A SURFACE SCIENCE APPROACH TO THE STUDY OF
UNDERPOTENTIAL DEPOSITION

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ABSTRACT

Submonolayer to multilayer coverages of Cu electrodeposited and vacuum-deposited onto a well-characterized Pt(111) surface were studied in both ultrahigh vacuum (UHV) and electrochemical environments using a combined UHV-electrochemical transfer apparatus. Linear sweep voltammograms obtained in 0.2 M HClO₄ for both types of surfaces displayed very similar electrochemical stripping profiles. The potential difference between the multilayer and the underpotential deposited (UPD) monolayer stripping peaks is ~0.43 V, which is equivalent to an absolute energy difference of 19.8 kcal/mole. In addition, these voltammetric results demonstrated that simple site blocking for hydrogen chemisorption on Pt(111) by both electrodeposited and vapor-deposited Cu occurs linearly with chemisorption being essentially eliminated at θ_{Cu} ~ 1.0 ML, much similar to analogous studies performed in UHV environment. Although the charge measured for the monolayer Cu stripping peak in both cases is lower than the theoretically expected value for a Cu monolayer...
in registry with the Pt(111) substrate surface, UHV studies of Cu overlayers on Pt(111) based on low-energy diffraction (LEED) analysis, Auger electron spectroscopy (AES) analysis, work function measurements and photoemission studies have shown that a complete Cu monolayer is formed prior to the formation of Cu multilayers.

To account for the discrepancy between these two values, we believe that the UPD Cu monolayers in the electrochemical environment near their stripping potentials are partially charged as a consequence of transfer of electronic charge from the metal overlayer to the Pt(111) substrate. In addition, substantial discrepancy is observed for submonolayer and monolayer coverages of Cu on Pt(111) and Ru(0001) between the voltammetrically measured faradaic charge and the theoretically expected value. Major contributions to this discrepancy are believed to be the partially charged nature of the Cu adlayers as well as the partial discharge of coadsorbed anions during the electrooxidative desorption of Cu.

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INTRODUCTION

The study of bimetallic surfaces in both gas-phase and liquid-phase environments has been a subject of many investigations over the last several years [1-6]. These studies are motivated in part by the selective improvement and degradation in catalytic activity, selectivity and resistance to poisoning of bimetallic surfaces over the monometallic surfaces. The modification of the metal substrate at the gas-solid interface is usually accomplished by vacuum deposition of the second metal [1-3], whereas at the liquid-solid interface, controlled submonolayer and monolayer deposits of a second metal can be electrochemically deposited onto the metal substrate by underpotential deposition (UPD) [4-7]. Moreover, while studies performed using modern techniques of surface science [8-10] give a detailed picture of the chemistry of bimetallic surfaces occurring at the gas-solid interface, the corresponding information is not easily obtained in the analogous electrochemical environment.

Although these bimetallic surfaces display strikingly similar properties in both gas- and liquid-phase environments as mentioned above, very few studies have addressed these similarities as well as the differences. In an effort to correlate the properties of these bimetallic surfaces at the gas-solid and liquid-solid (or electrolyte-electrode) interfaces, we have recently constructed a combined ultrahigh vacuum (UHV) and electrochemical apparatus [11] which allows easy and rapid controlled transfer of a
well-characterized single-crystal surface between UHV and atmospheric liquid electrochemical environments. This type of apparatus [7,12-17] is essential since it enables the powerful surface science techniques to be applied to characterize and study the electrode surface before and after electrochemical measurements.

In this paper we will demonstrate that ultrathin Cu films on Pt(111) prepared either by electrodeposition from Cu$^{2+}$-containing solution or by vacuum-deposition in UHV environment displayed essentially identical electrochemical stripping profiles in 0.2 M HClO$_4$. These results will show how copper affects the adsorption of hydrogen on Pt(111) in the electrochemical environment. We will also demonstrate that specific comparisons can be drawn between the present electrochemical data and that reported in the surface science literature [18]. In addition, our present studies show that substantial discrepancy is observed between the voltammetrically measured faradaic charge and the theoretically expected value based on UHV determined Cu coverages using Auger electron spectroscopy (AES) for submonolayer to monolayer coverages of Cu on Pt(111). More importantly, the degree and sign of this discrepancy is strongly coverage dependent. Also present here is a similar study for the Cu/Ru(0001) [7]. This later study is of interest since the thermal desorption spectra and the linear sweep voltammograms observed at comparable Ru coverages displayed remarkably similar profiles. Of special interest is this last system also displays significant discrepancy between the voltammetrically measured faradaic charge
and the theoretically expected value based on UHV determined Cu coverages using both AES and temperature programmed desorption (TPD) studies for submonolayer to monolayer coverages of Cu on Ru(0001).

