An EQCM Study of the Electrochemical Copper(I)/Copper(II)/Copper System in the Presence of PEG and Chloride Ions

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The charge-transfer reaction between copper(II) and copper is studied in electrolytes that are similar to galvanic copper baths, 2.2 M H$_2$SO$_4$ + 0.3 M CuSO$_4$ + chloride ions (c$_{Cl^-}$ ≤ 1 × 10$^{-2}$ M), and polyethylene glycol 1500 (PEG, c$_{PEG}$ ≈ 4 × 10$^{-5}$ M). Electrochemical quartz crystal microbalance (EQCM) measurements are conducted, mainly under conditions of cyclic voltammetry. The formation and dissolution of CuCl on the electrode surface at c$_{Cl^-}$ ≥ 2 mM is demonstrated, a notable shift of the pseudo-equilibrium potential associated with CuCl deposition is analyzed, and the inhibition of the charge-transfer reaction by the PEG/CuCl$_2$ surface layer is characterized. It is shown that the inhibiting layer forms by reaction between the adsorbate-covered copper electrode and PEG, i.e., neither Cu$^+$ nor Cu$^{2+}$ from the electrolyte are required. Numerical simulations of the processes as well as parallel experiments conducted with electrolytes not containing Cu(II) support the proposed mechanisms, in particular the role of the intermediate Cu$^+$.© 2003 The Electrochemical Society. [DOI: 10.1149/1.1602083] All rights reserved.

The use of galvanic copper deposits in the field of nanotechnology has aroused new interest in the mechanism of the electrochemical Cu(II)/Cu$_{metal}$ reaction, in particular in acid baths.1 Acid galvanic copper deposition baths contain H$_2$SO$_4$ + CuSO$_4$ in high concentrations. Traditionally, additives are added to the electrolyte at concentrations of up to a few millimoles per liter.2,9 In particular, chloride ions and polyethylene glycol (PEG) are known to act synergistically in improving the performance of the galvanic baths and the properties of the deposit.

In previous publications we studied phenomena resulting from chloride and bromide additions to the H$_2$SO$_4$ + CuSO$_4$ electrolyte.4,7 In the present work this investigation is extended to study the effects of adding PEG to the electrolyte in the presence and in absence of halide ions.

The added PEG adsors on the copper electrode. As long as the solution is free of halide, the adsorbed PEG only moderately affects the interfacial capacitance8,9 as well as the rate of charge-transfer reactions.10 The attenuation of the charge-transfer current can be explained as a rise in effective current density resulting from the reduction of active surface area (on the microscopic scale) by the adsorbed long-chain molecules, see the discussion for straight-chain carboxylic acids by Chu and Sukova.11,12

When both PEG and chloride are present, a surface layer forms on the copper electrode that constitutes a barrier for charge transfer.1,3,8,9,12,14 Yokoi et al. propose that the surface layer consists of Cu-Cl structures associated with PEG molecules that act as polydentate ether ligands.13,14 Healy et al. arrived at the conclusion that this CuCl/PEG layer is modified at more negative potentials (near the point of zero charge) such that the organic molecules adsorb directly on the copper electrode.3 This reorganization of the surface layer3,9 appears to resemble a phase transition of a kind that has been discussed recently in the field of nonlinear dynamics, for example, with camphor films.15 While the Cu/CuCl/PEG layer is effective in reducing both the anodic and the cathodic currents of the Cu(II)/Cu reaction, the slopes of the anodic and cathodic Tafel plots remain largely unaffected.3 This indicates that6,20–22 the Cu(II)/Cu$^+$ step is still rate determining.

