Polycrystalline gold electrode redox behavior in an ammoniacal electrolyte
Part II. A parallel RRDE, EQCM and TOF-SIMS study of copper underpotential deposition

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Abstract

The underpotential deposition (upd) of copper at polycrystalline gold in an ammoniacal electrolyte (0.1 M NH₃ + 0.1 M NaClO₄) was investigated. The rotating ring disk electrode (RRDE), the electrochemical quartz crystal microbalance (EQCM) and time of flight secondary ion mass spectrometry (TOF-SIMS) were all used in parallel to study this process. RRDE experiments showed that upd of Cu(0) occurred at −0.4 V < E < 0.1 V, at three different sites. Bulk deposition of Cu(0) began at −0.4 V. RRDE and EQCM data did not show the involvement of any ionic copper species during the upd discharge process. Static and dynamic TOF-SIMS results are consistent with the above experimental results. The rate-determining step is the reduction of a dissolved copper ammonia species to upd Cu(0). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Underpotential deposition; Copper; Polycrystalline gold; RRDE; EQCM; TOF-SIMS

1. Introduction

Upd is an electrochemical phenomenon in which foreign metal adatoms are deposited onto an electrode surface at potentials more positive than the reversible Nernst potential. Whenever a solid electrode is held at potentials where upd can occur, the possibility of upd of trace species must be considered. Upd plays an important role in many electrochemical processes, including electroplating, electrocatalysis, fuel cells and sensor applications. For example, the efficiency of gold plating is enhanced substantially by the upd of bismuth or thallium on the substrate (J.D.E McIntyre, private communication). Another example is the catalytic effect of lead or bismuth upd, and the poisoning effect of silver upd, on the electrooxidation of formic acid at platinum [1]. Often, trace metal impurities are unknowingly present in a solution, and this species undergoes upd with unpredictable effects. An example of this phenomenon is poisoning of the oxygen reduction process [2] because of the upd of trace copper impurities present in high purity sulfuric acid.

The copper electrodeposition process has been widely used in the electronics industry because of copper’s excellent electrical and thermal conductivity. The upd of copper at a platinum electrode has been studied in various aqueous acid media to gain insights into the principles of copper upd processes. Tindal and Bruckenstein [3] reported that the depositions of two monolayers of Cu(0) at underpotential are necessary before Nernst behavior for copper reduction is observed in sulfuric acid solution. The second monolayer is deposited just before bulk deposition occurs. Hepel et al.
[4], using EQCM, studied the electrodeposition of copper on a polymer-coated gold electrode. Gewirth [5] studied the structure of upd copper at (111) gold in different electrolytes using the atomic force microscope. He found changing the electrolyte can strongly affect both the structure and energetics of upd coverage. For example, the copper structure obtained in sulfate media is more open than that obtained in perchlorate media.

Most studies have involved species that are directly reduced to the upd metal, without the possibility of an intermediate oxidation state playing a role in the upd process. Also, the principal media studied have been acidic [6,7].

Upd studies in complexing media raise the possibility of mechanistic complications. Few studies of copper upd in complexing alkaline solution have been made. Without complexing agents, precipitation of cupric hydroxide would cause complications. To avoid this problem, in electroless copper baths, complexing agents for cupric and cuprous ions are added. One example is the use of ethylenediaminetetraacetic acid (EDTA) [8].

We chose to study a model system to develop techniques that could then be applied by others to these kinds of more complicated situations. The system we chose was Cu(II) in a solution of 0.1 M NH₃ + 0.1 M NaClO₄. In this medium, the equilibria shown in Fig. 1 exist.

The formation of Cu(NH₃)₂⁺ stabilizes the Cu(I) oxidation state as compared to the aquo Cu(I) complex, and makes it possible to observe the stepwise reductions

Cu(NH₃)₂⁺ + e⁻ → Cu(NH₃)⁺ + 2NH₃ (1)
Cu(NH₃)⁺ + e⁻ → Cu(0) + 2NH₃ (2)

which cannot be seen in non-complexing media. All the solution species in Eq. (1) and Eq. (2) can be reduced to upd copper. Previously used techniques are inadequate to address the complexity of this upd process. Fig. 2 summarizes possible mechanistic paths leading to the production of upd copper in this solution. Furthermore, as will be seen below, some possible reactions occur at potentials close to the upd process. A further complication involves the gold substrate oxidation and reduction processes [9].

Clarifying the details of the electrode surface processes occurring in this system becomes highly unlikely using cyclic voltammetry, the commonly used electrochemistry technique. Even the more powerful RRDE approach, by itself, is not sufficiently powerful. However, by combining the RRDE, EQCM and TOF-SIMS techniques, we can get a comprehensive view of the copper upd process at gold in ammonia medium.

