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Authors

Schwartz, D T

Mayer, S T

Muller, R H

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Extended Abstract

COPPER OXIDATION UNDER INTENSE ILLUMINATION
Effects of a Raman Probe Beam

Daniel T. Schwartz, Steven T. Mayer^{*}, and Rolf H. Muller

Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, CA 94720

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^{*}Lawrence Livermore National Laboratory

Introduction

Raman spectroscopy is being used increasingly as an *in situ* technique for identifying reaction products present at the electrode interface and within the electrolyte phase. Due to the low efficiency of Raman scattering, high intensity illumination of the sample is required. Incident beam power densities greater than 1000 W/cm^2 are routinely used in Raman spectroscopy in order to obtain an adequate signal-to-noise ratio in the spectra. Past investigators have expressed concern that high intensity illumination may modify interfacial electrochemical processes.¹ It is especially likely that laser illumination will modify the observed electrochemistry when the incident beam is sufficiently energetic to promote electrons to excited states, as is often found for semiconducting oxide thin films that form on metal electrodes.

For the case of oxidation products that form on copper electrodes, both cuprous oxide and cupric oxide phases are known to be p-type semiconductors with band gap energies in the visible spectral range (E_g for $\text{Cu}_2\text{O} \approx 2.2 \text{ eV}$ and E_g for $\text{CuO} \approx 1.7 \text{ eV}$).^{2,3} Yamashita, *et al.*³ found that a low intensity incident beam modified the current-potential behavior of an oxidized copper electrode through the addition of a photocurrent response. Other investigators have also analyzed the effects of low intensity illumination on the electrochemical behavior of oxidized copper electrodes,⁴ but the question remains as to the effect of high intensity illumination. We report here the results of a combined Raman spectroscopy and photocurrent study aimed at understanding the effects of high intensity illumination on the oxidation of copper in alkaline media.

Experimental

Experiments were performed using a copper working electrode (WE), a platinum counter electrode, and a Hg/HgO reference electrode in a single compartment cell with $1M$ KOH electrolyte. The initial studies employed a polished WE with geometric area of ≈ 2

cm^2 , but subsequent work (and all of the photocurrent studies) used a WE with geometric area of $\approx 5 \times 10^{-4} \text{ cm}^2$. All reported cyclic voltammograms (CV) were taken at a sweep rate of 1 mV/s.

The continuous power output from the Ar^+ laser (514.5 nm line) was 90 mW. The focussing optics provided a minimum beam waist of approximately 40 μm in diameter at the WE surface, but for the experiments reported here the typical beam waist was approximately 100 μm . Small amplitude, sinusoidal modulation of the laser beam intensity was accomplished in the photocurrent studies by including a Faraday cell and Glan-Thompson polarizing prism in the laser beam path. The plane of polarization emitted from the laser was modulated by the Faraday cell and then passed through the polarizing prism set at an angle of 45° to the mean polarization plane of the incident laser radiation. The focussing optics in the photocurrent studies were identical to those used for Raman spectroscopy, except that a plasma line filter was excluded from the optical path.

Results and Discussion

Raman Spectroscopy

Plotted in Fig. 1 is a series of Raman spectra acquired during the cathodic sweep of a 2 cm^2 Cu WE. Two distinct peaks are observed in the spectra; the peak centered near 640 cm^{-1} is associated with Cu_2O at the electrode surface and the peak centered near 480 cm^{-1} is from $\text{Cu}(\text{OH})_2$.⁵ In Fig. 2a the height of the 640 cm^{-1} Raman scattering peak (cuprous oxide) is plotted as the potential is swept anodically to 0.7 volts, and then reversed down to -1.4 volts vs. Hg/HgO. Similarly, Fig. 2b shows the 480 cm^{-1} peak height (cupric hydroxide) as a function of potential during the same potential sweep experiment. The experiments reported in Figs. 2a and 2b used the 2 cm^2 WE; the current-potential behavior of the system is therefore characterized by the dark current response, Fig. 2c, since the area of the illuminated spot is negligible compared to the WE area.