In the present work we studied the system with the electrochemical quartz crystal microbalance (EQCM). This technique permits simultaneous measurements of charge and mass changes during deposition or dissolution reactions. The basic electrode reaction

\[ Cu^{2+} + 2e^- = Cu_{metal} \quad E_{SME}^{0} = -0.353 \text{ V} \quad [1] \]

leads to the cathodic formation/anodic dissolution of 63.5 g of copper per two Faradays of charge (E$_{SME}$ is the electrode potential relative to the saturated mercocuric sulfate electrode operating in the acidic electrolyte). On the other hand, the following Reaction 2 does not require any net Faradaic charge for copper deposition/dissolution

\[ Cu^{2+} + Cu = 2Cu^{+} \quad pK = 6.2 \quad [2] \]

When the solution contains Cl$^-$ (or Br$^-$, etc.) and the activity of Cu$^+$ ions exceeds the value corresponding to the solubility product $K_s$,

\[ Cu^{+} + Cl^- = CuCl_{solid} \quad K_s = 1.72 \times 10^{-7} \quad [3] \]

CuCl (or CuBr, etc.) precipitates on the electrode surface. Thus, by comparing the current flow with mass change, valuable information on reaction mechanisms, e.g., of the Cu/halide system,22 may be obtained.

The basis for the analysis is the Sauerbrey equation

\[ \Delta m = -sA \Delta f \quad [4] \]

where $\Delta m$ is the mass change of the electrode in grams, $s$ is the sensitivity of the EQCM in gHz$^{-1}$ cm$^{-2}$, $\Delta f$ is the measurable change in resonance frequency, and $A$ is the electrode area.

According to Faraday’s law, an electrochemical current $I$ that is solely due to metal deposition/dissolution leads to a mass change, $\Delta m_1$,

\[ \Delta m_1 = \frac{M}{nF} \Delta q = \frac{M}{nF} \int_{t_1}^{t_2} Idt \quad [5] \]

where $M$ is the atomic mass of the metal, $n$ is the number of electrons exchanged per metal atom, and $\Delta q$ is the electric charge transferred for Faradaic metal deposition/dissolution.

Thus, by integrating the voltammetric current, voltamograms may be obtained. Their comparison with the mass changes measured directly with the EQCM$^7,21,26$ can yield valuable information on the electrochemical processes. Alternatively, if Faraday’s law is applicable, the mass change determined with the EQCM corresponds to a current flow $I_{EQCM}$.
Cyclic voltammograms obtained with a copper electrode in (a) the base electrolyte 2.2 M H₂SO₄ + 0.3 M CuSO₄, (b) after addition of 0.3 g/dm³ PEG = 0.2 mM, (c) after addition of 0.2 mM PEG and 4 mM chloride. Sweep rate, 20 mV/s; electrolyte deaerated with argon; electrode area, 0.28 cm².

**Experimental**

The electrochemical experiments were conducted with conventional potentiostatic equipment. A commercial (Schott, Germany) saturated Hg/Hg₂SO₄ reference electrode, SMSE, has been used throughout the work, and all potentials measured are given with respect to this reference. In the acidic electrolyte $E_{SMSE} = E_{SHE} - 0.69$ V. The electrolytes were prepared with analytical grade reagents and Milli-Q deionized water. The EQCM was described previously. With the HP 4194A impedance analyzer the response of the quartz was analyzed regularly to establish that the damping effect caused by roughening of the copper surface does not affect the mass analysis in a significant way. The 6 MHz quartzes were purchased from KVG, Germany. A central circular area of 6 mm diam was gold plated on both sides of the crystal. On the gold face exposed to the electrolyte a copper layer was deposited electrochemically before each experiment at −0.48 V. The film thickness was approximately 1 μm as determined by integrating the Faradaic current and by the reduction of resonance frequency (EQCM sensitivity, 12.8 ng Hz⁻¹ cm⁻²).