The RRDE gives, as a function of electrode potential, information about the oxidation state and surface coverage of the various species deposited on the working electrode. It also provides quantitative information about soluble species formed at any potential. The EQCM gives the charge consumed and how much mass deposited as a function of potential. TOF-SIMS provides additional information about the elemental composition of the surface that can validate the EQCM and RRDE studies. The complementary information provided by these three techniques uniquely identifies the...
Table 1
Summary of possible phenomena at RRDE and EQCM in Cu(upd) formation when stepping disk electrode potential from +0.6 to −0.4 V

<table>
<thead>
<tr>
<th>Process</th>
<th>$\mu^a_{\text{equiv}}/g$ equiv$^{-1}$</th>
<th>$E_{\text{ring}} = −0.4$ V</th>
<th>$E_{\text{ring}} = +0.4$ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(NH$_3$)$<em>4^{2+}$ + 2e$^−$ → Cu$</em>{\text{upd}}$ + 4NH$_3$</td>
<td>+63.5</td>
<td>Shielding</td>
<td></td>
</tr>
<tr>
<td>(i) Cu(NH$_3$)$_4^{2+}$ + e$^−$ → Cu(NH$_3$)$_2^{2+}$ + 2NH$_3$</td>
<td>0</td>
<td>Shielding</td>
<td>Collection</td>
</tr>
<tr>
<td>(ii) Cu(NH$_3$)$<em>4^{2+}$ + e$^−$ → Cu$</em>{\text{upd}}$ + 2NH$_3$</td>
<td>+63.5</td>
<td>Shielding</td>
<td></td>
</tr>
<tr>
<td>(i) Cu(NH$_3$)$_2^{2+}$ → Cu(NH$<em>3$)$</em>{\text{ads}}^{2+}$</td>
<td>+131.5</td>
<td>Shielding</td>
<td></td>
</tr>
<tr>
<td>(ii) Cu(NH$_3$)$<em>2^{2+}$ + 2e$^−$ → Cu$</em>{\text{upd}}$ + 4NH$_3$</td>
<td>−34</td>
<td>Shielding</td>
<td></td>
</tr>
<tr>
<td>(i) Cu(NH$_3$)$_4^{2+}$ + e$^−$ → Cu(NH$<em>3$)$</em>{\text{ads}}^{2+}$ + 2NH$_3$</td>
<td>+131.5</td>
<td>Shielding</td>
<td></td>
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<td>Shielding</td>
<td></td>
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<td>Shielding</td>
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<td>−34</td>
<td>Shielding</td>
<td></td>
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<tr>
<td>(i) Cu(NH$_3$)$_4^{2+}$ + e$^−$ → Cu(NH$<em>3$)$</em>{\text{ads}}^{2+}$</td>
<td>+97.5</td>
<td>Shielding</td>
<td></td>
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<tr>
<td>(ii) Cu(NH$_3$)$<em>2^{2+}$ + e$^−$ → Cu$</em>{\text{upd}}$ + 2NH$_3$</td>
<td>−34</td>
<td>Shielding</td>
<td></td>
</tr>
</tbody>
</table>

* Equivalent mass is preceded by a ‘+’ or a ‘−’ to indicate increase or decrease of mass.

coverage, oxidation state, and stoichiometry of surface species produced during the upd process.

2. Experimental

2.1. Reagents

A stock solution of cupric perchlorate was prepared by dissolving cupric oxide with 0.9 M perchloric and diluting it by a factor of 10. Its concentration was determined to be 0.1055 M by electrodeposition at constant current. This stock solution was diluted with the supporting electrolyte, 0.1 M NH$_3$ + 0.1 M NaClO$_4$, to produce either a $2 \times 10^{-4}$ M or a $2 \times 10^{-3}$ M Cu(NH$_3$)$_4^{2+}$ solution.

2.2. Experimental protocol

2.2.1. TOF-SIMS

TOF-SIMS experiments were carried out on the following samples.

2.2.1.1. Reference. One of the evaporated gold electrodes on a 10-MHz AT cut quartz crystal (of the sort...
Fig. 6. Current–potential (I–E) curve at a scan rate of 200 mV s\(^{-1}\). \(c_{\text{Cu(II)}} = 1.67 \times 10^{-3}\) M in 0.1 M NH\(_3\) + 0.1 M NaClO\(_4\). Solid line: first scan; dashed line: second scan.

Fig. 8. Mass–time (\(\Delta m–t\)) curves. Curve a: potential step from +0.6 to −0.4 V. Curve b: potential step from −0.4 to +0.6 V. \(c_{\text{Cu(II)}} = 3.5 \times 10^{-3}\) M in 0.1 M NH\(_3\) + 0.1 M NaClO\(_4\). Rinsed with deionized water. Then a TOF-SIMS spectrum was immediately obtained.

used for the EQCM experiments) was held at potential −0.1 V for 30 min in the ammoniacal electrolyte. It was then emersed from solution under potential control and rinsed with deionized water and a TOF-SIMS spectrum was immediately obtained.

2.2.1.2. Treated sample. Cu(ClO\(_4\))\(_2\) (0.1 M) was injected into the electrolyte to make the concentration of Cu(II) 2 mM. Nitrogen was bubbled through the solution both to remove oxygen and to mix it. The same reference gold electrode used in the blank experiment was introduced into the solution, held at −0.1 V for 30 min, emersed from solution under potential control and rinsed with deionized water. Then a TOF-SIMS spectrum was immediately obtained.

