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OXIDATION FILMS ON COPPER IN ALKALINE MEDIA: A LASER RAMAN AND PHOTOCURRENT SPECTROSCOPY STUDY

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Abstract

The composition of thin surface layers on copper oxidized in alkaline media has been determined by combining in-situ intensity modulated photocurrent measurements and laser Raman spectroscopy with cyclic voltammetry. Raman spectra confirmed that oxidized copper initially formed a thin Cu$_2$O film. Further oxidation produced a precipitated Cu(OH)$_2$ layer that coexisted with the Cu$_2$O underlayer. No CuO was detected at potentials where Cu(OH)$_2$ initially formed. At more positive potentials, the Cu(OH)$_2$ film was maintained while the Cu$_2$O underlayer was oxidized to CuO. Photocurrent measurements showed that the high intensity ($\leq$250 W/cm$^2$) laser Raman probe beam facilitated reduction of the oxidized surface. Laser-facilitated reduction provided a means to distinguish between CuO and Cu$_2$O films.
1. Introduction

The electrolytic oxidation and reduction of copper surfaces has received considerable attention because of the materials technological importance [1-15, and references therein]. Oxidized copper has been shown to form thin mono- and di-valent surface layers that affect the environmental stability and interfacial electronic properties of the material [6]. However, the complexity of films formed on copper oxidized in alkaline media has made discriminating between various oxide and hydroxide surface phases difficult [1-15]. In-situ spectroelectrochemical techniques have been employed to determine the composition of copper oxidation films with greater detail [4,7-15]. One technique, near-normal incidence reflectance spectroscopy, has shown sufficient sensitivity for distinguishing between oxide and hydroxide films on copper, but long signal acquisition times limited the dynamic capabilities of the method [13]. Other spectroelectrochemical techniques that are more suitable for dynamic studies—such as ellipsometry [4], photoacoustic spectroscopy [8], and photothermal deflection spectroscopy [15]—have been unable to differentiate between divalent copper oxide and hydroxide thin films.

Laser Raman spectroscopy (LRS) has been used as an in-situ technique for studying electrolytic surface films formed under dynamic potential control [14,16]. Past studies showed that LRS was valuable for identifying cuprous oxide (Cu$_2$O) and cupric hydroxide (Cu(OH)$_2$) surface species, but cupric oxide (CuO) was not detectable under dynamic in-situ conditions due to its low Raman scattering cross section [9,14,17]. Hamilton, et. al. [14] used LRS and cyclic voltammetry to verify that the initial oxidation film on copper in alkaline media was cuprous oxide. Upon further oxidation, their LRS spectra showed a poorly resolved new peak that was attributed to either cupric hydroxide or a polymeric cupric hydroxide species. Cuprous oxide gave a strong resonance enhanced Raman signal for 488 nm incident radiation [14]. The LRS results of Melendres, et. al. showed that electrolytic cuprous oxide was a stable phase in slightly acidic solutions, even at potentials that favored the formation of a divalent species [9].
In-situ intensity modulated photocurrent techniques have been used to detect thin oxide films on metals [18]. An electrode/electrolyte interface illuminated by an intensity-modulated source produces a modulated electrochemical response (current or potential) if the density of charge carriers in the electrode is modified by the illumination and the redox reaction is charge-carrier-limited [19,20]. Intensity modulation techniques have been valuable for copper oxidation studies because cuprous and cupric oxides are both p-type semiconductors [6,10,12,21]. The flat band potentials for cuprous and cupric oxides have been reported to differ by more than 200 mV [6,12], so the onset potential for photocurrent should, in principle, allow one to distinguish between the two oxide surface phases [22]. However, the multilayer structure of oxidized copper surfaces, and the superposition of numerous copper redox processes, has led to conflicting models for the origin of photocurrent response [6,7,10-12,23,24]. Moreover, a substantial range of values for the flat band potentials and growth mechanisms of electrolytic cuprous and cupric oxides have been reported in the literature [6,12,23-25]. In spite of inconsistencies in the quantitative models for electrolytic copper oxide films, intensity modulated photocurrent techniques have shown a high sensitivity for detecting the presence of copper oxides on surfaces [6,7,10,12,23,24,26].