**EXPERIMENTAL**

The combined UHV and electrochemical apparatus and procedures employed have been fully described elsewhere [11,19,20] and will only be briefly discussed below.

The Pt(111) and Ru(0001) sample, 10mm in diameter and 1.5mm thick, were heated resistively by tantalum leads spot welded to the edge of the crystal while the temperature measurement was made using a W-5% Re/ W-26% Re thermocouple spot welded to the back side. The Pt(111) and Ru(0001) samples were cleaned by heating to 1300K in $10^{-6}$ Torr O\textsubscript{2} followed by annealing in vacuum to 1500K and 1700K, respectively, to remove traces of oxygen. Surface cleanliness was verified by AES and the order of the Pt(111) and Ru(0001) samples was confirmed by low-energy electron diffraction (LEED).

A PAR model 273 potentiostat was used for the electrochemical measurements. The electrochemical cell is of conventional three-electrode configuration consisting of a platinum counter electrode and the Pt(111) and Ru(0001) samples as the working electrodes. Water was purified by means of Milli-Q system (Millipore).

Copper perchlorate and perchloric acid (doubly distilled) were from G. F. Smith. Deoxygenation of the solutions was accomplished by bubbling ultrapure N\textsubscript{2} through all solutions.
Cu was dosed in vacuum at a substrate temperature of ~300 - 400K by evaporation from copper wire wrapped around tungsten filaments. Prior to each deposition, the source was degassed extensively and AES showed no accumulation of impurities on the Pt(111) and Ru(0001) surfaces during metal deposition. Calibration of the metal surface coverage is described in the Results and Discussion section.

RESULTS AND DISCUSSION

A. Electrochemical Stripping of Electrodeposited and Vacuum-Deposited Cu Films on Pt(111)

To demonstrate the remarkable similarities in their electrochemical stripping profiles, Figs. 1A and 1B display series of linear sweep voltammograms at 0.05 Vs⁻¹ in 0.2 M HClO₄ for various coverages of Cu obtained for electrodeposited and vacuum-deposited Cu films on Pt(111), respectively. The former electrodeposited Cu films were prepared by setting the electrode potential at -0.2 V at various time intervals in a very dilute Cu²⁺ (100 µM)/0.2 M HClO₄ solution. The Cu²⁺ solution was then replaced with Cu²⁺ free 0.2 M HClO₄ solution prior to the stripping process. While the vacuum-deposited films were prepared as described in the Experimental section, it is important to note that following vacuum deposition of a given coverage of Cu, the Pt(111) electrode was introduced into the electrochemical cell under a controlled potential of -0.2 V to avoid any loss of Cu to the electrolyte.
The anodic peak at ~0.5 V observed for both surfaces shown in Figs. 1A and 1B can be attributed to the electrochemical stripping of submonolayer to monolayer copper layers (to form solution Cu$^{2+}$). The relatively more negative anodic peak at ~0.05 V, which is only observed at \( \theta_{\text{Cu}} > 1.0 \text{ ML} \), can easily be attributed to the desorption of Cu multilayers (i.e. \( \text{Cu}^0(s) \rightarrow \text{Cu}^{2+}(aq) + 2e^- \)). Interestingly, the electrochemical stripping voltammograms displayed in Figs. 1A and 1B provide useful information regarding the difference in desorption energies between multilayer and monolayer Cu on Pt(111) in the electrochemical environment. As shown in Fig. 1, the potential difference between the multilayer and the monolayer stripping peaks is ~0.43 V, which is equivalent to an absolute energy difference of 19.8 kcal/mole. To a first approximation, this represents the free energy change for Cu bound to Pt versus Cu bound to Cu. Although solvation effects could contribute to this free energy difference [21], this relatively large value does correlate with the well-known ease of alloy formation for the Cu/Pt(111) surface at temperatures above 520K [18,19,22].

