



## Spontaneous Potential Oscillations in the Cu(II)/Tartrate and Lactate Systems, Aspects of Mechanisms and Film Deposition

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Spontaneous oscillations in the cathode potential are observed in the alkaline Cu(II)/tartrate and lactate systems when applying current to the electrochemical cell. In the Cu(II)/tartrate system the oscillations induce formation of composite films of Cu and Cu<sub>2</sub>O on the cathode with a grain size ranging from about 5 to 15 nm. The oscillation period is a function of pH and deposition temperature. A mechanism for the oscillating Cu(II)/tartrate and lactate systems is proposed based on pH changes close to the electrode surface during the deposition process.

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Manuscript submitted November 2, 2000; revised manuscript received March 14, 2001. This was Paper 345 presented at the Washington, DC, Meeting of the Society, March 25-29, 2001. Available electronically June 21, 2001.

Materials properties are in general terms affected by phase, chemical composition, and microstructure. As the dimensions of the building blocks (particles, grains) are reduced, a rapid change in properties is observed. The recent strong interest in both science and technology for nanostructured materials is due to the dramatic changes in properties when the building blocks become a few nanometers in size.

There exists quite a lot of different material preparation techniques. However, when entering the nanometer range the requirements with respect to process control become more crucial. Electrochemical deposition is an example of an attractive technique, meeting the requirements in production of nanostructured materials. The recent observation of spontaneous oscillations in cathode potential, resulting in deposition of nanostructured materials, has further increased the interest for using electrochemical techniques for preparing nanostructured materials.

Switzer *et al.* have previously applied electrochemistry to deposit nanostructured layers of Cu and Cu<sub>2</sub>O.<sup>1-4</sup> By applying a constant cathodic current to an alkaline solution containing Cu(II) and lactate ions the electrochemical potential of the system oscillates spontaneously. This indicates formation of alternating layers of Cu<sub>2</sub>O and a composite of Cu and Cu<sub>2</sub>O. The existence of multilayer structures has also been verified by scanning tunneling microscopy (STM) and Auger depth profiling. Similar spontaneous potential oscillations have been observed by Panumis *et al.* during electroless deposition of Cu and Cu<sub>2</sub>O from the alkaline Cu(II)/glycerate and tartrate systems using formaldehyde as the reducing agent.<sup>5</sup>

Electrochemical oscillations are not an unknown phenomenon and have been reported in the literature for several systems by Wojtowicz<sup>6</sup> and Hudson and Tsotsis.<sup>7</sup> The great variety of electrochemical oscillating systems indicates that oscillations are not specific but are a general phenomenon and several explanations exist.

Switzer *et al.* believe that the oscillations in the Cu(II)/lactate system during galvanostatic deposition are either caused by the formation and breakdown of a rectifying Cu<sub>2</sub>O/solution interface, or by oscillations of the surface pH during the deposition or both.<sup>2</sup> However, detailed reaction mechanisms have not been clarified. The oscillation period is a strong function of pH, Cu(II) concentration, and temperature.<sup>4</sup> Bonnefont *et al.* have reported on an *in situ* atomic force microscopy (AFM) study of electrodeposition of mixed layers of copper/cuprous oxide from the Cu(II)/lactate system. They were able to follow the morphologic growth of the deposit during the galvanostatic deposition process. Their results suggest that the induction time, the time needed for the oscillations to start, has a crucial role for the growth mechanism.<sup>8</sup>

We have studied the electrochemical deposition of a nanosize composite of Cu and Cu<sub>2</sub>O from the spontaneously potential oscillating Cu(II)/tartrate and lactate systems, respectively. The aim of the work was to get an increased knowledge about the oscillating systems and the mechanisms behind the oscillations, resulting in composite film deposition. The two systems behave similarly in many aspects. Potential oscillations during galvanostatic deposition of Cu and Cu<sub>2</sub>O in the Cu(II)/tartrate system have never been reported before. Characteristics of the Cu(II)/tartrate system, additional information for the Cu(II)/lactate system, and a mechanism for the oscillations in the Cu(II)/tartrate and lactate systems are presented in this paper.