In this paper we report in-situ photocurrent and laser Raman spectroscopy results that identify the composition of thin films formed on copper in alkaline media during potentiodynamic experiments. The combined application of spectroelectrochemical and photoelectrochemical techniques is shown to distinguish between divalent copper oxide and hydroxide species. The laser Raman scattering results are acquired continuously during potential cycling in order to correlate voltammogram current peaks with surface phase formation. By using laser Raman spectroscopy and intensity modulated photocurrent techniques together, the composition of copper surface films can be determined without relying on difficult in-situ measurements of electronic properties for the thin oxidation films.
2. Experiment

A schematic of the apparatus used for the intensity-modulated photocurrent studies is shown in fig. 1. Intensity modulations were generated by passing the plane-polarized 488 nm beam from an argon ion laser (a) through the Faraday cell modulator (b) and Glan-Thompson polarizing prism (c). The Faraday cell modulated the plane of polarization of the laser beam transmitted through its core, where the difference between the polarization planes of the incident and emerging beams was $\varepsilon \cos(2\pi \sigma t)$ ($\varepsilon$ is the amplitude of the modulation angle in radians and $\sigma$ is the modulation frequency in Hz). The polarization-modulated beam then passed through the fixed polarizing prism set with a transmission direction of 45° relative to the polarization of the initial laser beam. After passing through the fixed polarizer, the intensity of the beam was modulated. The intensity-modulated laser beam was then expanded (d) and focussed (e) onto the working electrode (h). All intensity modulation experiments reported here were operated with $\varepsilon = 0.05$ and $\sigma = 50$ Hz, which resulted in the sample illumination

$$I(t) = \bar{I} + 2\varepsilon \bar{I} \cos(2\pi \sigma t),$$

(1)

where $\bar{I}$ is the mean (d.c.) intensity incident on the sample.

Beam profiling was performed using a Reticon 1024-element linear diode array. The focussed beam had a circular cross-section with a Gaussian intensity distribution. The fwhm of the beam at the sample was estimated to be 100±50 μm. Laser power was measured with a Coherent 2210 calibrated laser power meter. Intensities at the sample were based on estimates for the reflection loss at the electrochemical cell window and the fwhm of the focussed beam. Attenuation of the incident beam was accomplished using neutral density filters.

A single compartment, three electrode electrochemical cell containing approximately 10 ml of electrolyte was used in the photocurrent studies. The working electrode (h) was high purity copper wire (99.999%, 250 μm diameter) encased in a Teflon shroud that exposed only a cross-section of the wire to electrolyte (i). The geometrical area of the copper wire working electrode (WE) was approximately $5 \times 10^{-4}$ cm$^2$. New WE surfaces were prepared by immersing the
Teflon-covered wire in liquid nitrogen and then cutting the electrode with a clean razor blade, thereby exposing a fresh copper surface. The counter electrode (f) was platinum, and all potentials were referenced to a Hg/HgO electrode (g) that was immersed, without a liquid junction, directly in the 1M KOH electrolyte that was used throughout this study. Potential control of the electrochemical cell was performed with a PAR 273 potentiostat. All linear potential sweep experiments used a sweep rate of 1 mV/s. Reported current and photocurrent voltammograms were taken during the first potential cycle (initiated at -0.8 V and swept anodic), unless noted otherwise. The modulated current output (the a.c. photocurrent) was measured using lock-in amplifier detection (PAR model 5101).

Laser Raman spectroscopy (LRS) employed a large area working electrode (1cm x 2cm) that was polished to a mirror finish using standard metallographic techniques. The working electrode was placed in an electrochemical cell that provided optical windows for the incident laser beam and for collecting the scattered light. The incident beam focussing optics for LRS were similar to the intensity modulation apparatus shown in fig. 1, except that a plasma line filter was inserted between the beam expander (d) and the lens (e). Scattered light was collected at an angle of 60° from the surface normal with a f/1.4, 5 cm focal length camera lens. The intensity of the elastically scattered signal was attenuated by approximately 6 orders of magnitude using narrow band pass filters (Omega Optical), and then dispersed using a PAR OMA III single monochromator. Details of the LRS instrumentation and electrochemical cell, as well as evidence that thermal effects are unimportant for this system, are given elsewhere [27].