2.2.2. RRDE

The rotating gold disk–gold ring electrode had the following dimensions: disk electrode radius (\(R_1\)) = 0.3010 cm; ring electrode inner radius (\(R_2\)) = 0.3150 cm; and ring electrode outer radius (\(R_3\)) = 0.4055 cm. These geometric quantities yield the following theoretical values for the collection efficiency (\(N_c\)) = 0.4037, \(\beta^{2/3} = 1.190\). The gold electrode roughness factor was 2.8 [10].

Fig. 7. Scan rate effects on cathodic peaks and anodic peaks. Plot of \(I/r^{1/2}\) vs. \(v^{1/2}\).

Fig. 9. Mass–charge (\(\Delta m–Q\)) Curve. \(c_{\text{Cu(II)}} = 1.67 \times 10^{-3}\) M in 0.1 M NH\(_3\) + 0.1 M NaClO\(_4\); scan rate, 50 mV s\(^{-1}\).
Cu(I) detects cuprous ions by means of the oxidation reaction, reduction reactions, Cu(II) electrode detects both Cu(II) and Cu(I) by means of two reaction, Cu(II) electrode detects cupric ions by means of the reduction three ring potentials were used. 

The ring electrode can be detected by potentiostating the ring electrode current. Also, at this potential, Au(I) can be detected by choosing the appropriate ring electrode. Since neither Cu(I) nor Au(III) are present in the solutions we used, all Cu(I) and Au(III) detected must have been produced by some disk electrode process.

2.2.2.1. \( E_{\text{ring}} = 0.4 \) V. At this potential the ring electrode detects cuprous ions by means of the oxidation reaction, Cu(I) → Cu(II) + e\(^-\), that produces an anodic ring electrode current. Also, at this potential, Au(I) can be detected at the ring electrode by oxidizing it to Au(III). Since neither Cu(I) nor Au(III) are present in the solutions we used, all Cu(I) and Au(III) detected must have been produced by some disk electrode process.

2.2.2.2. \( E_{\text{ring}} = -0.4 \) V. At this potential, the ring electrode detects cupric ions by means of the reduction reaction, Cu(II) + e\(^-\) → Cu(I). Thus, disk electrode processes that consume Cu(II) will decrease the ring current (shielding), while disk processes that generate Cu(II) will increase the ring current (collection). Cu(I) is ‘invisible’ at this potential.

2.2.2.3. \( E_{\text{ring}} = -0.8 \) V. At this potential the ring electrode detects both Cu(II) and Cu(I) by means of two reduction reactions, Cu(II) + 2e\(^-\) → Cu(0) and Cu(I) + e\(^-\) → Cu(0), respectively. Thus, processes that consume Cu(II) or Cu(I) (reduction, or adsorption on the electrode) will cause shielding. Processes that produce Cu(II) and Cu(I) (oxidation of Cu(I) or Cu(0)) will produce collection. The ring electrode also detects Au(III) and Au(I) by reducing both to gold.

Adsortion or desorption of a copper species at the disk electrode, without any faradaic process, will produce shielding or collection of that particular species that can be detected by choosing the appropriate ring electrode potential. These processes can occur at any stage in a potentiodynamic experiment (i.e. cyclic voltammogram) because of the prior potential history of the electrode.

### Table 2

<table>
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<tr>
<th>Scan rate/mV s(^{-1})</th>
<th>( E/V )</th>
<th>( \mu_{\text{equiv}}^a/g) equiv(^{-1})</th>
<th>( E/V )</th>
<th>( \mu_{\text{equiv}}^a/g) equiv(^{-1})</th>
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<th>( \mu_{\text{equiv}}^a/g) equiv(^{-1})</th>
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<tr>
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<tr>
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<td>to</td>
<td>+0.42</td>
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</tbody>
</table>

* Equivalent mass is preceded by a ‘+’ or a ‘−’ to indicate increase or decrease of mass.

Electroactive species generated at the disk electrode surface can be detected by potentiostating the ring electrode at an appropriate potential. In this system, three ring potentials were used.

2.2.3. EQCM

2.2.3.1. Potential scan experiments. In these experiments, current (charge) and mass potential curves were obtained. Under some conditions, mixtures of diffusion-controlled and surface-controlled processes happened. These electrochemical peak current data were treated as follows. We assumed that the observed gold electrode peak currents (\( I_p \)) were the sums of three components. These are (1) faradaic diffusion currents (\( I_d \)) that are proportional to the square root of the scan rate (\( v^{1/2} \)) and bulk concentration (\( c^b \)), (2) surface faradaic processes (\( I_s \)) and (3) double layer charging currents (\( I_d \)) that are proportional to the scan rate. These assumptions give Eq. (3)

\[
I_p = k_eq^b + (k_s + k_d)v^{1/2}
\]

in which the subscripts for the constants represent diffusion, d, surface faradaic processes, s, and double layer charging, dl, currents. Eq. (3), that predicts a plot of \( I_p/v^{1/2} \) versus \( v^{1/2} \), should be linear and permits us to identify the diffusion and surface components of the peak currents.