**Results**

The experiments were conducted with an aqueous base electrolyte consisting of 2.2 M H₂SO₄ + 0.3 M CuSO₄, to which PEG of molecular weight 1500 and chloride ions (as HCl) were added. Figure 1 shows a set of typical cyclic voltammograms obtained with (a) the base electrolyte, (b) after addition of 0.3 g/dm³ = 0.2 mM PEG, (c) after both 0.2 mM PEG and 4 mM chloride had been added to the base electrolyte. For the results with only halide see Ref. 5-7. The corresponding EQCM results are represented in Fig. 2 and 3. In these figures calculated mass changes, $\Delta m_{\text{calculated}}$, are included as dashed lines, that were obtained with the currents of Fig. 1 with Eq. 5, with $M = 63.5$ and $n = 2$. Arrows indicate the sweep direction.
The Δm – E curve deviates dramatically from the Δm1 – E curve when the electrolyte contains both added chloride at cCl > 2 mM and PEG, Fig. 3. During the positive scan, at about −0.43 V, the actual mass increases strongly beyond the value expected from the current flow, and it decreases rapidly at about −0.49 V in the negative scan. Similar behavior has been observed previously in absence of PEG. At chloride concentrations cCl > 2 mM a deposit of CuCl was found to form reversibly on the electrode surface, in parallel with the electrochemical Cu(II)/Cu metal reaction. Clearly, under the conditions of Fig. 3 the same type of CuCl deposit forms.

In Fig. 4, the voltammetric current-voltage curves obtained in the presence of both PEG and several chloride concentrations are shown. Note that the apparent equilibrium potentials, i.e., the potentials at which the current/voltage curves cross the zero line, shift to more negative values as the chloride concentration increases. In Fig. 5, excess masses, Δ(Δm) obtained by subtracting Δm1 (derived from the currents of Fig. 4) from the corresponding Δm values, are plotted for three chloride concentrations.

In the experiment of Fig. 6, the copper electrode operates in an electrolyte that contains H2SO4, but not CuSO4. Note that the measured Cu-oxidation/reduction current is identical with IEQCM obtained with n = 2, Eq. 6. This indicates that the Cu(II)/Cu metal reaction proceeds as the only noticeable reaction in the anodic as well as in the cathodic scan. In the very negative potential region a small cathodic current is observed that is not associated with a mass change. This is apparently the onset of hydrogen evolution (note the rather sensitive current scale). In Fig. 7, the experiment of Fig. 6 is repeated in presence of both PEG and chloride in the electrolyte. The chloride concentration is so low that a CuCl precipitate does not form. In contrast to the results of Fig. 6, the measured Cu oxidation/reduction current deviates strongly from IEQCM if n = 2 is used in Eq. 6. The fit is better if n = 1 is used for transforming the mass change into current. This indicates that in the presence of PEG the formation of CuCl is the dominating anodic process. In the cathodic sweep mainly Cu⁺ is reduced back to Cu metal.

In the experiment represented in Fig. 8a, only chloride, at a concentration of 4 mM, was added to the H2SO4 electrolyte. Along with the measured current, the IEQCM results obtained from the corresponding EQCM data (not shown), with n = 2 (for Cu⁺/Cu) and n = 1 (for Cu²⁺/Cu) are presented. Note that up to −0.45 V in the anodic sweep the measured current is nearly identical with IEQCM obtained with n = 2. This indicates that under these conditions the oxidation of Cu is dominated by the Cu → Cu²⁺ reaction. However, the formation of CuCl also takes place. This follows from the negative deviation of IEQCM from I at E > −0.45 V in the positive sweep. It points to the formation of CuCl, indicating that at this potential the activity of Cu⁺ rises above the value demanded by Ke for CuCl precipitation. Note that the mass loss resulting from reducive dissolution of CuCl in the cathodic scan manifests itself as a positive IEQCM peak because via Eq. 6 with n = 2 it is interpreted as anodic Cu → Cu⁺ dissolution. When the electrolyte contains both Cl⁻ and PEG (Fig. 8b), in the positive scan up to −0.47 V the measured current I is practically identical with the corresponding IEQCM values obtained with n = 1. This demonstrates that mainly the reaction Cu → Cu²⁺ proceeds, similar to the situation of Fig. 7. At E > −0.47 V the strong negative deviation of IEQCM from I indicates that CuCl forms on the electrode, i.e., the activity of Cu⁺ near the electrode surface must have exceeded the value defined by Ke and the activity of chloride ions.