3. Results and Discussion

3.1 Effects of high intensity illumination

Cyclic voltammetry is used to analyze the potential regions where electron transfer reactions occur. Arrows on the voltammograms indicate the direction of the potential sweep. Positive values for the current denote anodic reactions. Figure 2 shows the fifth and sixth cycles of a cyclic
voltammogram for a copper wire working electrode that is illuminated (fig. 2a) and dark (fig. 2b). The measured current during anodic potential sweeps of illuminated and dark electrodes (figs. 2a and 2b, respectively) are nearly identical to each other and to comparable voltammograms reported in the literature [5,14], indicating that high intensity illumination does not substantially affect the oxidation of copper. The first current peak during the anodic sweep, labeled A1, is due to the oxidation of Cu metal to cuprous oxide, Cu$_2$O, via the reaction [6,10,15]

$$2\text{Cu} + 2\text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} + 2\text{e}^- .$$  \hspace{1cm} (2)

The second anodic sweep peak, labeled A2, arises from the oxidation of Cu and Cu$_2$O to divalent surface and solution phase species [1-4,13-15]. The precise composition of the divalent surface film at the A2 peak (and at more positive potentials) is uncertain [4,10-12,14,15], but the most probable divalent surface species are Cu(OH)$_2$, CuO, or a mixed phase of both species. A low current tail is observed at potentials positive of the A2 peak. The composition of divalent species is addressed in §3.2.

Oxidation products generated during the anodic sweep are reduced during the cathodic sweep. The cathodic potential sweep results shown in fig. 2 illustrate that reduction processes (i.e. the cathodic current) are different for illuminated and dark electrodes. In the voltammogram of the dark electrode, fig. 2b, no current is evident as the potential is swept from 0.5 V to -0.3 V. A small cathodic peak in the dark voltammogram is observed at -0.4 V (labeled C2) and a large composite cathodic peak (labeled C1) is seen over the potential range -0.55 V to -0.85 V. The voltammogram of the illuminated electrode, on the other hand (fig. 2a), shows a series of reduction peaks labeled α, β, δ, and γ; no large composite peak comparable to C1 is observed in fig. 2a. It is unlikely that differences between the cathodic sweep results of fig. 2a and 2b are explained by illumination-induced modification of the anodic sweep, since illumination does not change the anodic sweep much (cf. figs. 2a and 2b). The most likely origin for the cathodic sweep illumination effects observed in fig. 2 is the p-type conductivity of semiconducting oxides that form on copper in alkaline media [6-8,10-12]. The results in fig. 2 show that high intensity illumination photo-facilitates reduction of the oxidized copper surface. Photo-facilitated reduction
results in the individual peaks \( \alpha, \beta, \delta, \) and \( \gamma \) rather than the composite C1 peak found in the absence of illumination.

Intensity modulated photocurrent measurements are especially sensitive to photoelectrochemical processes because the a.c. photocurrent signal exists only when there is photo-induced modification of an electron transfer reaction. In addition, the d.c. current is comparable to a cyclic voltammogram of the illuminated electrode. Figure 3 shows the a.c. in-phase and quadrature photocurrent signal and the d.c. current signal for the first potential cycle of a typical intensity modulation photocurrent voltammogram. The low frequency a.c. photocurrent signal reported in this study is proportional to \( \mathcal{E} \left( \frac{\partial j_{ph}}{\partial I} \right)_T \), where \( \frac{\partial j_{ph}}{\partial I} \) is the derivative of photocurrent with respect to intensity (evaluated at \( T \)).

During the anodic potential sweep, a.c. photocurrent (figs. 3a and 3b) is observed in the A2 peak and A2 tail region of the illuminated cyclic voltammogram (fig. 2a). However, the a.c. photocurrent response is dominated by two large in-phase peaks observed during the cathodic sweep. The two in-phase cathodic photocurrent peaks (fig. 3a) are centered near 0.0 V and -0.5 V, and are labeled \( \alpha_{ph} \) and \( \beta_{ph} \) since their potentials correspond roughly to the \( \alpha \) and \( \beta \) peak regions in fig. 2a. The cathodic sweep a.c. photocurrent peaks in fig. 3a confirm the results from fig. 2 showing that the major effects of illumination appear during reduction of the oxidized surface (i.e. the \( \alpha \) and \( \beta \) peak regions). Further discussion of the a.c. photocurrent results is limited to the in-phase component since it is characteristic of the total a.c. response during the cathodic sweep.