Under linear potential scan conditions, the change of mass with potential is proportional to the change of mass with time, that is in turn proportional to the current. Consequently, the instantaneous slope \( d\Delta m/dt \propto I \). When this relationship holds, one participant in the electrochemical reaction must be a surface immobilized species. An analogous relationship exists between \( \Delta q \) and \( \Delta m \).
2.2.4. Combining EQCM and RRDE experimental protocols

The potential step method, as described in Cadle and Bruckenstein’s paper [11], was used. This method requires the deposition process to be convective–diffusion controlled. Let us explain the approach by considering a Cu(II) solution in an ammonia electrolyte. Assume that the disk electrode potential is jumped from a potential at which there is no disk current to one at which the reactions shown in Fig. 3 occur during the time \( t \leq \tau \) of upd and adsorption, while the reaction

\[
\text{Cu(NH}_3\text{)}_2^{2+} + e^- \rightarrow \text{Cu(NH}_3\text{)}_2^{+} + 2\text{NH}_3 \quad t > \tau
\]  

(4)

occurs after the completion of upd and adsorption at \( t > \tau \).

As discussed above, RRDE and EQCM data by themselves cannot unequivocally yield the molar mass of a copper adsorbate. This is because the charge measured by both techniques contains unknown contributions from electrode processes not involving the copper species. However, the actual consumption of Cu(II) at the disk during an RRDE experiment can be determined from the shielding at the ring electrode (see shielding charge, RRDE experiments in Table 1). Note that at a constant ring electrode potential there are no steady-state ring double layer charging or surface process currents. Consequently, the oxidation state and molar mass \( \left( \mu_{\text{molar}} \right) \) of any copper adsorbates can be found combining RRDE \( (\Delta q_{\text{ring}}, \text{change in ring charge}) \) and EQCM \( (\Delta m, \text{change in disk mass}) \) data.

We employ the fundamental definition of the RRDE collection efficiency \( (N = \text{the ratio of the ring flux to the disk flux}) \) and Faraday’s law to obtain the expression we use with RRDE and EQCM data to find molar masses:

\[
\mu_{\text{molar}} = \pm \frac{\Delta m z_{\text{ring}} FN}{\Delta q_{\text{ring}}}
\]  

(5)

In Eq. (5), \( z_{\text{ring}} \) is the number of electrons per mole of copper species involved in the ring electrode process.

### 3. Results and discussion

#### 3.1. RRDE experiments

3.1.1. Disk potential jumps from +0.6 to −0.34 V

The gold disk electrode of the RRDE was oxidized at +0.6 V for 5 min in 0.1 M NH₃ + 0.1 M NaClO₄ supporting electrolyte containing \( 2 \times 10^{-5} \) M Cu(II) before stepping it to −0.34 V. The transient disk current (Fig. 4, curve a) and ring currents obtained at \( E_{\text{ring}} = -0.4 \) V and \( E_{\text{ring}} = +0.4 \) V (Fig. 4, curves b and c) were recorded. The transient disk current contains contributions from double layer charging, gold oxide reduction, and non-steady-state convection–diffusion reduction of Cu(NH₃)₄²⁺ to an adsorbate.

The disk current decreases rapidly after the potential step from +0.6 to −0.4 V, until, after 13 s, either the upd process

\[
\text{Cu(NH}_3\text{)}_2^{2+} + 2e^- \rightarrow \text{Cu(upd)} + 4\text{NH}_3 \quad t \leq 13 \, \text{s}
\]  

(6)

or an adsorption process such as

\[
\text{Cu(NH}_3\text{)}_2^{2+} + e^- \rightarrow \text{Cu(NH}_3\text{)}_4^{+} - x(\text{I})_{\text{ads}} + x\text{NH}_3 \quad t \leq 13 \, \text{s}
\]  

(7)

is completed. Then, as shown by the ring current collection at \( E_{\text{ring}} = +0.4 \) V, the disk current reaches the limiting convection–diffusion-controlled reduction process

\[
\text{Cu(NH}_3\text{)}_2^{2+} + e^- \rightarrow \text{Cu(NH}_3\text{)}_2^{+} + 2\text{NH}_3 \quad t > 13 \, \text{s}
\]  

(8)

The ring current transient at \( E_{\text{ring}} = -0.4 \) V (shown in Fig. 4, curve b) exhibits a small collection peak, followed by decrease in the ring current to a value that corresponds to complete shielding. It remained at this value throughout the experiment; accordingly, the surface concentration of Cu(II) at the disk electrode became zero because of either reactions (6), (7) and/or (8). Some soluble Au(III) species are generated during the reduction processes on changing disk electrode potential from +0.6 to −0.34 V [10]. Consequently, we