The Cu coverages depicted in Figs. 1A and B were determined by assuming the faradaic charge measured under the saturated stripping peak at 0.5 V is a full monolayer as well as from the AES [Cu(920 eV)/Pt(237 eV)] ratios [19,20]. Surprisingly, the faradaic charge measured for the saturated monolayer Cu stripping peak at 0.5 V is approximately 340 ± 25 µCcm$^{-2}$, which is substantially lower than the theoretically expected value for a monolayer of Cu in
registry with the Pt(111) substrate surface (480 µCcm\(^{-2}\) for the present system). There are several important pieces of data obtained in the present and previous studies [19,20] which support our Cu coverage estimation.

First of all, UHV studies of Cu overlayers on Pt(111) [18,23,24] based on LEED analysis, AES analysis, work function measurements, and photoemission studies have shown that a complete monolayer is formed prior to the formation of Cu multilayers. Secondly, it has long been recognized that hydrogen chemisorbs strongly on Pt both in UHV environment [18,25] and in acidic electrolyte solution [16,17,26-28]. Moreover, both UHV studies [18] and electrochemical studies [4,5,29] have demonstrated that total blockage of hydrogen chemisorption on this surface requires a complete monolayer of Cu.

Close inspection of Figs. 1A and B reveals that the voltammetric wave, corresponding to the removal (oxidation) of adsorbed hydrogen on Pt(111) within the electrode potential region between -0.2 and 0.1 V [16,17,26,27], is increasingly suppressed as \(\theta_{Cu}\) is progressively increased for both surfaces. Eventually, this adsorbed hydrogen wave is compressed at \(\theta_{Cu} > 1\) ML.

To further illustrate this last point, Fig. 2 displays plots of saturation coverages of adsorbed hydrogen, \(\theta_h\), as deduced from the faradaic charge under the voltammetric wave at -0.2 to 0.1 V as a function of copper pre-coverage, \(\theta_{Cu}\), in 0.2 M HClO\(_4\). (The saturation coverage of hydrogen on the clean Pt(111) surface is assumed to be 1.0 ML.) The data points plotted in Fig. 2 were obtained
from the corresponding linear voltammograms for electrodeposited (filled circles) and vacuum-deposited (open squares) Cu overlayers on Pt(111). As mentioned above, Fig. 2 clearly shows that both electrodeposited and vacuum-deposited Cu overlayers linearly attenuate the hydrogen adsorption capacity of the Pt(111) electrode in a 0.2 M HClO₄ environment with chemisorption being essentially eliminated at $\theta_{Cu} = 1.0$ ML. We also note here that this linear attenuation of the hydrogen adsorption capacity resembles closely that reported in a recent UHV study in which hydrogen adsorption on Pt(111) was blocked linearly by vacuum-deposited Cu layers [18].

The fact that complete blocking of hydrogen adsorption on the Pt(111) electrode at the completion of the UPD Cu layer deposited electrochemically or in vacuum strongly indicates that this UPD Cu layer represents a complete Cu monolayer.

Finally, comparisons of the AES [Cu(920 eV)/Pt(237 eV)] ratios for the vacuum-deposited Cu monolayer before and after immersion in the electrolyte under controlled potential (-0.2 V) reveal no measurable loss of Cu. In addition, the observed AES ratio is in close agreement (within 5%) with that found for the electrodeposited UPD Cu layer. Moreover, both aforementioned Cu monolayers displayed (1x1) LEED patterns at room temperature, confirming the pseudomorphic structure of each. The above observations imply that the UPD Cu layer deposited electrochemically or in vacuum are essentially identical and therefore represent a complete Cu monolayer.
B. The Nature of the Cu Monolayer on Pt(111)

As mentioned earlier, we have observed that the faradaic charge measured for the monolayer Cu stripping peak in both electrodeposited and vacuum-deposited Cu films on Pt(111) is substantially lower than the theoretically expected value for a Cu monolayer in registry with the Pt(111) substrate surface. One simple explanation is that the monolayer Cu adatoms are significantly partially charged under the electrochemical conditions near their stripping potentials. As a result, the charge measured for the UPD stripping peak will lead to a lower value than the theoretically expected value, which assumes a full two-electron-transfer process to occur within the UPD peak potential region.