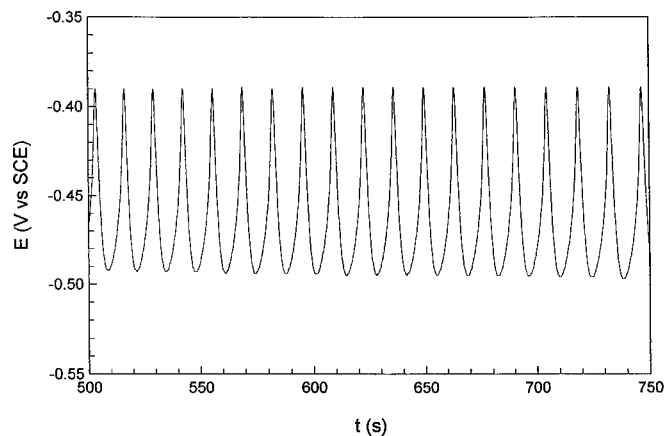
### Experimental

The Cu(II) tartrate solution, (0.4 M Cu(II), 0.4 M tartrate) was prepared by first dissolving 19 g sodium potassium tartrate tetrahydrate (L-tartrate, purity >99%) into 130 mL deionized 18 MΩ water with stirring. 15 g copper(II) sulfate pentahydrate (purity >99%) was added to the solution, and then 20 mL of 6.6 M NaOH was added in small increments over a period of a few minutes. The solution was left overnight, and the pH in the solution was adjusted to the final pH by adding a few drops of 95-97% sulfuric acid.<sup>9</sup> The Cu(II) lactate deposition solution [0.6 M Cu(II), 3 M lactate], was prepared by adding 37.5 g copper(II) sulfate pentahydrate to 62.5 mL >88% DL-lactic acid with stirring, and then 187.5 mL of 5 M NaOH was added in 50 mL increments over a period of a few minutes. The solution was left stirred overnight and the pH in the solution was then adjusted to the final value with the addition of 5-10 mL of 5 M NaOH.<sup>1</sup> A rotating disk electrode made of a Pt rod (area = 0.126 cm<sup>2</sup>) or a Cu rod (area = 0.785 cm<sup>2</sup>) was used as working electrode. It was mechanically polished down to a grit size of 1 μm and cleaned in deionized water in an ultrasonic bath for 10 min. All potentials were measured and reported vs. the saturated calomel electrode (SCE). A Cu sheet was used as a counter electrode. The rotation speed was varied from 0 to 500 rpm. The deposition current was controlled by a Solartron 1285 or EG&G PAR 273 potentiostat. The deposition temperature was controlled with a Neslab water bath for depositions not performed at room temperature.

The phase composition of the deposited films was analyzed by X-ray diffraction (XRD) using a Siemens D5000 diffractometer (Cu Kα radiation). The surface microstructure was examined with a high resolution LEO 1550 field emission gun (FEG) scanning electron microscope (SEM). Transmission electron microscope (TEM) analysis was performed, using a JEOL 2000 FX II TEM, operated at 200 kV.

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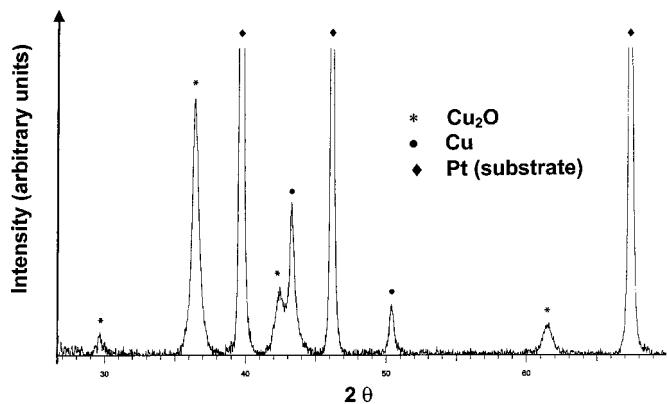
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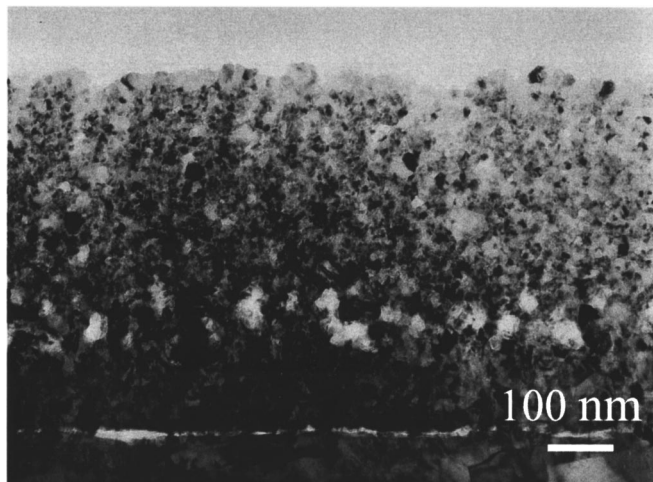
**Figure 1.** Spontaneous potential oscillations in an unstirred Cu(II)/tartrate solution at pH 10,  $T = 30^\circ\text{C}$ ,  $[\text{Cu(II)}] = 0.4 \text{ M}$ ,  $[\text{tartrate}] = 0.4 \text{ M}$  on a Pt electrode and cathodic current density of  $1 \text{ mA/cm}^2$ .