#### Table 3

<table>
<thead>
<tr>
<th>Region</th>
<th>Cathodic process</th>
<th>Potential range/V (( e = 10 ) mV s⁻¹)</th>
<th>Reaction</th>
<th>( \mu_{\text{equiv}}/g ) equiv⁻¹</th>
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<td>(1) Gold oxide reduction</td>
<td>+0.6 to +0.05</td>
<td>( \text{AuO-(H}<em>2\text{O)}</em>{\text{ads}} + 2e^- + \text{H}_2\text{O} \rightarrow \text{Au-(H}<em>2\text{O)}</em>{\text{ads}} + 2\text{OH}^- ) (3.1)</td>
<td>8.0</td>
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<td>(2) Gold amine reduction</td>
<td></td>
<td>( \text{AuNH}_2\text{-}(\text{H}<em>2\text{O)}</em>{\text{ads}} + e^- + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{Au-(H}<em>2\text{O)}</em>{\text{ads}} + \text{OH}^- ) (3.2)</td>
<td>16</td>
</tr>
<tr>
<td>BC</td>
<td>Cu upd formation</td>
<td>+0.05 to −0.13</td>
<td>( \text{Cu(NH}_3\text{)}_2^{2+} + 2e^- \rightarrow \text{Cu(upd)} + 4\text{NH}_3 ) (3.3)</td>
<td>31.8</td>
</tr>
<tr>
<td>CD</td>
<td>Solution reaction</td>
<td>−0.13 to −0.46</td>
<td>( \text{Cu(NH}_3\text{)}_2^{2+} + e^- \rightarrow \text{Cu(NH}_3\text{)}_2^{+} + 2\text{NH}_3 ) (3.4)</td>
<td>0</td>
</tr>
<tr>
<td>DE</td>
<td>Bulk Cu deposition</td>
<td>−0.46 to −0.66</td>
<td>( \text{Cu(NH}_3\text{)}_2^{2+} + 2e^- \rightarrow \text{Cu(bulk)} + 4\text{NH}_3 ) (3.5)</td>
<td>31.8</td>
</tr>
<tr>
<td>EF</td>
<td>Bulk Cu deposition</td>
<td>−0.66 to −0.8</td>
<td>( \text{Cu(NH}_3\text{)}_2^{2+} + 2e^- \rightarrow \text{Cu(bulk)} + 4\text{NH}_3 ) (3.6)</td>
<td>31.8</td>
</tr>
<tr>
<td>FG</td>
<td>Bulk Cu deposition</td>
<td>−0.8 to −0.42</td>
<td>( \text{Cu(NH}_3\text{)}_2^{2+} + 2e^- \rightarrow \text{Cu(bulk)} + 4\text{NH}_3 ) (3.7)</td>
<td>31.8</td>
</tr>
</tbody>
</table>

* Equivalent mass is preceded by a ‘+’ or a ‘−’ to indicate increase or decrease of mass.
Table 4
Mechanisms for the anodic processes

<table>
<thead>
<tr>
<th>Region</th>
<th>Process</th>
<th>Potential range/V (t = 10 mV s⁻¹)</th>
<th>Reaction</th>
<th>( \mu_{\text{equiv}}/\text{g equiv}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>GH</td>
<td>Stripping bulk Cu to Cu(I)</td>
<td>−0.42 to −0.2</td>
<td>Cu(bulk) + 2NH₃ → Cu(NH₃)₂⁺ + e⁻ (4.1)</td>
<td>−63.5</td>
</tr>
<tr>
<td>HI</td>
<td>Solution reaction</td>
<td>−0.2 to 0.0</td>
<td>Cu(NH₃)₂⁺ → Cu(NH₃)₂⁺ + e⁻ (4.2)</td>
<td>0</td>
</tr>
<tr>
<td>IJ</td>
<td>Stripping bulk Cu to Cu(II) and upd Cu to Cu(II)</td>
<td>0.0 to +0.24</td>
<td>Cu(bulk) + 4NH₃ → Cu(NH₃)₂⁺ + 2e⁻ (4.3)</td>
<td>−31.8</td>
</tr>
<tr>
<td>JK and KL</td>
<td>(1) Continuously stripping upd Cu</td>
<td>+0.24 to +0.4</td>
<td>Cu(upd) + 4NH₃ → Cu(NH₃)₂⁺ + 2e⁻ (4.4)</td>
<td>−31.8</td>
</tr>
<tr>
<td></td>
<td>(2) Au surface oxidation</td>
<td>+0.4 to +0.6 to +0.05</td>
<td>Cu(upd) + 4NH₃ → Cu(NH₃)₂⁺ + 2e⁻ (4.4)</td>
<td>−31.8</td>
</tr>
<tr>
<td></td>
<td>(3) NH₃ oxidation</td>
<td>(1) Au-(H₂O)ads + 2OH⁻ → AuO-(H₂O)ads + 2e⁻ + H₂O (4.5)</td>
<td>0.05</td>
<td>+8.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2) NH₃ + Au-(H₂O)ads + OH⁻ → AuNH₂-(H₂O)ads + e⁻ + H₂ (4.6)</td>
<td></td>
<td>+17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3) NH₃ + 3OH⁻ → 1/2N₂ + 3H₂O + 3e⁻ (4.7)</td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

*Equivalent mass is preceded by a ‘+’ or a ‘−’ to indicate increase or decrease of mass.

assign the initial, small ring collection peak when \( E_{\text{ring}} = −0.4 \) V, to the reduction of this soluble Au(III) species. After correction for charge associated with the reduction of the gold surface, \( \Delta q_{\text{ring}} \) was 62 µC cm⁻². At \( E_{\text{ring}} = −0.4 \) V, \( \tau_{\text{ring}} = 1 \) since Cu(II) is reduced to Cu(I), and all values other than \( \Delta m \) in Eq. (9) are now known. An analogous EQCM experiment that yielded the value of \( \Delta m \) is given in Section 3.2.3 (below), and the \( \mu \) is calculated there.