Past intensity modulation studies (all of which employed lower intensities than used here) have observed a single a.c. photocurrent peak comparable to \( \beta_{ph} \) [7,10,12], but no peak comparable to \( \alpha_{ph} \). In order to determine whether the \( \alpha_{ph} \) peak in fig. 3 arises as an artifact of oxidation under high intensity illumination, a series of a.c. photocurrent measurements for copper oxidized in the dark and reduced under high intensity illumination were performed (fig. 4). Curve (a) of fig. 4 shows the course of an experiment. A fresh working electrode is started at -0.8 V and the potential is scanned in the dark up to 0.7 V, at which point a dark cathodic scan begins. No photocurrent is observed during any portion of the dark scan. At a particular potential during the
cathodic scan (0.0 V for curve (a), fig. 4), the working electrode is illuminated and an a.c. photocurrent signal is observed. In going from curve (a) through curve (d), illumination is initiated at successively more anodic potentials. The dark scans in curves (b)-(d) are omitted for clarity. Each curve in fig. 4 displays both photocurrent peaks \( \alpha_{ph} \) and \( \beta_{ph} \). The fact that both \( \alpha_{ph} \) and \( \beta_{ph} \) photocurrent peaks remain whether the electrode is oxidized in the dark or light shows that neither cathodic photocurrent peak arises simply as an artifact from photoelectrochemical or thermal processes that occur during the anodic potential sweep.

In order to reconcile our high intensity results with lower intensity literature (in which only a single cathodic photocurrent peak has been reported), a series of a.c. photocurrent experiments subject to different incident intensities was performed. Plotted in fig. 5 are the cathodic sweeps of a.c. photocurrent voltammograms with mean illumination intensities that vary by three orders of magnitude. For clarity the anodic sweeps are not included in the figure. Figure 5 shows that attenuating the incident beam intensity by a factor of 800 reduces the magnitude of \( \alpha_{ph} \) relative to \( \beta_{ph} \) and also shifts the \( \alpha_{ph} \) peak potential from -10 mV in curve (a) to -170 mV in curve (e). An illumination-induced potential shift of voltammogram peaks has been observed before [8]. The dominance of \( \beta_{ph} \) over \( \alpha_{ph} \) at low intensities (fig. 5d) is caused mainly by the different intensity dependencies of the \( \alpha_{ph} \) and \( \beta_{ph} \) peak heights. The height of the \( \alpha_{ph} \) peak depends linearly on \( \bar{I} \), thereby reducing the \( \alpha_{ph} \) peak size by a factor of nearly 800 in going from curve (a) to (d). By comparison, curves (a)-(d) show that the \( \beta_{ph} \) peak size decreases only by a factor of 10. Thus, the photocurrent efficiency for the \( \beta_{ph} \) peak increases approximately 80-fold between curves (a) and (d) in fig. 5, while the photocurrent efficiency for the \( \alpha_{ph} \) peak remains essentially unchanged. (Here we use the term photocurrent efficiency to denote the quantity \( \langle \delta j_{ph}/\delta I \rangle \).) The nonlinear dependence of the \( \beta_{ph} \) peak height on illumination intensity, and the potential shifting of the \( \alpha_{ph} \) peak, accounts for the appearance of a single cathodic photocurrent peak in studies that employ low intensity illumination.

The linear intensity dependence of the a.c. photocurrent in the \( \alpha_{ph} \) peak region is characteristic of a photoelectrochemical reaction that is limited by the density of minority charge
carriers at the interface (i.e., electrons for a p-type layer). The photocurrent response in the $\beta_{\text{ph}}$ peak region of fig. 5 exhibits a saturation behavior, where an increase in the incident intensity results in a less than linear increase in a.c. photocurrent. The nonlinear intensity dependence of the $\beta_{\text{ph}}$ peak height is not explained by either a charge-carrier-limited or a mass-transfer-limited model for the photoelectrochemical charge transfer process. The photocurrent in a mass-transfer-limited photoelectrochemical reaction is independent of intensity, leading to no a.c. photocurrent signal. The nonlinear photocurrent saturation behavior observed in $\beta_{\text{ph}}$ is the subject of a future report.