In the experiments of Fig. 9 bromide is used as an additive instead of chloride. At bromide concentrations above 0.5 mM, both in
the presence and in absence of PEG, strong negative \( I_{ECQM} \) peaks in the anodic scans, and positive \( \Delta m \) peaks in the negative scans point to the formation and reductive dissolution of CuBr. Formation of a precipitate at a lower halide concentration than in the case of \( Cl^- \) is the consequence of the smaller solubility product of \( KBr \) (\( K_{sp} = 5.9 \times 10^{-5} \) M\(^2\)). Note that in the presence of the inhibiting combination of halide and PEG under otherwise the same conditions significantly more CuBr forms, and the CuBr formation starts earlier than in absence of PEG.

**Discussion**

The rates of the two consecutive charge-transfer reactions.—The II/E curves of Fig. 1 as well as literature results\(^{3,8,9}\) indicate that the rate of the Cu(II)/Cu(I) reaction is reduced considerably if both chloride and PEG are added to the electrolyte. It has been shown\(^{16-20}\) that the current/voltage curves can be analyzed efficiently on the basis of the Butler-Volmer equations\(^{3,9}\) for the two consecutive reaction steps, i.e., for Cu\(^{2+}+/Cu^+\):

\[
i_{1} = i_{1}^{0} \frac{a_{Cu^{2+}}}{a_{Cu^{+}}} \exp \left[ \frac{\alpha_{1}(E - E_{1}^{0})}{RT} \right] - \frac{a_{Cu^{2+}}}{a_{Cu^{+}}} \exp \left[ \frac{(1 - \alpha_{1})(E - E_{1}^{0})}{RT} \right]
\]

and for Cu\(^{+}+/Cu\):

\[
i_{II} = i_{II}^{0} \left\{ \exp \left[ \frac{\alpha_{II}(E - E_{II}^{0})}{RT} \right] - \frac{a_{Cu^{+}}}{a_{Cu^{2+}}} \exp \left[ \frac{(1 - \alpha_{II})(E - E_{II}^{0})}{RT} \right] \right\}^{1,2}
\]

where \( i_{1} \) and \( i_{II} \) are the charge-transfer controlled current densities of the two consecutive reactions, \( i_{1}^{0} \) and \( i_{II}^{0} \) are the exchange current densities at the reference activities \( a_{Cu^{2+}} = a_{Cu^{+}} = 1 \) M, and \( E_{1}^{0} \) and \( E_{II}^{0} \) are the corresponding standard potentials

\[
Cu^{2+} + e^- = Cu^+ \quad E_{1}^{0} = -0.537 \text{ V}
\]

\[
Cu^+ + e^- = Cu_{\text{metal}} \quad E_{II}^{0} = -0.169 \text{ V}
\]

The current/potential curve from Fig. 4 for the system 2.2 M H\(_2\)SO\(_4\), 0.3 M CuSO\(_4\), 4 mM chloride, and 0.4 mM PEG was analyzed, using an estimated value of \( \gamma_{Cu^{2+}} = 0.05 \) as the activity coefficient for Cu\(^{2+}\), and a constant activity of Cu\(^{+}\) \( (a_{Cu^{+}} = \text{const}) \), and the assumption that all charge transfer (CT) coefficients are equal (\( \alpha_{1} = \alpha_{II} = 0.5 \)). Thus, values of 0.03 and 0.08 A cm\(^{-2}\) for the exchange current densities \( i_{1}^{0} \) and \( i_{II}^{0} \) respectively, are derived. If the PEG concentration is reduced, the values of \( i_{1}^{0} \) and \( i_{II}^{0} \) both increase. In the case of 0.2 mM PEG, Fig. 1, the values \( i_{1}^{0} = 0.05 \) and \( i_{II}^{0} = 0.1 \) A cm\(^{-2}\) are obtained. If the chloride concentration is increased above 0.4 mM (Fig. 4), the cathodic reduction current rises. Apparently, the known catalytic mechanism of chloride is still operating. For the system in the absence of chloride and PEG, exchange current densities of \( i_{1}^{0} = 0.6 \) and \( i_{II}^{0} = 1.2 \) A cm\(^{-2}\) were

**Figure 5.** The excess mass, \( \Delta (\Delta m) \), obtained by subtracting \( \Delta m_{I} \) (the mass change expected from the measured current in Fig. 4, i.e., under the assumption that only the reaction \( Cu^{2+} + 2e^- = Cu \) would take place (\( n = 2 \)) from the corresponding EQCM mass change, \( \Delta m \).