An interesting feature of Fig. 2 is that the Cu_2O Raman signal increases during the cathodic sweep from 0.4 to -0.1 volts (Fig. 2a), yet there is neither a decrease in the $\text{Cu}(\text{OH})_2$ signal (Fig. 2b) nor does there appear to be any current flowing over that potential range (Fig. 2c). The rising Cu_2O signal suggests that the concentration of cuprous oxide is increasing at the surface, but the source of the Cu_2O is unresolved from the results in Fig. 2. Clearly, $\text{Cu}(\text{OH})_2$ is not being reduced during the cathodic sweep until the electrode potential is more negative than -0.2 volts, as shown by Fig. 2b. The absence of current during the cathodic potential sweep from 0.4 to -0.1 volts (Fig. 2c) may indicate that a nonfaradaic chemical transformation is forming Cu_2O on the electrode. A more plausible explanation for the increasing Cu_2O signal is that a photoactive surface species is being reduced in the 10^{-4} cm^2 illuminated region of the electrode, but not over the remaining dark portion of the 2 cm^2 electrode. The likely photoreduced surface species is CuO . Though CuO is not observed in the Raman spectra of Fig. 1 (CuO is a poor Raman scatterer¹), it has been reported as an oxidation product of Cu .

Photocurrent Studies

In order to test for the presence of CuO , intensity modulated photocurrent studies were performed using a $5 \times 10^{-4} \text{ cm}^2$ Cu WE. CuO , being a p-type semiconductor, should have a cathodic photocurrent response if it is present at the interface. Shown in Fig. 3a is the in-phase component of the photocurrent plotted against potential for an intensity modulation frequency of 50 Hz. Figure 3b shows the 90° quadrature component of the photocurrent and Fig. 3c shows the mean current. The most prominent features of the photocurrent signal are the two peaks that occur in the in-phase component during the cathodic sweep. The photocurrent peak centered near -0.5 volts has been noted in the literature and is attributed to the photo-assisted reduction of Cu_2O to Cu ,⁴ but the photocurrent peak centered near 0.0 volts has not been reported to the best of our knowledge. Note that the photocurrent peak near 0.0 volts actually extends from 0.2 to

-0.3 volts, coinciding well with the potential range where the Cu_2O Raman signal rises in Fig. 2a. Also note in Fig. 3c that a small Faradaic current is noticeable on the illuminated $5 \times 10^{-4} \text{ cm}^2$ WE for potentials more negative than 0.15 volts during the cathodic sweep. No similar current is observed for a dark electrode, Fig. 2c. These photocurrent results strongly support our hypothesis that CuO is present at the interface, and is photoreduced to form Cu_2O .

Conclusions

We have shown that photo-induced effects must be considered if one is to understand the potential dependence of Raman spectra for Cu oxidation in alkaline media. The rising Cu_2O Raman signal in the initial region of the cathodic sweep is a result of cathodic photo-decomposition of CuO. Moreover, the reduction of Cu_2O is also facilitated by illumination. Finally, we have shown that the Cu(II) valence state is present as a thin film containing both $\text{Cu}(\text{OH})_2$ and CuO phases, at least when oxidation occurs under intense illumination.

Acknowledgments

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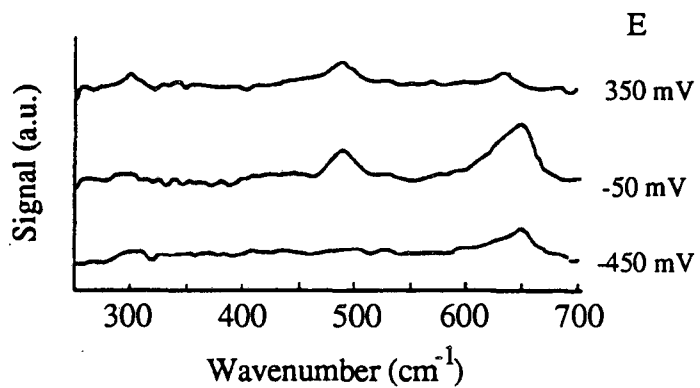


Fig. 1. Raman spectra acquired sequentially during cathodic sweep of a copper working electrode in alkaline media. The peak near 480 cm^{-1} is from cupric hydroxide and the peak near 640 cm^{-1} is from cuprous oxide. E vs. Hg/HgO. (XBL 8911-4319)