### Results and Discussion

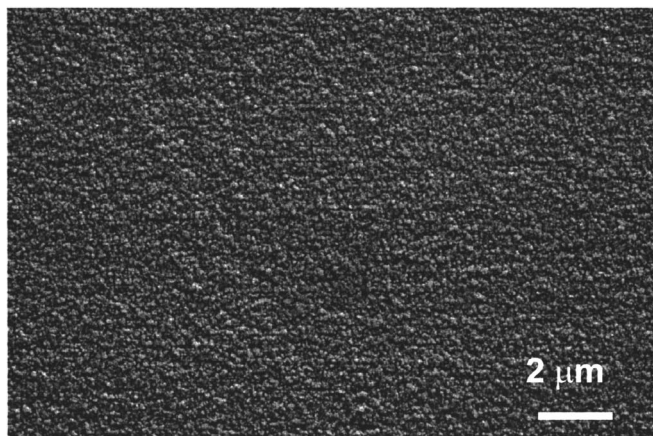
*Oscillations in the Cu(II) tartrate system.*— Typical potential oscillations observed in the Cu(II) tartrate system are shown in Fig. 1. The potential oscillates between  $-0.4$  and  $-0.5 \text{ V vs. SCE}$ . The oscillation period is about 15 s. This is a typical example of the oscillating potential behavior in this system. The XRD pattern shows that the film deposited consists of both Cu and  $\text{Cu}_2\text{O}$  (Fig. 2). The XRD peaks are broadened which indicate that the grains are small. This is also confirmed by the TEM investigation (Fig. 3). The size of the particles varies from about 5 to 15 nm. SEM images show that the grains in the film are uniformly deposited (Fig. 4a). At higher resolutions the film shows a tendency to be porous (Fig. 4b). Cu and  $\text{Cu}_2\text{O}$  are believed to be deposited alternately during the oscillations and, as confirmed by Switzer *et al.* for the Cu(II) lactate system,<sup>4</sup>  $\text{Cu}_2\text{O}$  is believed to be deposited during the positive-going potential shift and mainly Cu is believed to be deposited during the negative-going potential shift. We failed to show the evidence of a layered structure by Auger depth profiling and TEM. Probable reasons could be very thin layers and/or not completely covered layers and/or a very rough growth of the deposit. Further studies have to be done to characterize the Cu/ $\text{Cu}_2\text{O}$  deposits. Auger depth profiling shows that the films are not contaminated by species from the electrolyte.



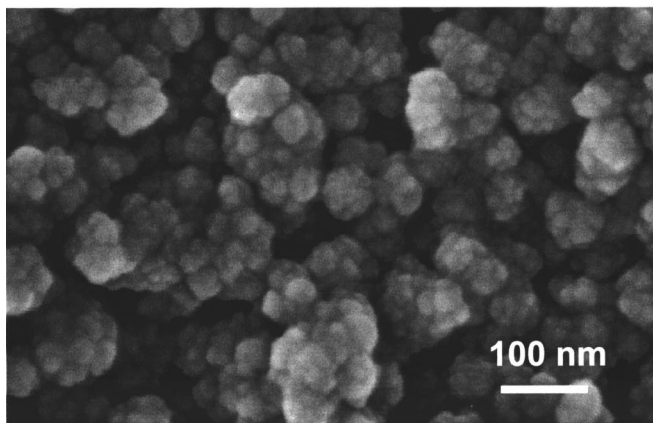
**Figure 2.** XRD pattern (Cu  $K\alpha$  radiation) of a film deposited from the oscillating Cu(II)/tartrate system onto a Pt-electrode at pH 11.5,  $T = 30^\circ\text{C}$ ,  $[\text{Cu(II)}] = 0.4 \text{ M}$ ,  $[\text{tartrate}] = 0.4 \text{ M}$ , and cathodic current density of  $1 \text{ mA/cm}^2$ . The diffractogram shows that the film consists of Cu and  $\text{Cu}_2\text{O}$ .