**Figure 6.** Current/potential curves obtained from voltammetric experiments, \( \dot{I} \), and from the corresponding mass changes, \( \dot{m}_{ECQM} \) via Eq. 6 with \( n = 2 \). Electrolyte 1.8 M H\(_2\)SO\(_4\), sweep rate 20 mV/s, electrode area 0.28 cm\(^2\); arrows indicate the sweep direction.
obtained previously. One concludes that the Cu/Cl/PEG barrier layer acts rather unspecifically in about the same way on both the two consecutive charge-transfer reaction steps Cu$^{+1}$/Cu$^{+}$ and Cu$^{+}$/Cu.

CuCl deposition in presence of the Cu/Cl/PEG layer.—In Fig. 2 and 3 the EQCM mass changes, $\Delta m$, are compared with the mass changes $\Delta m_I$ obtained via Eq. 5 from the currents of Fig. 1, assuming that the current would be due only to the reaction Cu$^{+1}$ + 2e$^-$ = Cu. The deviation of $\Delta m_I$ from $\Delta m$ is caused by the CuCl deposit. We have shown previously that the formation/disappearance of CuCl proceeds by a precipitation/dissolution mechanism, i.e., CuCl forms in the anodic scan as the stationary concentration of Cu$^+$ exceeds the value required for fulfilling the condition of the solubility product, Eq. 3. The mass of CuCl formed (Fig. 3) depends nearly linearly on the concentration of chloride, as observed previously in the absence of PEG, indicating that the growth rate of the deposit is limited by transport of Cl$^-$ toward the electrode surface. In the negative potential range, the CuCl deposit dissolves when the stationary concentration of Cu$^+$ falls below the value defined by the solubility product. The Cu$^+$ ions may then be reduced to Cu metal while Cl$^-$ undergoes transport into the bulk electrolyte. Note that in this analysis we disregard the contribution of the direct electrochemical reaction according to CuCl + e$^- = Cu_{metal} + Cl^-$, that may take place at the three-phase interface between Cu, CuCl, and the electrolyte solution. Of course, this direct reaction is thermodynamically indistinguishable from the precipitation/dissolution mechanism.

As long as one may disregard any consumption of Cu$^+$, either by diffusion away from the electrode surface or by deposition as CuCl, the stationary state of the system is characterized by $i_1 = i_{11}$.
the stationary activity of Cu

Voltaometric currents and the corresponding EQCM results as in Fig. 8, but with 1 mM KBr added instead of HCl to the H₂SO₄ electrolyte as indicated in the figure.

\[ i = \frac{1}{2} i_a \]

In this case, Eq. 7 and 8 yield the following expression for the stationary activity of Cu⁺ near the electrode surface

\[ a_{Cu^+} = a_{Cu^+}^{0} \exp \left( \frac{F(E - E_{Cu^+}^{0})}{2RT} \right) \]

\[ a_{Cu^+} = a_{Cu^+}^{0} \frac{i_0}{i_i} \exp \left( \frac{F(E - E_{Cu^+}^{0})}{2RT} \right) + a_{Cu^+}^{0} \frac{i_0}{i_i} \exp \left( -\frac{F(E - E_{Cu^+}^{0})}{2RT} \right) \]

With Eq. 11 and the exchange current densities for the system containing both chloride and PEG (Fig. 4), the potential dependence of the stationary concentration of Cu⁺ not limited by CuCl deposition can be calculated. These data are represented in Fig. 10 as curve (a). The corresponding calculated current/voltage curve is shown in Fig. 11 as curve (a).

The CuCl precipitation reaction will limit the concentration of Cu⁺, as shown in Fig. 10 curves (b) and (c) for two chloride concentrations. The current/voltage curve Fig. 11 curve (b) is calculated as \( i = i_1 + i_2 \) with the truncated \( a_{Cu^+}/i \) relations of Fig. 10(c). It shows that the current rises above the values observed in the absence of CuCl precipitation, crossing the zero line at a potential more negative than the equilibrium potential. It is concluded that the conspicuous current rise observed in Fig. 4 around −0.4 V and the corresponding shift of apparent equilibrium potential are the result of CuCl formation following this mechanism.