The results from this section show the potential regimes where a high intensity laser probe beam affects the electrochemistry of copper in alkaline media. Photoelectrochemical effects are mainly observed during the reduction of the oxidized surface, where two distinct regions of photocurrent activity are found ($\alpha_{\text{ph}}$ and $\beta_{\text{ph}}$). The $\alpha_{\text{ph}}$ peak becomes more prominent at high illumination intensity because of the $\beta_{\text{ph}}$ peak saturation. It is also shown that high intensity illumination shifts some of the cathodic reactions to more positive potentials, resulting in a separation of otherwise overlapping current peaks. Figure 5 shows that the properties of the illuminated electrode are very different in the $\alpha_{\text{ph}}$ and $\beta_{\text{ph}}$ peak regions; the chemical species responsible for the photoelectrochemical activity of oxidized copper are identified in the following sections.

3.2 In-situ identification of surface species by laser Raman spectroscopy

In-situ laser Raman spectroscopy is used here to identify the composition of thin oxidation films that form on the copper working electrode. Since the intensity of the Raman probe beam is comparable to the highest intensities studied in §3.1, interpretation of the resulting spectra must consider the effects of illumination on the chemistry. Shown in fig. 6 is a series of Raman spectra taken during the anodic (fig. 6a) and cathodic (fig. 6b) sweeps of a cyclic voltammogram with potential limits identical to fig. 2. The signal for each Raman spectrum is acquired over a 100 mV (i.e. 100 second) potential window, where the potential reported next to each spectrum in fig. 6 is the average potential of the acquisition window. For clarity every other spectrum is omitted in fig.
6 (i.e. 200 mV potential increments are shown). Two characteristic peaks are seen in the Raman spectrum; one peak is located near 488 cm\(^{-1}\) and the other is near 633 cm\(^{-1}\). Reference standards in previous work verify that the 488 cm\(^{-1}\) peak is from cupric hydroxide, Cu(OH)\(_2\), and the 633 cm\(^{-1}\) peak is from cuprous oxide, Cu\(_2\)O [14,27]. The 633 cm\(^{-1}\) peak is detectable for cuprous oxide films thicker than \(~4\) nm due to its strong scattering [14,27], but cupric hydroxide films must be considerably thicker for a 488 cm\(^{-1}\) peak to appear in the spectrum. The distinct 488 cm\(^{-1}\) peak shown in fig. 6 was not observed by either Melendres, et. al. [14] or Hamilton, et. al. [9] during \textit{in-situ} spectroelectrochemical Raman studies using lower pH electrolytes.

Plotted in figs. 7(a) and 7(b) are the integrated areas under the 633 cm\(^{-1}\) and 488 cm\(^{-1}\) peaks, respectively, as a function of electrode potential. The integrated Raman signal is a measure of the material sampled on the copper surface. Presenting the potential dependence of the \textit{in-situ} integrated Raman signals, as in figs. 7(a) and 7(b), allows a more transparent comparison of Raman spectroscopy results with cyclic voltammetry and a.c. photocurrent results. Note that the integrated Raman signals in fig. 7 are not expected to show changes precisely at the potentials of cyclic voltammogram peaks since the spectra are acquired over a 100 mV window. Smooth lines are drawn through the data in fig. 7 to indicate the general features of the potential dependent Raman signal, and arrows on the lines indicate the direction of the potential sweep.

For an anodic sweep along the cyclic Raman response curves, fig. 7, one observes a rising Cu\(_2\)O signal starting near -0.3 V and a rising Cu(OH)\(_2\) signal near -0.1 V. The potential where a Cu\(_2\)O Raman signal is first observed correlates well with the A1 voltammogram peak (see fig. 2), while the potential where Cu(OH)\(_2\) is observed correlates with the A2 peak. Continuing the anodic sweep past 0.0 V in fig. 7, one observes that the Cu\(_2\)O Raman signal begins to decline and the Cu(OH)\(_2\) signal remains essentially unchanged. The declining Cu\(_2\)O signal is apparently the result of a Faradaic process, with the film conversion occurring in the tail region following the A2 peak in fig. 2a.