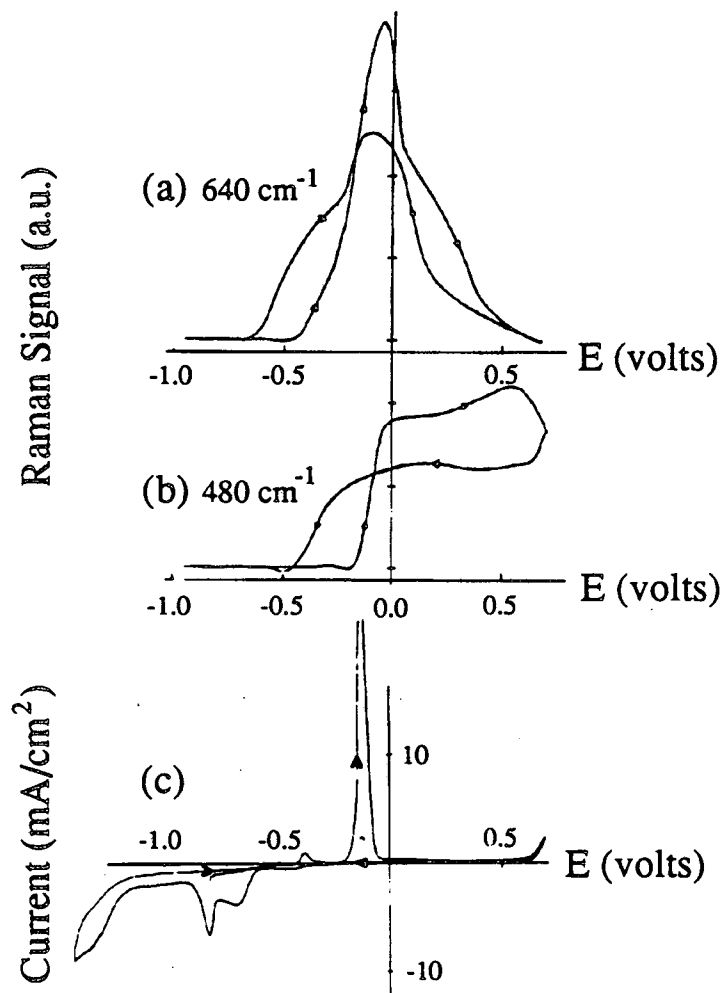


Fig. 2. Raman signal intensity as a function of potential: (a) Cuprous oxide signal at 640 cm^{-1} . (b) Cupric hydroxide signal at 480 cm^{-1} . (c) CV for the dark electrode. E vs. Hg/HgO . (XBL 8911-4320)

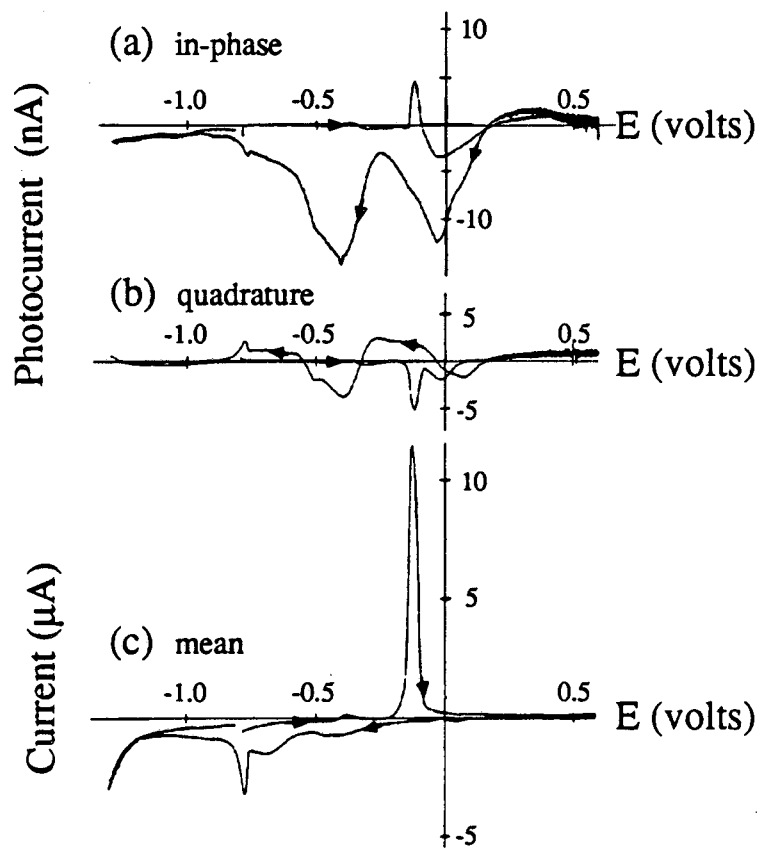


Fig. 3. Cyclic photocurrent response for 50 Hz intensity modulation: (a) In-phase photocurrent. (b) Out-of-phase photocurrent. (c) CV of the mean current from the illuminated electrode. E vs. Hg/HgO. (XBL 8911-4321)

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TECHNICAL INFORMATION DEPARTMENT
1 CYCLOTRON ROAD
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