**Figure 3.** TEM image of a film deposited from the oscillating Cu(II)/tartrate system onto a Cu electrode at pH 12,  $T = 25^\circ\text{C}$ ,  $[\text{Cu(II)}] = 0.4 \text{ M}$ ,  $[\text{tartrate}] = 0.4 \text{ M}$ .

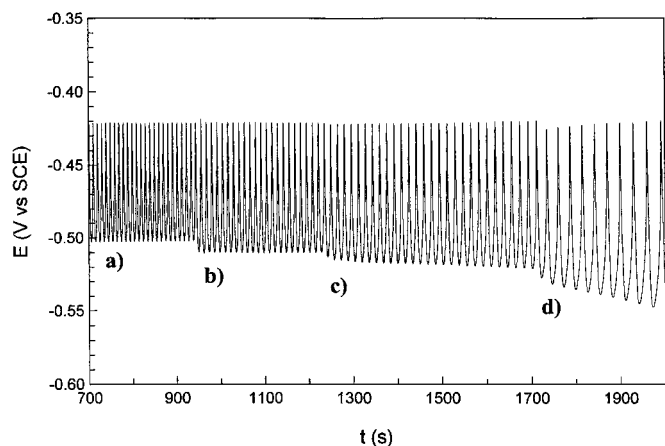


(a)



(b)

**Figure 4.** SEM images of a film deposited from the oscillating Cu(II)/tartrate system at pH 10.6,  $T = 30^\circ\text{C}$ ,  $[\text{Cu(II)}] = 0.4 \text{ M}$ ,  $[\text{tartrate}] = 0.4 \text{ M}$  onto a Cu electrode at an applied cathodic current density of  $1 \text{ mA/cm}^2$ : (a) low magnification image and (b) high resolution image.



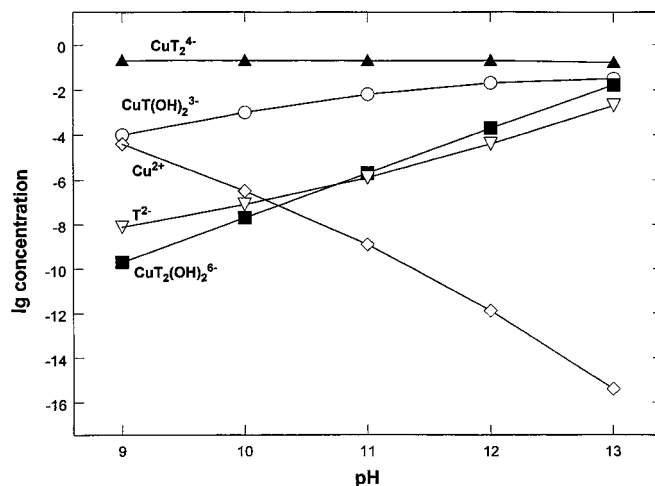
**Figure 5.** Spontaneous potential oscillations on a Pt-electrode in the Cu(II) tartrate system at pH 10.4,  $T = 25^\circ\text{C}$ ,  $[\text{Cu(II)}] = 0.4 \text{ M}$ ,  $[\text{tartrate}] = 0.4 \text{ M}$ . Different rotation speeds: (a) 500, (b) 200, (c) 100, and (d) 50 rpm.