As the electrode potential is swept in the cathodic direction, the integrated Raman signal for Cu\(_2\)O rises over the potential region from 0.15 V to -0.15 V, while the Cu(OH)\(_2\) signal remains
essentially unchanged until -0.25 V is reached. The potential window where the Cu$_2$O Raman signal rises corresponds to the $\alpha$ peak region in fig. 2a. Both the Cu$_2$O and Cu(OH)$_2$ integrated Raman signals decrease monotonically as the cathodic sweep reaches potentials more negative than -0.25 V, showing that the $\beta$ and $\delta$ voltammogram peaks in fig. 2a result from the reduction of the detectable surface layers. The increasing Cu$_2$O Raman signal at the A1 peak agrees with reaction (2). The only divalent species observed with laser Raman spectroscopy is Cu(OH)$_2$, which is formed at the A2 peak. *Ex-situ* scanning electron micrographs [2,27] and *in-situ* light scattering measurements [27] show that the surface morphology becomes rough and needle-like at the A2 peak, presumably due to the formation of a Cu(OH)$_2$ layer by precipitation from solution. However, some investigators suggest that CuO is the major divalent surface species [11], while others suggest that CuO and Cu(OH)$_2$ form a mixed phase at the A2 peak [5,13].

The declining Raman signal observed in the tail region of the A2 peak (fig. 7a) shows that the thin Cu$_2$O underlayer is either consumed or it is obscured by another layer. Two possible oxidation reactions with products that would cause the 633 cm$^{-1}$ Raman signal to decline in the A2 tail region are

\[ \text{Cu}_2\text{O} + 2\text{OH}^- \rightarrow 2\text{CuO} + \text{H}_2\text{O} + 2\text{e}^- \tag{3a} \]

and

\[ \text{Cu} + 2\text{OH}^- \rightarrow \text{Cu(OH)}_2 + 2\text{e}^- \tag{3b} \]

In reaction (3a) the Cu$_2$O layer is oxidized to form CuO, a species not readily detectable with Raman spectroscopy. In reaction (3b) it is assumed that the Cu(OH)$_2$ layer, initiated at the A2 peak, grows to sufficient thickness in the A2 tail region to obscure the Cu$_2$O underlayer. On reversal of the potential sweep direction, fig. 7a shows that the Raman signal response in the $\alpha$ peak potential region is essentially the inverse of the Raman signal in the A2 tail. This indicates that charge transfer in the $\alpha$ peak originates in part from the reduction of the products formed in the A2 tail region. Recall from §3.1 that charge transfer in the $\alpha$ peak region occurs only when the electrode is illuminated (see figs. 2 and 3). The fact that reduction in the $\alpha$ peak region is from a photoelectrochemical reaction favors (3a) over (3b) since electrolytic CuO is known to be a p-type
semiconductor whereas Cu(OH)$_2$ is an insulator. However, it is also possible that reduction of Cu(OH)$_2$ is photo-facilitated in the $\alpha$ peak region due to an enhancement of electronic conductivity in the illuminated Cu$_2$O underlayer.

In order to further differentiate between the reactions (3a) and (3b), both of which are consistent with the Raman signal response for potentials positive of the A2 peak, a series of a.c. photocurrent experiments taken to different anodic excursion potentials have been performed. Figure 8, curve (a) shows that scanning the potential to a maximum anodic value of 0.5 V produces an a.c. photocurrent voltammogram with $\alpha_{ph}$ and $\beta_{ph}$ peaks of comparable size, as in fig. 3(a). The $\alpha_{ph}$ peak is shown to diminish as the maximum anodic excursion potential decreases from curve (a) (0.5 V) to curve (d) (-0.1 V). Each curve in fig. 8 has an anodic excursion that is sufficient to pass completely through the A2 peak, where it is known from the Raman spectroscopy results (figs. 6 and 7) that Cu(OH)$_2$ is formed. If Cu(OH)$_2$ is the species photo-reduced in the $\alpha$ peak region, then $\alpha_{ph}$ should not diminish in fig. 8 since a Cu(OH)$_2$ layer exists on the surface for each curve plotted. Rather, the a.c. photocurrent sequence in fig. 8 verifies that CuO is formed in the tail of the A2 peak according to the anodic reaction given by of (3a). The CuO formed by oxidation in the A2 tail is then photo-reduced in the $\alpha_{ph}$ region.