Two factors could contribute to the presence of a charged Cu monolayer at the Pt/solution interface: (1) a charge transfer from Cu to Pt in the first monolayer is expected based upon the lowering work function upon vacuum-deposition of Cu onto Pt(111) in UHV studies [18,23]; and (2) the adsorption of solution anions near the stripping potential of monolayer Cu could facilitate charge transfer from the Cu overlayer to the Pt substrate. From the work function difference between monolayer Cu on Pt and bulk Cu, the contribution of (1) to the development of the partial Cu charge is estimated to be relatively minor [30]. The contribution of (2), then, clearly is seen to dominate the development of the partial charge on the Cu prior to the onset of the UPD stripping peak. In this regard it is noteworthy that a partially charged UPD Cu adlayer electrodeposited on a
polycrystalline platinum electrode, using thermodynamic and kinetic arguments, has been proposed [31]. In addition, a recent radiochemical study [32] has provided direct evidence that, in the presence of submonolayer and monolayer coverages of electrodeposited Cu on polycrystalline gold, an enhanced adsorption of (bi)sulfate is induced by the Cu adatoms. This enhanced anion adsorption [32] likely is a consequence of the positive charge developed at the Cu sites via transfer of electronic charge from the Cu to the metal substrate. An "electrosorption valency" [31,33] of Cu that is significantly less than 2 can be ascribed to a polarization of the Cu to optimize the destabilizing Cu-anion electronic interaction [34], which involve primarily occupied orbitals, and the stabilizing Cu$^{\delta+}$-anion electronic interactions. In this regard, it is of interest to note that recent X-ray photoelectron spectroscopy (XPS) studies [3,34] have demonstrated that chemisorption of CO onto bimetallic surfaces, in general, induces a large positive shift in the core level of the metal overlayer. The mechanism by which the metal overlayers become partially charged has been ascribed to an adsorbate-induced charge transfer from the overlayer metal to the substrate.

It is also of interest to note that a recent study [35] of UPD Cu on carbon-supported platinum by XANES (X-ray Absorption Near Edge Structure) has shown that the adsorbed copper had an oxidation state close to Cu$^{+1}$. Similarly, Stuwe, et al., [36] using XPS, have identified the positively charged nature of the emersed UPD lead
C. Coverage-Dependent Behavior of Ultrathin Cu Films on Pt(111)

More importantly, the aforementioned discrepancy between the measured faradaic charge and the theoretically expected value is also observed for submonolayer coverages of Cu on Pt(111) \[20\]. Interestingly, the degree and sign of the discrepancy is strongly coverage dependent. In addition, AES analysis of the emersed Cu/Pt(111) electrodes indicates the presence of substantial amounts of chlorine and oxygen (from perchlorate ions) which vary linearly as a function of Cu coverage. These results therefore strongly indicate that the Cu adlayer is partially charged at submonolayer to monolayer coverages in the electrochemical environment.

Fig. 3 shows plots of the ratio of measured to theoretical faradaic charge, $Q_{\text{meas}}/Q_{\text{theo}}$, as a function of Cu coverage in monolayer (ML), $\theta_{\text{Cu}}$, on Pt(111). The $Q_{\text{meas}}/Q_{\text{theo}}$ values were obtained by ratioing the faradaic charge measured from the stripping peak at $\sim 0.5$ V in 0.2 M HClO$_4$ to the theoretically expected value which was deduced from the $\theta_{\text{Cu}}$ value determined from AES. The Cu/Pt(111) surfaces were prepared from UHV and the $\theta_{\text{Cu}}$ values determined precisely by AES \[19,20\]. The deviation of the $Q_{\text{meas}}/Q_{\text{theo}}$ ratio from unity displayed in Fig. 3 is of central importance since a ratio of unity is expected if the Cu adlayer on Pt(111) in 0.2 M HClO$_4$ is fully discharged. Close inspection of Fig. 3 reveals that the resulting plots can in general be separated into three regions: (1) for $\theta_{\text{Cu}} < 0.4$, the ratio
lies above unity; (2) at $0.4 \leq \theta_{\text{Cu}} \leq 0.6$, the ratio is close to unity; and (3) at $\theta_{\text{Cu}} > 0.6$, a ratio below unity is obtained.