Anodic formation of Cu⁺ and Cu⁴⁺ in electrolytes not containing CuSO₄.—For the experiment of Fig. 6 pure H₂SO₄ is used as the electrolyte while the results of Fig. 7 are obtained with an electrolyte of H₂SO₄, PEG, and chloride at a concentration below the minimum value required for CuCl deposition. Comparison of the results of Fig. 6 and 7 indicates that the Cu/Cl/PEG layer induces the anodic formation of Cu⁺, while in the absence of the barrier layer the main product is Cu⁴⁺. This notable finding can be understood by considering first that the Cu/Cl reaction is relatively fast, also when the layer is present. Thus, the equilibrium activity of Cu⁺ will tend to be established according to the Nernst equation

\[ a_{Cu^+} = \exp \left( \frac{F}{RT} (E - E_{Cu^+}^{0}) \right) \]

Curve (a) of the concentration/potential plots of Fig. 12 is obtained with Eq. 12, with \( \gamma_{Cu^+} = 0.32 \). The corresponding current for the reaction Cu → Cu⁺ will be determined by two processes, first, by the rate of transport of Cu⁺ away from the electrode surface (\( i_d \)), second, by the rate of oxidation of Cu⁺ to Cu⁴⁺ (Eq. 7). We assume diffusion-controlled transport away from the electrode, then

\[ i_d = \frac{FDa_{Cu^+}}{\delta} \]

where \( D \) is the diffusion coefficient of Cu⁺ and \( \delta \) is the Nernst diffusion layer thickness. For the following simulation we assume simply a constant value of \( \delta \) that corresponds to very slow rotation (1 rps) of the (actually stationary) electrode. With a diffusion coefficient of \( 1.38 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \) for Cu⁺ and \( \delta = 0.00715 \text{ cm} \), the \( i_d = E \) plot (a) of Fig. 13 is obtained.

With the exchange-current densities for the Cu⁺ → Cu⁴⁺ reaction in the presence of the Cu/Cl/PEG film, \( i_0^0 = 30 \text{ mAm}^{-2} \), and that observed in the absence of the film, \( i_0 = 0.6 \text{ A cm}^{-2} \), the oxidation currents of Cu⁺ designated with (b) and (c) in Fig. 13 are obtained.
Assuming diffusion control as above, from the Cu\(^{+}\) oxidation currents (b) and (c) of Fig. 13, concentrations of Cu\(^{+}\) near the electrode can be calculated. With the diffusion coefficient of 3.3 \times 10^{-6} \text{ cm}^2 \text{s}^{-1} for Cu\(^{+}\),\(^{39}\) and \(d = 0.00444 \text{ cm}, the results represented in Fig. 12 are obtained, (b) in the presence of the inhibiting film, and (c) in the absence of the film.

The representations of the surface concentrations and oxidation currents of Fig. 12 and 13 explain straightforwardly the results of Fig. 6 and 7. In the potential region where the current rises in the anodic sweep (around \(-0.5 \text{ V}, \text{Fig. 6 and 7}\), in the presence of the CuCl/PEG film the oxidation current yields mainly Cu\(^{+}\) that diffuses from the electrode into the solution, while the reaction producing Cu\(^{+}\) is relatively slow [Fig. 13(a) and (b)]. Consequently, the anodic oxidation product near the electrode is mainly Cu\(^{+}\), see Fig. 12(a) and (b). On the other hand, in the absence of the surface film, the rate of Cu\(^{+}\) formation from Cu\(^{+}\) is larger than that of Cu\(^{+}\) diffusing from the electrode into the solution [Fig. 13(a) and (c)], so that the concentration of Cu\(^{+}\) near the electrode surface rises above the Cu\(^{+}\) value [Fig. 12(a) and (c)].