Fig. 4, curve c, for which \( E_{\text{ring}} = +0.4 \) V, shows that no Cu(I) escapes from the disk electrode until \( t \geq \tau \), presumably the time the electrode surface coverage with adsorbates has reached equilibrium. Since Cu(II) is consumed quantitatively at the disk (the shielding result), while no Cu(I) escapes from the disk during the interval \( t < \tau \), either Cu(0) is deposited at underpotential or Cu(I) is adsorbed, or both are occurring.

3.1.2. Disk potential jump from −0.34 to −0.8 V

Suppose the disk electrode is covered with Cu(I)ads at −0.34 V. Then, on jumping the disk potential from −0.34 to −0.8 V, we would expect to see a charge corresponding to the reduction of Cu(1)ads to Cu(0). However, this experiment produced a total charge of only 37.6 µC. This charge hardly differs from the charge, 36 µC, found for the same potential jump done in a copper-free solution. Consequently, this electrochemical result is best understood if the adsorbate formed at the disk electrode at −0.34 V consists only of upd Cu(0). Additional electrochemical and TOF-SIMS experiments, reported below, confirm this conclusion.

3.1.3. Disk potential jump from −0.40 to 0 V

After the disk electrode surface had reached equilibrium at −0.40, it was producing soluble Cu(I) species. Then, its potential was jumped to 0.0 V while holding the ring potential at −0.4 V. At this disk potential, copper species adsorbed on the disk electrode are oxidized from it as soluble, ionic copper species.

![Fig. 10. TOF-SIMS difference spectra of sample. Difference between a gold electrode held at −0.1 V in \( c_{\text{Cu(II)}} = 1.67 \times 10^{-3} \) M + 0.1 M NH₃ + 0.1 M NaClO₄ and the corresponding blank without \( c_{\text{Cu(II)}} \).](image1)

![Fig. 11. TOF-SIMS depth profile for a gold electrode held at −0.1 V in \( c_{\text{Cu(II)}} = 1.67 \times 10^{-3} \) M + 0.1 M NH₃ + 0.1 M NaClO₄. Curve a: Cs⁺ sputtering for longer sputtering times. Curve b: Cs⁺ sputtering for shorter times.](image2)
Also, disk electrode oxidation is not important. At the chosen ring electrode of potential $-0.4$ V, Cu(II) produced at the disk electrode can be detected by reduction to Cu(0). Therefore, we determined both the ring electrode reduction charge, $Q_{\text{ring}}$, corresponding to the disk electrode oxidation charge, $Q_{\text{disk}}$, and found $Q_{\text{ring}} = 44.6$ $\mu$C and $Q_{\text{disk}} = 230$ $\mu$C.

These two charges are related via the relationship $Q_{\text{disk}} = (n_{\text{disk}}/n_{\text{ring}})(Q_{\text{ring}}/N)$. Since $n_{\text{ring}} = 1$, we calculate $n_{\text{disk}} = 2.08$. In other words, a ring electrode charge that is only half the disk charge reduces the species produced by oxidizing the adsorbate from the disk electrode. Since the ring electrode reaction is a one-electron process ($\text{Cu(II)} + e^- \rightarrow \text{Cu(I)}$), the disk electrode oxidation reaction must be the two electron oxidation of upd copper, i.e. Cu(upd) + 2e$^- \rightarrow \text{Cu(II)}$.

3.2. EQCM experiments

3.2.1. Cyclic voltammetry

Fig. 5, curves a and b, show the cyclic current–potential ($I$–$E$) and mass–potential ($\Delta m$–$E$) curves obtained during an EQCM experiment using 1.67 mmol/l Cu(II) in the ammoniacal electrolyte. The $\Delta m$–$E$ curve shows that the mass slowly decreases during the scan from +0.6 to 0.0 V; in this potential region AuO and AuNH$_2$ formed at +0.6 V, are reduced in Cu(II)-free electrolyte [9]. Then the mass increases from 0.0 to
- 0.4 V. This mass increase corresponds to upd Cu(0) deposition. At potentials more negative than -0.4 V, the mass increased sharply because bulk copper deposited.

There is an obvious difference between the first and second J-E scans. Three cathodic peaks (A, B, C) exist in the first current–potential scan at a scan rate of 50 mV s⁻¹. However, peaks A and peak B merged after the first potential scan. When scan rates are very fast, e.g. 200 mV s⁻¹, there are only two cathodic peaks even in the first scan, peak A (sum of peak A and peak B) and peak C, as shown in Fig. 6. The larger peak current and the more positive peak potential for peak A’ in the first scan characterize the difference among the first and subsequent scans. Peak C’s peak current height and peak potential do not change.

