at 0.15 V and the appearance of a new state at 0.04 V. In parallel with these changes is the growth in the Pt(111) copper adsorption peaks at ≈ 0.4 V. Continued potential cycling was found to eliminate entirely the 0.04 V state with subsequent restoration of the Pt(111) voltammogram features shown already in Figure 5a. This implies that no structural transformations have occurred to the Pt(111)substrate as a consequence of complete palladium desorption. Furthermore, so long as the positive potential limit was maintained at 0.5 V (Cu²⁺/Cu), the Pd₃Cu alloy phase remained stable, as signified by the constancy of the voltammetric response of the electrode shown in Figure 7b. Finally, within the constraints of a 0.5 V (Cu^{2+}/Cu) potential limit, sweep rate was found to have no discernible effect on the stability of the alloy phase.

Copper UPD in 0.1 M H₂SO₄ in the Presence of 10⁻³ M Bromide. Having already investigated the effect of chloride on the dissolution of palladium, it was thought prudent to examine whether or not bromide ions also had a catalytic influence over the desorption kinetics. Previous studies^{4b,11,18} have concluded that a copper-bromide bilayer is formed during the initial copper adsorption step on clean Pt(111). The second peak at more negative potentials may, as for chloride, be related to place exchange with copper of residual bromide ions bonded to the Pt(111) substrate. The total copper stripping charge for copper in the presence of bromide (not shown) was found to be 490 μ C cm⁻², slightly less than the stripping charge in chloride but greater than the charge in pure sulfuric acid. Figure 9 shows the oxidative stripping of a palladium film ($\theta_{Pd} > 1$) in the bromide-containing copper electrolyte. Although peak resolution is not as good as for chloride, it is still possible to discern the preferential stripping of second layer palladium (UPD peak at 0.17 V, negative-going sweep) and the subsequent



Figure 8. Schematic of oxidative stripping of palladium in the presence of halide ions.



Figure 9. Oxidative stripping of palladium irreversibly adsorbed on Pt(111) in 10^{-3} M $Cu_{(aq)}^{2+}$ + 0.1 M H_2SO_4 + 10^{-3} M NaBr. The gradual decrease in the magnitude of the copper adsorption state corresponding to second layer palladium and the simultaneous growth in the first layer palladium state are evident. Sweep rate = 10 mV/s. Insert: Effect of oxidative stripping of a monolayer of palladium. Sweep rate = 50 mV/s.

growth in the intensity of the first layer palladium peak (0.16 V, negative going sweep). The palladium film was stable up

to 0.3 V, but significant oxidative currents associated with palladium desorption could be generated at potentials > 0.3 V. This behavior is identical with that found for chloride-catalyzed desorption whereby preferential desorption of palladium multilayers takes place prior to any stripping of the palladium monolayer. The charge under the copper stripping peak from a monolayer of palladium derived from stripping of second and third layer palladium was estimated to be 466 μ C cm⁻². The resemblance between the behavior of bromide and chloride becomes even more striking when oxidative desorption of the palladium monolayer is facilitated. The insert of Figure 9 shows the effect of repetitive potential cycling up to 0.75 V at 50 mV/s on the palladium monolayer. As with chloride, new copper adsorption states are generated close to the potential of the UPD peak on Pt(111) and simultaneously at potentials negative of the copper UPD state associated with the palladium monolayer. It is proposed that the same microscopic model outlined for chloride applies in this case. That is, place exchange of bromide ions with simultaneous desorption of a palladium bromide complex occurs at the edges of palladium monolayer islands, leading subsequently to the formation of a copper desorption state at ~0.44 V. Copper UPD onto the Cu-Pd alloy formed as a result of bromide-copper place exchange (peak at 0.32 V) manifests itself as the adsorption state at potentials negative of the UPD copper peak associated with the palladium monolayer. Eventually, after continued potential cycling, recovery of the UPD response of the palladium-free Pt(111) substrate was obtained. Hence, the behavior of bromide ions in controlling the oxidative desorption of palladium films on Pt(111) is demonstrated to be almost identical with that of chloride.