In the experiments of Fig. 6 and 7 discussed above, the chloride concentration was kept below the value required for CuCl deposition. In the subsequent experiments of Fig. 8 and 9 the halide concentration is increased such that CuCl or CuBr deposits can form. Consider the formation of CuCl in Fig. 8. Since in the absence of PEG the main oxidation product will be Cu\(^{+}\), the CuCl deposition reaction is a relatively unimportant side reaction (Fig. 8a). On the other hand, in Fig. 8b CuCl production is the dominating process because chloride and PEG have formed the inhibiting surface layer with the consequence that Cu\(^{+}\) is the main oxidation product. In the experiment of Fig. 9 the preferential production of Cu\(^{+}\) in the presence of PEG and halide manifests itself in the remarkable finding that the CuBr deposit forms more efficiently in the presence of the inhibiting PEG/halide layer than on the clean Cu electrode.

The mechanism of formation of the CuCl/PEG layer.—It is interesting to note that in the case of PEG + Cl\(^-\) as well as with PEG + Br\(^-\) the inhibiting surface layer also forms when the electrolyte does not contain CuSO\(_4\), and also at potentials where neither Cu\(^+\) nor Cu\(^{+}\) establish appreciable Nernstian equilibrium concentrations with Cu\(_\text{metal}\). This follows from the observation of copper electrodes that were freshly immersed into the H\(_2\)SO\(_4\) + PEG + Cl\(^-\) (or Br\(^-\)) electrolyte at a negative potential (e.g., \(-0.65 \text{ V}\)). When the potential is scanned for the first time in the anodic direction with these fresh electrodes, exactly the same small copper-oxidation current is observed as in the subsequent scans, see Fig. 7, 8b, and 9b. This means that the inhibiting surface layer forms already between the adsorbate-covered copper electrode and PEG. Neither Cu\(^+\) nor Cu\(^{+}\) from the electrolyte are required.

**Conclusions**

Copper electrodes are studied with electrochemical methods and with the EQCM in H\(_2\)SO\(_4\) electrolytes containing varying concentrations of CuSO\(_4\), Cl\(^-\) (or Br\(^-\)), and PEG. The following was found:

1. When both halide and PEG are present in the electrolyte the well-known inhibiting layer forms on the copper surface. This layer reduces both the Cu(II)/Cu\(^+\) and the Cu\(^+\)/Cu exchange current densities by an order of magnitude. However, the Cu(II)/Cu\(^+\) reaction
The slow step in the sequence of consecutive reactions
remains the slow step in the sequence of consecutive reactions Cu(II)/Cu(I)/Cu(n)

2. In the presence of the inhibiting CuCl/PEG film [in fact, whenever the rate of the Cu(II)/Cu reaction is attenuated], in the course of anodic copper oxidation near the electrode the stationary concentration of Cu** relative to that of Cu** rises. This phenomenon may be understood straightforwardly on the basis of the Butler-Volmer equations for the two consecutive charge-transfer reactions (Cu**/Cu**/Cu(n)) taking into account the variation of the exchange current densities.

3. In the anodic potential sweep a conspicuous current rise is observed in the potential range where bulk CuCl (or CuBr) precipitates on the electrode surface. It leads to a shift in the negative direction of the apparent equilibrium potential (i.e., the potential of zero current of the current/voltage curves), that is clearly noticeable when both PEG and chloride (or bromide) are present in the electrolyte at appropriate concentrations. Simulations show that the cause for this phenomenon is the asymmetry introduced into the system of two consecutive reactions (Cu/Cu**/Cu**) when the intermediate Cu** is consumed for the formation of the precipitate.

4. The surface film forms between the halide-covered copper electrode and PEG. Neither Cu nor Cu** from the electrolyte are required. The precipitation of bulk CuCl (or CuBr) on the electrode surface at the larger halide concentrations is a parallel process and not a requirement for formation of the inhibiting layer.

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References


Figure 13. (a) Diffusion-controlled current density for anodic formation of Cu** from Cu; (b) charge-transfer controlled current density due to oxidation of Cu** from equilibrium activity to Cu** with an exchange current density i** = 0.03 A cm~2 (CuCl/PEG film present); (c) the same for the electrode without an inhibiting film (i** = 0.6 A cm~2).