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# Current oscillations during chronoamperometric and cyclic voltammetric measurements in alkaline Cu(II)-citrate solutions

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## Abstract

It is demonstrated that current oscillations can be observed during chronoamperometric and cyclic voltammetric experiments in solutions containing 0.4 M $CuSO_4$ and 1.2 M citrate at pH 11 and 50 °C. The oscillations, which are shown to originate from local variations in the pH, result in the deposition of nanostructured Cu and $Cu_2O$ materials. It is concluded that the current oscillations are analogous to the previously described potential oscillations obtained under controlled current conditions in alkaline Cu(II)-lactate, -tartrate and -citrate solutions. Rotating disk electrode results clearly show that the reduction of the Cu(II)-complexes is kinetically controlled and that the rate of the reduction increases with increasing pH and temperature. It is also shown that the presence of a cathodic peak on the anodic scan in the cyclic voltammograms can be used to identify the experimental conditions leading to the spontaneous current (or potential) oscillations. Electrochemical quartz crystal microbalance results indicate that the cathodic peak stems from an increased rate of the reduction of the Cu(II)-citrate complexes due to a rapid increase in the local pH. This causes $Cu_2O$ rather than Cu to be deposited which, however, results in a decrease in the local pH and a decreasing current. In situ ellipsometry data confirm that $Cu_2O$ deposition replaces that of Cu in the potential region of the cathodic peak. The present findings should facilitate syntheses of nanolayered materials based on spontaneous potential or current oscillations.

*Keywords:* Current oscillations; Cu; $Cu_2O$; Nanolayers; Local pH variations; Citrate

## 1. Introduction

Nanostructured materials have been extensively studied during the last decade due to their interesting electronic, magnetic, electrochemical and optical properties and potential use as catalytic- and electrode materials in various devices. The preparation of nanostructured metals and semi-conducting materials has consequently become an important research area particularly due to the presence of quantum effects [1]. The presence of nanosized metal particles in materials has also been found [2] to influence the absorption, scattering and luminescence properties of materials.

One promising approach to the synthesis of nanostructured materials involves electrodeposition. Switzer et al. [3] have elegantly demonstrated that layered nanostructures of copper/cuprous oxide can be deposited from alkaline copper(II)-lactate solutions by the application of a constant cathodic current so that spontaneous potential oscillations are obtained. The latter type of material, which has been proposed for use in devices based on quantum mechanical tunnelling effects [4], has been shown to exhibit negative differential resistance in perpendicular transport measurements at room temperatures due to resonant tunnelling [4]. Similar electrical transport properties were recently reported for $Cu_2O$ nanoparticles embedded in a polyimide matrix [5]. $Cu_2O$ is a semiconductor with a direct band gap of about 2 eV at room temperature [6] and the p-type conductivity of single crystal $Cu_2O$ prepared by high temperature grain growth methods has been reported to be due to the presence of Cu vacancies [7]. The charge carrier density of $Cu_2O$ deposited from an alkaline Cu(II)-lactate solution has been reported to be $10^{12}$–$10^{14}$ $cm^{-3}$ [8] while the resistivity of a $Cu_2O$ film grown at $-0.555$ V vs. SCE in a Cu(II)-lactate solution at pH 9 and 70 °C was found to be $5 \times 10^6\ \Omega\,cm$ [9].

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Electrochemical quartz crystal microbalance measurements [10] have shown that the material obtained during spontaneous potential oscillations was composed of $Cu_2O$ layers situated between composite layers containing Cu and $Cu_2O$. The composite layer was proposed to consist of copper oblate spheroids embedded in a cuprous oxide matrix, based on non-linear optical measurements and comparisons with theory for the second harmonic generation (SHG) intensity [2]. The thickness of the $Cu_2O$ and composite layers has been tuned in the range between 0.4 and 2.5 nm and 5 nm and 20 nm, respectively, by alteration of the current density [10]. The thickness and composition of the layers could, however, not be tuned independently and the copper concentration in the composite layer was found to increase with increasing current density. The size of the particles in the copper composite layer was found to be increased when illumination with laser light was used during the deposition [11].