*Characteristics of the Cu(II)/tartrate and lactate systems.—The influence of pH, temperature, and current density.*—The oscillation period is a function of solution pH. As the solution pH is increased, the oscillating period is decreased. When increasing pH in the Cu(II) tartrate system, from 10 to 12, the oscillation period generally decreases by a factor of about two, e.g., from about 10 to 5 s at  $25^\circ\text{C}$ . An increase in pH from 10 to 12 shifts the oscillating potential range from  $-0.5/-0.4 \text{ V}$  to  $-0.6/-0.5 \text{ V}$ .

The oscillating period is decreased when the temperature is increased. In the Cu(II)/tartrate system, an increase in temperature from  $25$  to  $35^\circ\text{C}$  affects the oscillation period in a similar manner as the pH increase, by a factor of two. At a fixed pH value, where no oscillations are being observed and mainly Cu is being deposited, the deposition of  $\text{Cu}_2\text{O}$ , i.e., to start the oscillations, can be triggered by an increase in deposition temperature.

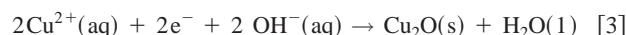
A high current density favors Cu deposition and a low current density favors  $\text{Cu}_2\text{O}$  deposition in both systems. Current densities from  $\sim 0.05$  to  $\sim 1 \text{ mA/cm}^2$  yield oscillations in the Cu(II) tartrate system. At current densities above  $\sim 1 \text{ mA/cm}^2$  copper is being deposited and the resulting potential is about  $-0.7 \text{ V vs. SCE}$ , and no oscillations are seen. Only  $\text{Cu}_2\text{O}$  is being deposited at current densities below  $\sim 0.05 \text{ mA/cm}^2$  and the resulting deposition potential in that case is about  $-0.45 \text{ V vs. SCE}$ . Therefore, lower current densities favor  $\text{Cu}_2\text{O}$  deposition and higher current densities favor Cu deposition. The deposition of  $\text{Cu}_2\text{O}$  during the lower current densities could be explained by a more pronounced two-step electron transfer  $[\text{Cu(II)} \rightarrow \text{Cu(I)} \rightarrow \text{Cu(s)}]$ . The lower current density causes a longer "life time" of the Cu(I) species and thereby an increased possibility of the  $\text{OH}^-$  species to react with Cu(I) to produce  $\text{Cu}_2\text{O}$ . The influence of the applied current density on the phase composition of Cu and  $\text{Cu}_2\text{O}$  during oscillations has not been evaluated.

*The influence of stirring.*—Oscillations are observed in stirred and unstirred solutions. In the Cu(II)/tartrate system, stirring has been seen to inconsistently trigger and suppress the start of oscillation. Oscillations in an unstirred solution are less frequently observed than in a stirred solution. The oscillation period is shorter in the beginning than after some minutes. Initially, in a stirred solution, the oscillation period is not affected by the rotation speed, but after oscillating for some minutes the oscillation period can be varied by changing the rotation speed (Fig. 5). Since the oscillating period can be affected by the amount of stirring, depletion of the reacting species is believed to take place. Before oscillation starts, a small dip in potential is generally seen (down to  $-0.55 \text{ V vs. SCE}$  and then the system oscillates between  $-0.50$  and  $-0.40 \text{ V vs. SCE}$ ).

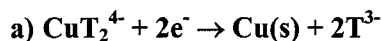


**Figure 6.** Concentration of different Cu(II)/tartrate complexes at pH 9-12.

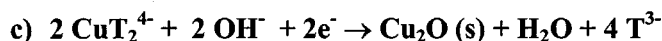
*Mechanism for the oscillations in the Cu(II)/tartrate and lactate systems.*—We propose a mechanism that is based on variations in pH close to the electrode surface during the deposition process. The complexing anion has a key role in causing the pH changes. The potential oscillations are due to the alternating deposition of Cu and  $\text{Cu}_2\text{O}$  (see Reactions 1, 2, and 3). Cu is believed to be deposited during the negative potential shift and  $\text{Cu}_2\text{O}$  during the positive potential shift. In the oscillating deposition process alternatively Reactions 1, 2, and 3 are the most favorable. A simultaneous codeposition of a small amount of  $\text{Cu}_2\text{O}$  during the deposition of Cu (during the negative potential shift) is not excluded. The reduction of Cu(II) in the complex with tartrate and lactate takes place in a two-step reduction process 1 and 2. The anion favors a pronounced two-step reduction process of the  $\text{Cu}^{2+}$  to Cu by stabilizing the Cu(I) state effectively