As mentioned earlier, a ratio below unity obtained for $\theta_{\text{Cu}} = 1.0$ can be explained by the partially charged nature of the Cu monolayer in the electrochemical environment [19]. The charged nature of the first monolayer of Cu is demonstrated in Fig. 4 which displays plots of Cl coverage, $\theta_{\text{Cl}}$, as a function of $\theta_{\text{Cu}}$ as determined by AES for an emersed Pt(111) electrode [20]. The $\theta_{\text{Cl}}$ values were determined from the AES [Cl(181 eV)/Pt(237 eV)] ratio and a saturation coverage of $\sim 0.45$ ML [37]. The presence of oxygen in amounts consistent with stoichiometric ClO$_4$ was indicated by an Auger feature at 510 eV. The linear sweep voltammograms in these studies were characteristic of those published voltammograms for a chloride-free electrolyte [38]. The monotonic increase in $\theta_{\text{Cl}}$ with increasing $\theta_{\text{Cu}}$ displayed in Fig. 4 can be attributed to the partially charged nature of the Cu adlayer at the emersion potential.

While the presence of a partially charged Cu adlayer can fully explain the observed deviation of the $Q_{\text{meas}}/Q_{\text{theo}}$ ratio from unity at $\theta_{\text{Cu}} > 0.6$ (Fig. 3), questions do arise regarding the possibility of additional interactions between the electrolyte and the Cu/Pt(111) surface at $\theta_{\text{Cu}} \leq 0.6$ where $Q_{\text{theo}}/Q_{\text{theo}} \geq 1.0$. Although a marked change in the double-layer structure during the electrooxidative desorption of Cu could possibly lead to the aforementioned deviation, it is unrealistic that such modification could be the major contributor to the observed deviation [39]. We therefore believe that for $\theta_{\text{Cu}}$
≤ 0.6, significant partial discharge of coadsorbed anions, likely hydroxide, occurs during the electrooxidative desorption process, thus accounting for the excess faradaic charge. The dispersed and partially charged nature of the Cu adlayer at θ_{Cu} ≤ 0.6, in principle, could allow the coadsorbed anions to be interdispersed with the Cu adatoms, possibly in correlated positions [40]. This arrangement, in turn, would facilitate the discharging process during the electrooxidative desorption of Cu. Clearly, the more dilute the Cu within these structures, the larger the partial charge will be on the Cu. Thus the contribution of the anions to the measured charge during the oxidative stripping more than compensates for the increase in the oxidation state of the Cu at θ_{Cu} < 0.6. At θ_{Cu} > 0.6, where the Cu adlayer is believed to be in the form of large 2-D islands [18,23,24], anion coadsorption and their accompanying discharge during the Cu electrooxidation would be minimal. The maintenance of the large 2-D Cu morphology during the electrooxidative desorption process for θ_{Cu} > 0.6 is consistent with the observed desorption kinetics [41].

Recent work by Magnussen and coworkers [40] using in-situ scanning tunneling microscopy (STM) indicates that Cu coverages on Au(111) deduced from the STM images differ markedly from the coverages evaluated coulometrically. For example, an STM image which can accommodate only 0.33 ML Cu yielded a charge corresponding to θ_{Cu} ≥ 0.5 ML. This ratio of the coulometrically measured Cu coverage to the actual Cu coverage is very close to that found for Cu/Pt(111)
in Fig. 3. Similarly, Chen et al. [42], using atomic force microscopy (AFM), have identified discreet structures for UPD Ag on Au(111) which are interpreted as metal–anion complexes. Furthermore, little agreement was found in this study between AFM-determined Ag coverages and those predicted from coulometric measurements.

More recently Tadjeddine, et al. [43], have used SEXAFS to characterize three distinct structure at of Cu on Au(111), a $\sqrt{3}\times\sqrt{3}$ structure at $\theta_{\text{Cu}} = 0.3$, a c(5x5) structure at $\theta_{\text{Cu}} = 0.6$, and a (1x1) structure at $\theta_{\text{Cu}} = 1.0$. This work, along with another recent study [35], also showed, using XANES, that the oxidation state of the high coverage Cu to be +1, very close to the value estimated by us for high coverage Cu on Pt. In view of these latter results, the changes observed in the normalized charge for the stripping of Cu from Pt are believed to be associated with discreet structures related to specific Cu coverages.

**D. Coverage-Dependent Behavior of Ultrathin Cu Films on Ru(0001)**

In addition to the Cu/Pt(111) system, we have studied the Cu/Ru(0001) system since this system has been widely investigated in both UHV and electrochemical environments [1–3,7]. Interestingly, using a similar approach as mentioned earlier, our results indicate
that significant discrepancy is also obtained between the voltammetrically measured faradaic charge and the theoretically expected value based on UHV determined Cu coverages. It is noteworthy that precise Cu coverages on Ru(0001) can be obtained by TPD as well as AES analysis [1-3,7].