3.3 The origins of a.c. photocurrent

The results and discussion in §3.2 show that the $\alpha_{ph}$ a.c. photocurrent peak arises from the photo-facilitated reduction of CuO to Cu$_2$O. In addition, the combined Raman spectroscopy and a.c. photocurrent measurements show that the broad $\beta_{ph}$ peak results, in part, from the photo-facilitated reduction of the semiconducting Cu$_2$O layer via the reverse reaction of (2). Therefore, the $\alpha_{ph}$ and $\beta_{ph}$ a.c. photocurrent peaks originate primarily from the photo-facilitated reduction of the p-type semiconducting oxide films CuO and Cu$_2$O, respectively. This model of the interfacial electrochemistry provides a self-consistent description of the Raman spectroscopy and photocurrent results presented here and is in basic agreement with the photoelectrochemically-derived results of Collisi and Strehblow [12].
The electrochemical film reduction scheme described above does not fully account for the prominent shoulders observed on the $\alpha_{ph}$ and $\beta_{ph}$ a.c. photocurrent peaks. It is known that electrons photo-injected into p-type oxide layers will reduce solution-phase oxidizing agents when certain constraints on the energy levels in the solid and solution are satisfied [22]. Copper oxidized in alkaline media has been reported to form mono-, di-, and tri-valent soluble species [1]. These soluble species are likely to be reduced when the oxide-covered surface is illuminated since the thermodynamic reduction potentials for the soluble oxidation products are comparable to the reduction potentials for the solid oxidation films. The shoulders on $\alpha_{ph}$ and $\beta_{ph}$ indicate that each peak is a composite peak, where the oxide films and solution-phase species are photo-reduced. Note that the shoulders on the $\alpha_{ph}$ peak in fig. 4 are considerably larger than those normally observed when the entire potential scan is illuminated (cf. fig. 4 and figs. 3 and 8). If the shoulders on $\alpha_{ph}$ and $\beta_{ph}$ arise from the photo-facilitated reduction of soluble copper species, then fig. 4 shows that changing the illumination conditions during oxidation modifies the selectivity between soluble species and film formation.

4. Summary

This study shows that the composition of surface layers formed on copper in alkaline media can be analyzed under dynamic potential control using in-situ a.c. photocurrent measurements and laser Raman spectroscopy. As the metallic copper surface is initially oxidized, a thin cuprous oxide layer forms. On further increase in potential a soluble divalent species is formed that results in a precipitated layer of cupric hydroxide on top of the cuprous oxide layer. Cupric oxide is formed by oxidation of the cuprous oxide underlayer at potentials greater than those needed to form the cupric hydroxide precipitate layer. Illumination does not substantially change the composition of surface oxidation films. During the cathodic sweep, surface layers formed in the anodic sweep are reduced, but the reduction processes depend on illumination. When illuminated, the thin cupric oxide underlayer is reduced to cuprous oxide. Further reduction of the illuminated electrode results in the removal of cupric hydroxide and cuprous oxide layers from the surface. In the absence of
illumination, reduction occurs principally at a single voltammogram peak where the cathodic reactions overlap.

Two cathodic a.c. photocurrent peaks ($\alpha_{ph}$ and $\beta_{ph}$) with very different illumination-dependent properties are observed at high illumination intensities. It is shown that p-type CuO and Cu$_2$O layers form next to the copper substrate and facilitate cathodic charge transfer reactions. The photo-facilitated reduction is selective for CuO and Cu$_2$O layers, occurring at the potential of the $\alpha_{ph}$ and $\beta_{ph}$ peaks, respectively. However, shoulders on the $\alpha_{ph}$ and $\beta_{ph}$ peaks suggest that solution-phase species are also reduced when the CuO- and Cu$_2$O-covered electrode is illuminated.

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References


[25] The flat band potential reported by K.L. Hardee and A.J. Bard, J. Electrochem. Soc. 124 (1977) 215, for CuO has later been erroneously assigned to Cu2O by numerous authors (see for example ref. [10,13,24]).

Figure Captions

Fig. 1. Schematic of intensity modulation optics and electrodes. (a) Ar$^+$ laser operating at 488 nm, (b) Faraday cell polarization modulator, (c) Glan-Thompson polarizing prism, (d) diverging lens for beam expansion, (e) f/10 focusing lens, (f) Pt counter electrode, (g) Hg/HgO reference electrode, (h) copper wire working electrode, (i) expanded view of copper wire working electrode.