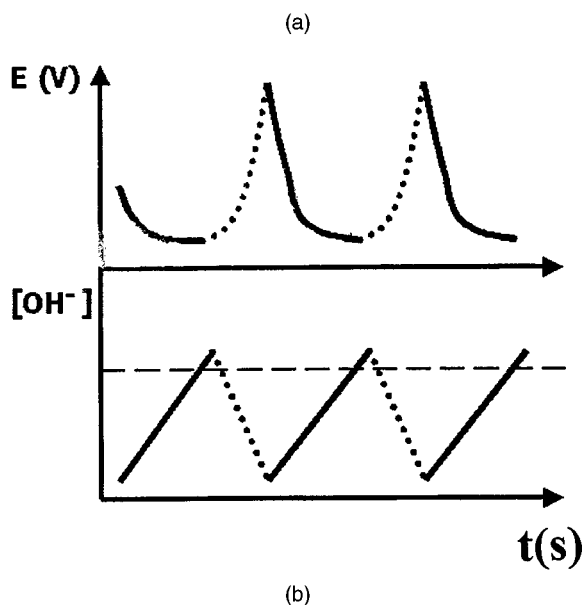
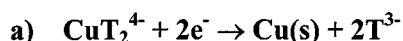
*The role of the complex binding species.*—The complex binding of the Cu(II) ion by the organic anion is important in obtaining the oscillations. The Cu(II)/tartrate complexes in the alkaline region have been studied by Norkus *et al.*<sup>10</sup> It has been shown that three different Cu(II)/tartrate complexes,  $\text{CuT}(\text{OH})_2^{3-}$ ,  $\text{CuT}_2^{4-}$ , and  $\text{CuT}_2(\text{OH})_2^{6-}$ , exist in the studied pH region ( $11.5 < \text{pH} < 14.4$ ). The logarithms of the stability constants for these complexes are  $18.6 \pm 1.2$ ,  $20.5 \pm 0.2$ , and  $21.9 \pm 0.3$  (L-tartrate). The concentration of the different complexes, existing at different pH values, has been calculated by solving adequate equilibrium equations (Fig. 6). The dominating complex throughout the pH range is the  $\text{CuT}_2^{4-}$  complex and the concentration of  $\text{CuT}_2^{4-}$  is almost constant. According to the study done by Norkus *et al.* the tartrate exists in the form of  $\text{T}^{3-} [^- \text{OOC}-\text{C}(\text{OH})-\text{C}(\text{O}^-)-\text{COO}^-]$ , which means that one of the  $\alpha$ -hydroxyl protons is also dissociated. Oscillations in the Cu(II)/tartrate system are observed at pH 10, which is lower than the pH value for dissociation of the proton in the hydroxyl group. But, when having the possibility of complexing the Cu(II) ion, the hydroxyl proton is dissociated at a lower value than the actual dissociation value because of the very stable chelating Cu(II)/tartrate complex formed. Chelating complexes are very stable as confirmed by the high stability constants for these complexes. The tartrate anion exists only as  $\text{T}^{3-}$  in complex with Cu(II). As  $\text{T}^{3-}$  is released from the metal central atom it is protonated to  $\text{HT}^{2-}$ .<sup>4</sup> This causes

**Reaction scheme:**

$[\text{OH}^-] \uparrow$  promotes  $\text{Cu}_2\text{O}$  deposition:



$[\text{OH}^-] \downarrow$  promotes Cu deposition:

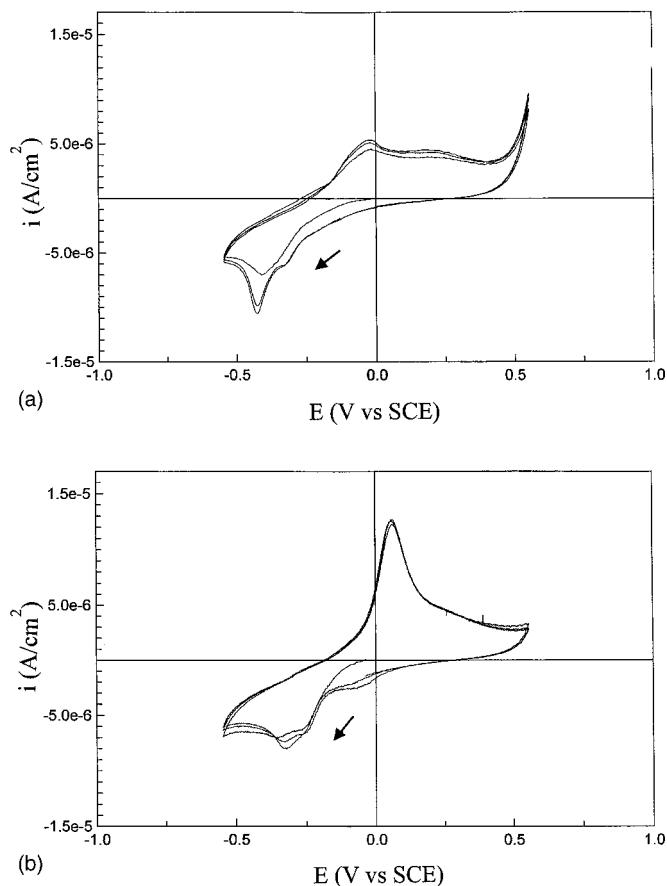


**Figure 7.** (a, top) Reaction scheme for the spontaneous oscillations. (b, bottom) Schematical sketch of the variation in  $\text{OH}^-$  concentration during the spontaneous potential oscillations, inducing the alternating deposition of Cu and  $\text{Cu}_2\text{O}$ : (—) Cu deposition and (·····)  $\text{Cu}_2\text{O}$  deposition.

the pH to increase. The protonation of  $\text{T}^{3-}$  and resulting pH increase play key roles in the oscillating mechanism



*The mechanism for the potential oscillations.*—In the following, a mechanism for the potential oscillations, based on variations in  $\text{OH}^-$  concentrations, is proposed according to the reaction scheme above (Fig. 7a). The alternating deposition originates from variations in concentration of  $\text{OH}^-$  during the deposition process (Fig. 7b). The process starts with deposition of Cu (Fig. 7a). As Cu is being deposited,  $\text{T}^{3-}$  ligands are liberated. Once  $\text{T}^{3-}$  is dissociated from the complex it is protonated to  $\text{HT}^{2-}$  (Fig. 7b). This causes the pH to increase only at the surface. As long as Cu is being deposited, the pH is increased (Fig. 7b). Then at a certain critical concentration of  $\text{OH}^-$ , the production of  $\text{Cu}_2\text{O}$  is more favorable than Cu deposition and deposition of  $\text{Cu}_2\text{O}$  starts (Fig. 7c). As  $\text{Cu}_2\text{O}$  is being deposited,  $\text{OH}^-$  is consumed and Cu deposition starts again when the concentration of  $\text{OH}^-$  is lowered due to  $\text{OH}^-$  consumption. This mechanism requires that the kinetics for  $\text{Cu}_2\text{O}$  deposition is faster than the protonation of  $\text{T}^{3-}$  since liberation of  $\text{T}^{3-}$  also occurs during  $\text{Cu}_2\text{O}$  deposition. In addition the proposed mechanism also requires that



**Figure 8.** Cyclic voltammograms (sweep rate: 10 mV/s and 0 rpm) on a Pt electrode in the (a) Cu(II)/tartrate system at pH 11.6,  $T = 25^\circ\text{C}$ ,  $[\text{Cu(II)}] = 0.4\text{ M}$ ,  $[\text{tartrate}] = 0.4\text{ M}$ , (b) Cu(II)/lactate system at pH 9.4,  $T = 25^\circ\text{C}$ ,  $[\text{Cu(II)}] = 0.6\text{ M}$ ,  $[\text{lactate}] = 3\text{ M}$ .

the  $\text{Cu}_2\text{O}$  production, once it has started, continues after reaching the critical  $\text{OH}^-$  concentration for  $\text{Cu}_2\text{O}$  deposition. This is plausible if the kinetics is fast and the nucleation of  $\text{Cu}_2\text{O}$  already has taken place. The pH changes are believed to occur very close to the surface. The Cu(II)/lactate system is assumed to follow an analogous mechanism.