The current of Peak A’ is the sum of three surface reduction processes, namely gold surface oxide reduction, gold surface nitrogen compound reduction and upd Cu formation. The first two processes depend on how long the gold electrode is oxidized at +0.60 V. The electrode is held +0.6 V for 5 min only before the first potential scan. Accordingly, it is at oxidizing potentials for a shorter time during the second potential scan. Therefore, Peak A has the greatest contribution from these two surface oxidation processes in the first potential scan. Peak C is the bulk Cu deposition process, and is not affected by the time spent at oxidizing potentials.

3.2.2. Effect of potential scan rate

A plot of I vs. v produces straight lines with zero intercept for peak A (the reduction of the oxidized gold surface), confirming that it corresponds to a surface process. The same plot for peak G shows straight line with non-zero intercept because of the contribution of oxidation of a small amount of ammonia. Fig. 7 shows I versus v¹/² plots for peaks C, B, D + E, and F. Peak B (copper upd deposition), peak F (stripping of upd copper) and peak (D + E) (stripping bulk copper) show diffusion-controlled behavior. All the peak current data fit the predictions from Eq. (3).

3.2.3. Potential jump experiments

EQCM experiments analogous to the RRDE potential jump experiments described in Section 3.1 were done. Using a range of Cu(II) concentrations, potentials were jumped from +0.6 to 0.0 or -0.4 V in the 0.1 M NH₃–0.1 M NaClO₄ supporting electrolyte. Mass transients were recorded. No differences in the limiting mass response were found in any experiments after the Cu(II) concentration reached 3 × 10⁻³ M, i.e. saturation coverage was achieved. At shorter times, the limiting mass response was reached earlier using the higher concentrations of Cu(II).

Fig. 8 shows the Δm vs. t curve obtained when jumping the potential from +0.6 to -0.4 V in a 3.5 mM Cu(II) solution. An initial small decrease of mass corresponding to reduction of the oxidized gold surface was followed by a mass increase, reaching a steady-state value of 116 ng cm⁻². This result was combined with the charge data of Q_{ring} = 62 µC cm⁻² when E_{ring} = -0.4 V obtained in the analogous RRDE experiment and substituted into Eq. (5) to give μ = 73 g mol⁻¹. The molar mass of the adsorbate existing at -0.4 V was determined also by jumping potential from -0.4 to 0 V to desorb it. This experiment gave Δm = 106 ng cm⁻², and Q_{ring} = 59.4 µC cm⁻², so that μ = 69.5 g mol⁻¹.

EQCM experiments alone were done to find the molar mass of the adsorbate. In one experiment, the potential was jumped from -0.4 to 0.0 V, conditions in which no significant mass change occurs in a Cu(II)-free supporting electrolyte. Both the charge and mass change were recorded. The electrode’s roughness factor was irrelevant because both charge and mass change were determined at the same electrode. We found that Δm = 82 ng and Q = 256 µC. In a blank experiment in Cu(II)-free supporting electrolyte, Δm = 19 ng and Q = 53 µC. Using these values to correct for the blank charge and mass changes, the molar mass of the adsorbate was calculated to be 68 g mol⁻¹. Consequently, we conclude the primary reaction forming the adsorbate at -0.4 V involves a soluble Cu(II) species, and is

\[
\text{Cu(NH}_3\text{)}_2^{2+} + 2e^- \rightleftharpoons \text{Cu(0)upd} + 4\text{NH}_3 \tag{9}
\]

All three methods gave experimental molar masses ~10% higher than the value of 63.5 g mol⁻¹ predicted by Eq. (9) for upd Cu. We believe this to be due to small changes in double layer structure not accounted for by the various blank corrections. The blank experiments differ from the upd ones in that no upd copper is ever present.

3.2.4. EQCM study explaining equivalent mass values at different potential

Fig. 9 is the Δm–Q plot obtained for 1.67 mmol/l Cu(ClO₄)₂ in 0.1 M NaClO₄ + 0.1 M NH₃ electrolyte, using cyclic voltammetry at a scan rate of 50 mV s⁻¹. Three slopes in the negative scan and two in the positive scan can be seen. From these slopes, we can obtain the equivalent masses (μ_{equiv} = μ_{molar}/z) of the surface and solution processes.

Table 2 lists the equivalent masses found for 1.5 mM Cu(II) in 0.1 M NaClO₄ + 0.1 M NH₃ electrolyte at different potential scan rates and directions over different potential ranges. There is only a small charge difference between the anodic and cathodic process. This is in contrast to what is observed in Cu(II)-free electrolyte where there is substantial charge difference due to the reaction.
NH$_3$ + 3OH$^-$ → 1/2N$_2$ + 3H$_2$O + 3e$^-$ (10)

This difference suggests that copper upd permanently affects the gold electrode surface even after all the upd copper appears to have been stripped. We suggest two possible reasons. First, trace amounts of upd copper remain, and poison the ammonia oxidation process. Second, the upd copper deposition and stripping process changes the principle crystallographic faces present in the surface of the gold to ones that are not catalytic for the ammonia oxidation processes.