Fig. 2. Consecutive cyclic voltammograms of a Cu wire working electrode. (a) Electrode illuminated with an intensity of approximately 250 W/cm$^2$. (b) Dark electrode.

Fig. 3. Cyclic photocurrent response for an intensity modulation given by eq. (1) with $I=250$ W/cm$^2$. (a) In-phase component of the modulated photocurrent signal. (b) Quadrature component of the modulated photocurrent signal. (c) D.C. current.

Fig. 4. In-phase a.c. photocurrent response when the anodic sweep is performed without illumination. Illumination with 250 W/cm$^2$ is initiated during the cathodic sweep at the potentials (a) 0.0 V, (b) 0.1 V, (c) 0.2 V, and (d) 0.3 V. Included for reference at the bottom of the plot is fig. 3c.

Fig. 5. Cathodic sweeps of the in-phase a.c. photocurrent response for the mean illumination intensities $\bar{I} = (a) 250$ W/cm$^2$, (b) 31 W/cm$^2$, (c) 2.5 W/cm$^2$, and (d) 0.31 W/cm$^2$. The 2 nA scale bar is for curve (a); other photocurrent axes have been expanded by the multiplying factor given next to each respective curve. Curve (e) is an expanded view of the $\alpha_{ph}$ peak region of (d).
Fig. 6. *In-situ* laser Raman spectra taken sequentially as the electrode potential scans (a) anodically up to 0.7 V and then switches to the (b) cathodic scan. Spectra are acquired over a 100 mV potential window, but for clarity every other spectra is omitted. Reference spectra assign the 488 cm\(^{-1}\) peak to Cu(OH)_2 and the 633 cm\(^{-1}\) peak to Cu_2O.

Fig. 7. Integrated area under the (a) 633 cm\(^{-1}\) and (b) 488 cm\(^{-1}\) Raman peaks (see fig. 6) as a function of electrode potential. Open circles (O) denote data points for the anodic sweep, filled circles (●) denote data points for the cathodic sweep, and the solid line is a smoothing of the data.

Fig. 8. In-phase a.c. photocurrent response for various anodic potential excursions beyond the A2 peak. The anodic sweeps are reversed at (a) 0.5 V, (b) 0.3 V, (c) 0.1 V, and (d) -0.1 V. Included for reference at the bottom of the plot is fig. 3c. \(\bar{I} = 250\) W/cm\(^2\).
Fig. 1. Schematic of intensity modulation optics and electrodes. (a) Ar+ laser operating at 488 nm, (b) Faraday cell polarization modulator, (c) Glan-Thompson polarizing prism, (d) diverging lens for beam expansion, (e) f/10 focussing lens, (f) Pt counter electrode, (g) Hg/HgO reference electrode, (h) copper wire working electrode, (i) expanded view of copper wire working electrode.
Fig. 2. Consecutive cyclic voltammograms of a Cu wire working electrode. (a) Electrode illuminated with an intensity of 250 W/cm². (b) Dark electrode.
Fig. 3. Cyclic photocurrent response for an intensity modulation given by eq. (1) with $I = 250 \, \text{W/cm}^2$. (a) In-phase component of the modulated photocurrent signal. (b) Quadrature component of the modulated photocurrent signal. (c) D.C. current.
Fig. 4. In-phase a.c. photocurrent response when the anodic sweep is performed without illumination. Illumination with 250 W/cm² is initiated during the cathodic sweep at the potentials (a) 0.0 V, (b) 0.1 V, (c) 0.2 V, and (d) 0.3 V. Included for reference at the bottom of the plot is fig. 3c.
Fig. 5. Cathodic sweep of the in-phase a.c. photocurrent response for the mean illumination intensities $\bar{I}$ = (a) 250 W/cm$^2$, (b) 31 W/cm$^2$, (c) 2.5 W/cm$^2$, and (d) 0.31 W/cm$^2$. The 2 nA scale bar is for curve (a); other photocurrent axes have been expanded by the multiplying factor given next to each respective curve. Curve (e) is an expanded view of the $\alpha_{ph}$ peak region of (d).
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