Fig. 5 shows plots of the ratio of measured to theoretical faradaic charge ratio as a function of copper coverage on Ru(0001) obtained in a similar fashion as that shown in Fig. 3. Interestingly, the results obtained for the Cu/Ru(0001) system shown in Fig. 5 display remarkable similarities in the submonolayer region to those of Fig. 3 for the Cu/Pt(111) system. We therefore believe that the partially charged nature of the Cu adlayers as well as the partial discharge of coadsorbed anions during the electrooxidative desorption of Cu contribute significantly to the observed charge discrepancy for the Cu/Ru(0001) system as well.

**SUMMARY**

(1) Both electrodeposited and vacuum-deposited Cu at various coverages on a well-characterized Pt(111) surface display remarkably similar electrochemical stripping profiles in 0.2 M HClO₄.

(2) Similar to that reported in UHV studies, simple site blocking
of hydrogen chemisorption on Pt(111) by both electrodeposited and vacuum-deposited Cu occurs linearly with chemisorption being eliminated at $\theta_{\text{Cu}} \sim 1.0$ ML.

(3) The apparent discrepancy between the measured faradaic charge for the UPD Cu stripping peak and the theoretically expected value for a complete monolayer is likely due to the partially charged nature of the Cu monolayer. This partial charge arises as a consequence of the transfer of electrons from the metal overlayer to the Pt(111) substrate.

(4) For both the Cu/Pt(111) and the Cu/Ru(0001) systems, the apparent discrepancy between the voltammetrically measured faradaic charge and the theoretically expected value for submonolayer and monolayer Cu coverages is believed to be due to the partially charged nature of the Cu adlayers as well as the partial discharge of coadsorbed anions during the electrooxidative desorption of Cu.

(5) Results obtained in the present studies imply that coulometric determination of UPD Cu coverage on Pt(111) and Ru(0001) in HClO$_4$ can lead to substantial error. Whether this is generic to other UPD overlayers and to other adsorbates is of considerable interest and is the focus of studies in progress.

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REFERENCES

39. Although it is difficult to evaluate the nonfaradaic charge during the electrooxidative process, a rough estimation can be made as follows. If we assume a capacitance of roughly 30 - 40 µFcm² for the Cu/Pt(111) surface, to compensate for the difference
between the measured and theoretically expected charge (40 – 100 μCcm⁻²), a change of 1 – 2 V in the potential of zero charge during the Cu stripping process would be required. Such a change is highly unlikely in the present system.


41. The stripping curves for various coverages of Cu from θ_{Cu} = 0.05 – 1.0 ML do not constitute a "family" of curves. That is, the curve for 0.5 ML Cu, for example, does not fall within the 1.0 ML curve, but is shifted significantly cathodic. The implication of this is that the kinetics of the structural transformation from one Cu coverage to a second is very slow relative to the rate of the potential sweep.


**FIGURE CAPTIONS**

Figure 1. Linear sweep voltammograms for various coverages of (A) electrodeposited and (B) vacuum-deposited Cu on a well-characterized Pt(111) surface in 0.2 M HClO₄ at 0.05 Vs⁻¹.

Figure 2. Plots of saturation coverages of adsorbed hydrogen, θ_H, as a function of Cu pre-coverage, θ_Cu, in 0.2 M HClO₄. The Cu overlayers were prepared electrochemically (closed circles) and under vacuum condition (open squares).

Figure 3. Plots of the ratio of voltammetrically measured to theoretically expected faradaic charge, Q_meas/Q_theo, in 0.2 M HClO₄ as a function of copper coverage, θ_Cu, for vacuum-deposited Cu on Pt(111).

Figure 4. Plots of chlorine coverage, θ_Cl, as a function of copper coverage, θ_Cu, for emersed Cu/Pt(111) electrodes.

Figure 5. As for Fig. 3, but obtained for vacuum-deposited Cu on Ru(0001).
Fig. 1

Pt(111)/0.2 M HClO₄, 0.05 V s⁻¹

VACUUM-DEPOSITED Cu

E (V vs Ag/AgCl)

CURRENT (µA)

ELECTRODEPOSITED Cu

E (V vs Ag/AgCl)

CURRENT (µA)
Fig. 2
Fig. 3
Fig. 4
Coulometry of Cu/Ru(0001)
0.2 M Perchloric Acid

Measured/Theoretical Charge Ratio

Copper Coverage (ML)