Table 3 gives the detailed mechanism of the upd process for Cu in 0.1 M NH$_3$ + 0.1 M NaClO$_4$ we propose based on the $\mu$$_{equiv}$ values given in Table 2.

Process AB is the reduction of the gold substrate via reactions (3.1) and (3.2). When the scan rate is very fast, i.e. 200 mV s$^{-1}$, the first process, reaction (3.1) predominates. At the slower scan rates of 10 mV s$^{-1}$, the second process, reaction (3.2), predominates, as shown in Table 2.

Process BC is mainly the Cu(II) underpotential deposition reaction. However, at fast scan rates, reaction (3.2) still occurs in the potential region where process BC takes place. This causes the experimental $\mu$$_{equiv}$ values in Table 2 to be smaller than the theoretical value of 31.8. The slower the scan rates, the closer the experimental $\mu$$_{equiv}$ values approach the theoretical result.

Process CD is the reduction of copper(II) ammonia complex in solution to the copper(I) complex. This reaction can be separated from other reactions at slow scan rates. Then process BC that forms upd copper will be completed before the potential reaches the reduction potential of reaction (3.4). When the scan rate is fast, upd formation in process BC is not completed before reaching the potential at which the CD process occurs. Under these conditions, the current response is the sum of contributions from reactions (3.3) and (3.4). Consequently, the charge is a sum for these two reactions and this produces smaller experimental values of $\mu$$_{equiv}$.

Processes DE, EF, and FG are bulk copper deposition processes that occur at different polycrystalline gold sites. They manifested themselves by the slight changes of $\mu$$_{equiv}$ slopes in the Q–Am curves shown in Fig. 8. Scan rates do not affect these processes as long as the rate of nucleation is fast, as is the case here.

The anodic mechanism of stripping upd Cu in 0.1 M NH$_3$ + 0.1 M NaClO$_4$ is listed in Table 4. Process GH is stripping of bulk Cu to a cuprous ammonia complex, and process HI is the oxidation of the cuprous ammonia complex in the diffusion layer formed in process GH to cupric ammonia complex. Process IJ is the continued stripping of bulk Cu to cupric ammonia complex. The stripping of upd copper to the soluble copper(II) ammonia complex starts at the end of potential region IJ and finishes in the JK potential range.

Process KL shows a very small mass increase that is accompanied by a big charge increase caused by the oxidation of the gold electrode and a small amount of ammonia to nitrogen.

3.2.5. TOF-SIMS studies of copper upd

The TOF-SIMS positive ion spectra obtained at the treated gold electrode potentiostated at $-0.1$ V, and the corresponding reference electrode were normalized with respect to the Au$^+$ intensity. Their difference spectrum is given in Fig. 10. There are two Cu isotope peaks at $m/z$ = 63 and 65, with a ratio of ~2, proving the presence of copper in the surface, either as upd copper or an adsorbed cupric or cuprous ion. No signal was found in Fig. 10 at the $m/z$ value for adsorbed Cu(NH$_3$)$_2$$^{2+}$ ($m/z$ = 131, 133) and Cu(NH$_3$)$_2$$^{+}$ ($m/z$ = 97, 99). These results confirmed that no adsorbed Cu(NH$_3$)$_2$$^{2+}$ or Cu(NH$_3$)$_2$$^{+}$ species exist on the gold surface in upd copper region. The blank spectrum contained more peaks in the $m/z$ range 0–150 than the sample held at $-0.1$ V because the amount of surface contamination at a upd copper surface is less than at a clean gold surface.

Fig. 11 gives the TOF-SIMS Cu$^+$ intensity ($m/z$ = 63) as a function of time for a gold electrode held at $-0.1$ V using Cs$^+$ primary ion sputtering. Experiment 1 is the depth profile at longer sputtering times and Experiment 2 is the depth profile at shorter sputtering times. Initially the Cs$^+$ primary ion only bombarded the surface copper upd layer and there was a steep decrease of Cu$^+$ intensity with time. When the sputter front reached the Cu$|$Au interface, the copper that was sputtered decreased. However, mixing of Cu and Au now occurred, leading to slower copper removal, as reflected in the very slow decrease of Cu$^+$ intensity with time. Even at longer sputtering times, the Cu$^+$ intensity does not reach zero, because of the ‘knock in’ effect.

4. Conclusions

Parallel use of three techniques, RRDE, EQCM and TOF-SIMS, to study the Cu upd process at gold in the ammoniacal electrolyte showed that Cu(NH$_3$)$_2$$^{2+}$ diffuses to the electrode surface where it is reduced to upd copper atoms. Four NH$_3$ molecules are released in the potential range $-0.4$ V $< E < 0.1$ V. No adsorbed ionic copper species are detected during this process. The detailed mechanism we propose is shown in Fig. 12.

Acknowledgements

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References