Further Discussion

The adsorption of palladium on Pt(111) leads to the formation of well-defined epitaxial films.^{7–10} In 0.1 M H₂SO₄, copper UPD may be used to determine the palladium coverage for $\theta_{Pd} \le 1$ mL. However, oxidative desorption of palladium multilayers in copper-containing electrolytes in the absence of halide

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ions always led to a disordered Pt/Pd phase. This behavior contrasts strongly with that found in halide solutions. A reasonable explanation of this difference would be to consider the extent to which surface oxides can form on the palladium deposit and the ability of the palladium to form complexes with the anions in the electrolyte phase. It is well-known that halides possess the ability to inhibit the onset of oxide formation on transition metal electrodes.³⁴ One of the striking consequences of electrochemical oxide formation on electrode surfaces is reported to be a significant perturbation of the surface crystallinity.³⁵ Thus, if oxide formation is precluded, surface roughening by this mechanism should not happen. This would be consistent with the present halide results whereby surface roughening via oxide formation and adsorption is prevented due to the strong interaction of the halides with the electrode surface. However, in the presence of the more weakly adsorbed bisulfate anion, surface oxide formation is more likely to take place in competition with anion adsorption with a corresponding increase in the surface disorder upon desorbing the oxide. The ability of strongly adsorbed anions to weaken the bonding between a metal atom and a metallic substrate (for example, during "electrochemical annealing"7,25) may also play in part in facilitating the dissolution of palladium. Having discussed possible reasons as to why chloride and bromide catalyze the dissolution of palladium without encouraging the growth of surface defects, it remains to explain why second layer palladium should be removed exclusively via oxidative desorption, even though palladium monolayer sites are available (see Figure 6b). If the proposed model of dissolution occurring from island boundaries into the island center is correct, it means that step sites (at the junction between palladium first and second layers) are highly susceptible to dissolution. This phenomenon could be attributed to the lower PZTC exhibited by step sites versus terraces.³⁰ That is, at a given potential, the excess positive charge at the step site would always be greater than at a terrace site, and therefore, a greater interaction with adsorbed anions would be exhibited. To obtain a similar degree of interaction at a terrace site, the electrode potential would need to be increased toward more positive potentials. In fact, it was found during the stripping experiment in chloride that, if a bulk palladium layer was desorbed by cycling between 0 and 0.5 V (Cu²⁺/Cu) until a "perfect" palladium monolayer was evolved, to cause further place exchange of the chloride with the palladium monolayer, the overpotential had to be increased to at least 0.6 V (Cu²⁺/Cu), consistent with the absence of step defect sites in such an electrochemically formed palladium monolayer. Thus, from a fundamental viewpoint of excess charge at local sites, the rate of palladium dissolution at steps must always be greater than at a terrace, giving rise to the behavior reported above. Strong evidence in support of our model has recently been published in which in situ STM was used to monitor the iodine-catalyzed dissolution of palladium single crystals. Both layer-by-layer dissolution and selective corrosion at steps were observed.³⁶ One further advantage of using a thin palladium layer to observe halide-catalyzed palladium desorption is that it demonstrates unambiguously that the initial step in dissolution must involve a place exchange with the halide anion. This finding is revealed only as a consequence of the fact that a halide anion bonded to platinum exhibits an adsorption/desorption state some 200 mV removed from an equivalent palladium site.

Conclusion

Copper UPD may be used to estimate the surface coverage of irreversibly adsorbed palladium films on Pt(111). The range of potential in which the palladium film was stable depended upon the type of anion present in the electrolyte. Whereas in the absence of halide ions, the palladium deposit was stable up to 0.6 V (Cu²⁺/Cu), in the presence of chloride and bromide, oxidative desorption could be observed at potentials greater than 0.3 V (Cu²⁺/Cu). The morphology of the palladium film after oxidative stripping was also dependent upon the extent of oxide formation which could be minimized by specifically adsorbed halide ions. As reported by Soriaga and co-workers³⁶ in the case of iodide monolayers, the halide-induced dissolution of palladium occurs in a layer-by-layer fashion with selective corrosion at step sites. In addition, it is asserted that the initial step in the dissolution process is place exchange of the halide anion at defect sites contained within the palladium film.

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