Further work has to be done to experimentally verify the mechanism. At this stage we have experimentally verified that the pH is increased as copper is deposited. An experiment with a small amount of electrolyte above the surface and a pH indicator (phenolphthalein) added to the solution has been performed. The aim was to observe color changes (colorless to red) when the surface pH changed. The Cu(II) lactate electrolyte itself is very dark blue. We were not able to set up the experiment to be able to observe the color shift during the oscillations. However, during conditions where no oscillations were seen and only copper was deposited, a shift in color (from dark blue to lilac) was observed which means that surface pH is increased as copper is being deposited. The increase in pH as copper is deposited supports the mechanism, but further work has to be done to verify the proposed mechanism.

*Anion criteria.*—The organic anion has a crucial role in the origin of the oscillations. The anion must favor a pronounced two-step reduction process of the  $\text{Cu}^{2+}$  to Cu by stabilizing the Cu(I) state effectively. Otherwise the  $\text{OH}^-$  ion would have no chance to react with  $\text{Cu}^+$  to produce  $\text{Cu}_2\text{O}$ . Information about the two-step electron transfer properties can be extracted from cyclic voltammetry measurements. Figure 8 shows cyclic voltammograms for the Cu(II)/lactate and tartrate systems. In Fig. 8a the tartrate serves as the

anion, and in Fig. 8b the lactate serves as the anion. In both systems reduction occurs at two different potentials. The deposition of Cu is started at potentials below  $-0.5$  V and at about  $-0.35$  V a current peak is seen indicating reduction from Cu(II) to Cu(I). Another criterion for obtaining oscillations in the Cu(II)/tartrate and lactate systems is the presence of a hydroxyl group at the anion that can be deprotonated when forming strong chelating complexes with  $\text{Cu}^{2+}$ . Both the tartrate and the lactate have a  $\beta$ -hydroxyl group. The protonation and deprotonation of the  $\beta$ -hydroxyl group is responsible for the concentration variation of  $\text{OH}^-$  and thereby the oscillations.

*Terminating the oscillations.*—The oscillations can be terminated by adding a strong Cu(I) complex binder. The reaction between  $\text{Cu}^+$  and  $\text{OH}^-$  is then suppressed. Experiments have been performed with a small amount of ammonia (10 mM) added to the solution. Ammonia terminates the oscillations by forming a strong complex with the  $\text{Cu}^+$  ion. When adding  $\text{NH}_3$  to an oscillating system no oscillations are observed and only Cu is being deposited. Hence the reaction between  $\text{Cu}^+$  and  $\text{OH}^-$  and the deposition of  $\text{Cu}_2\text{O}$  is suppressed. Experiments with other potential  $\text{Cu}^+$  ligands have also been performed. Two halides,  $\text{Cl}^-$  and  $\text{I}^-$ , have been added to the solution, respectively. At a concentration of 5 mM of  $\text{I}^-$ , no oscillations are seen. At the same concentration of  $\text{Cl}^-$ , the system still oscillates and a concentration of about 50 mM of  $\text{Cl}^-$  is needed to terminate the oscillations. A lower concentration of  $\text{I}^-$  terminates the oscillations since the  $\text{I}^-$  ion is a soft Lewis base and therefore forms a stronger complex with the  $\text{Cu}^+$  ion (soft Lewis acid) than the  $\text{Cl}^-$  ion does.

### Conclusions

Spontaneous potential oscillations are observed during the galvanostatic deposition of a nanocomposite of Cu and  $\text{Cu}_2\text{O}$  from the alkaline Cu(II)/tartrate and lactate systems. The oscillation period is

a function of solution pH and temperature. The tartrate and lactate systems show the same main characteristics. The films deposited from the Cu(II) tartrate system consist of grains ranging from 5 to 15 nm. A mechanism for the oscillations in the Cu(II)/tartrate and lactate systems is proposed based on variations in pH close to the electrode surface during the oscillating process. Initially, Cu is deposited followed by a simultaneous increase in pH close to the surface due to the protonation of the organic anion liberated from the copper(II) complex. As the pH is increased, the deposition of  $\text{Cu}_2\text{O}$  becomes more favorable and a positive shift in potential is observed.

### Acknowledgments

Financial support by the Swedish Natural Science Research Council (NFR) and the Swedish Research Council for Engineering Sciences (TFR) is gratefully acknowledged.

*Uppsala University assisted in meeting the publication costs of this article.*

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