The stacked Cu/$Cu_2O$ nanolayers [11–14] have so far only been obtained using constant current electrolysis under conditions that yielded spontaneous potential oscillations. In the latter case, high concentrations of copper ions in the presence of an excess of an organic ligand such as lactate [3,14], tartrate [14,15] or citrate [16] are generally used in alkaline solutions (pH 8–11), often at elevated temperatures (30–50 °C). As was recently discussed by Eskhult et al. [16], the oscillations are only anticipated for Cu(II)-complexes, (such as Cu(II)-lactate, -tartrate or -citrate complexes) which contain ligands that undergo protonation upon their liberation. The potential oscillations, during which Cu and $Cu_2O$ are sequentially deposited, have been shown to originate from local changes of the pH close to the working electrode [14]. Since the Cu(II)-citrate speciation is well-known, Eskhult et al. [16] recently employed this system as a model system for studying the origin of the spontaneous potential oscillations under galvanostatic conditions. It was found that the potential became more positive during the deposition of copper as a result of a local increase in the pH (due to the protonation of the hydroxyl group of the liberated citrate). This eventually gave rise to the deposition of $Cu_2O$ rather than Cu. The local pH then, however, dropped due to the presence of a comproportionation reaction involving Cu(II) and Cu and the lack of $OH^-$ production during the deposition of $Cu_2O$. This caused Cu to be deposited again and the initiation of a new oscillation cycle. Eskhult et al. [16] also demonstrated that a fraction of the deposited $Cu_2O$ underwent reduction to Cu when the local pH was decreased.

Our model for the potential oscillations [16], based on variations in the local pH, also implies that it should also be possible to observe oscillations in the current during potentiostatic conditions. Such current oscillations, yielding Cu/$Cu_2O$ layered materials, have, however, so far not been described for the present Cu(II)-ligand systems although they could constitute an alternative way for the synthesis of these materials. At this point it should be stressed that oscillations are relatively common in electrochemical systems and that a large number of other systems exhibiting electrochemical oscillations have been described in the literature as discussed by e.g. Strasser et al. [17], Krischer [18] and Hudson and Tsotsis [19]. As discussed by Strasser et al. [17] and Krischer [18], the oscillating systems can be classified into different categories (e.g. chemical oscillators, negative differential resistance (NDR) oscillators and hidden negative differential resistance (HNDR) oscillators) depending on the oscillation mechanism. While the NDR and HNDR oscillators depend on alterations in the double layer potential caused by changes in the iR drop, chemical oscillators depend on periodic variations of the rate of chemical reactions. Although a large number of NDR and HNDR systems have been identified [17–19], only a few examples of chemical oscillators have so far been described in the literature. As has been shown by several groups [20–23], NDR current oscillations can, for example, be seen during copper and tin codeposition from solutions containing a surface active compound. These oscillations were found to give rise to multilayer nanostructures composed of two alloy layers of different composition [21,22].

Another important and related question concerns the possibility to straightforwardly identify the experimental conditions giving rise to the desired oscillations. It is well known [11–16] that spontaneous potential oscillations only are obtained under rather specific experimental conditions (e.g. pH, current density, temperature, ligand concentration and hydrodynamic conditions). For an unknown system, a series of trial-and-error experiments hence generally has to be carried out to explore whether oscillations can indeed be obtained for that particular system or not. Since cyclic voltammetry often is used as one of the first techniques in the characterization of an electrochemical system, it is important to investigate if the shapes of the cyclic voltammograms can be used to predict the behaviour of the system with respect to the possibilities to obtain oscillations in the potential or current. Such possibilities would clearly facilitate the optimisation of the manufacturing of nanolayered materials based on spontaneous potential (or current) oscillations.

The voltammetry of Cu(II) in citrate solutions has been studied previously [24] using TaN and Pt electrodes to study copper nucleation on barrier layers. Studies of partial-current polarization curves for copper deposition for a wide range of bulk pH values and free citrate concentrations have likewise been carried out [25] to investigate the copper deposition mechanism. In addition, the kinetics of copper electrodeposition from alkaline citrate solutions has been studied [26] with platinum rotating disc electrodes. Current–potential curves for rotating Cu-disc-Pt-ring electrodes have also been recorded in the presence of various additives with the aim to find the optimal conditions for damascene copper plating [27].

In the present study, the possibilities to obtain current oscillations during constant potential and cyclic voltammetric conditions are investigated on the basis of the Cu(II)-citrate system and the oscillation model proposed by Eskhult et al. [16]. The possibilities to use cyclic voltammetric experiments as a straightforward way to predict whether a system will exhibit spontaneous oscillations in the potential or current are likewise discussed based on electrochemical quartz crystal microbalance (EQCM) and in situ ellipsometry measurements in alkaline Cu(II)-citrate solutions composed of 0.4 M $CuSO_4$ and 1.2 M citrate. The influence of different experimental conditions (e.g. pH, temperature, hydrodynamic conditions) on the behaviour of the system under controlled potential conditions is also discussed, as well as the implications of the findings on the synthesis