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# Quasiperiodic Behavior in the Electrodeposition of Cu/Sn Multilayers: Extraction of Activation Energies and Wavelet Analysis

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**Abstract**

This work reports the observation of quasiperiodic behavior during the oscillatory electrodeposition of Cu/Sn multilayers. By employing a wavelet transform on the current from the time-series, and by varying the temperature, it was possible to extract two apparent activation energies from the oscillation frequencies, of two different domains: one believed to be mainly activation limited (near 50 kJ/mol), extracted from a higher frequency oscillation, and one thought to be mainly diffusion limited (near 20 kJ/mol), extracted from a lower frequency oscillation. These energies are comparable to those calculated using current values from the cyclic voltametry in different temperatures.

***Key words:***

*Electrodeposition, nonlinear dynamics, quasiperiodicity*

## Introduction

Research of self-organized materials is an ever-growing field, as it can yield products with unique physicochemical properties.[1] A known method for preparing these materials is the electrodeposition of multilayers. More specifically for the Cu/Sn system, it has been reported the emergence of a period-one oscillations, even though the mechanism behind this nonlinear behavior is not well understood.[2]

In this work, the previously undescribed quasiperiodic behaviour of the electrodeposition of Cu/Sn multilayers is studied. In addition to reporting this complex behaviour, the main objective is to provide some insights on the electrodeposition mechanism of the formation of these Cu/Sn multilayers, through the extraction of apparent activation energies. This work has been submitted for publication in a peer-reviewed journal.

## Results and Discussion

To study the electrodeposition mechanism, a constant potential, *c.a.* -0.46 V *vs.* SCE, was applied, and the current was monitored over time. Different temperatures were employed (15 ºC, 20 ºC and 25 ºC) to calculate apparent activation energies.

Image 1 presents regions of three distinct time-series, each one from the experiments done at different temperatures. On each of them, two oscillation patterns have emerged: the period-one oscillations, seen early in the time-series, and the quasiperiodic oscillations, seen later.

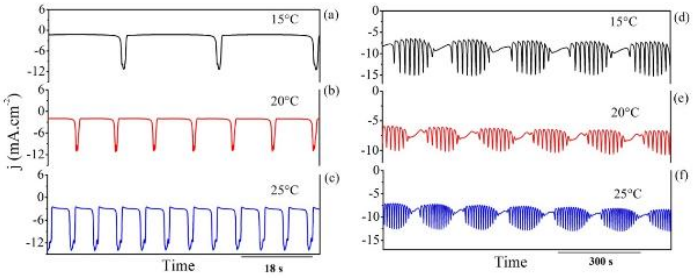


**Image 1.** Different parts of the time-series for each temperature. (a), (b) and (c) depicting the period-one oscillations and (d), (e) and (f), the quasiperiodic behaviour.

Using the continuous wavelet transform, the following oscillation frequencies were extracted: period-one oscillation frequency (denominated P1), and both oscillation frequencies observed in the quasiperiodicity (the faster oscillation frequency, denominated QP1, and the modulating slower oscillation frequency, denominated QP2). With these frequencies in hand, it was possible to calculate the apparent activation energies: 95 ± 5 kJ/mol for P1, 48 ± 10 kJ/mol for QP1, and 26 ± 6 kJ/mol for QP2.

The two calculated apparent activation energies from the QP, one ~48 kJ/mol and the other ~26 kJ/mol, were compared with data from the literature, and it was hypothesized that the first might be mainly activation limited, while the second would be mainly diffusion limited, thus providing some information regarding the electrodeposition mechanism.[3]

Corroboration for the calculated apparent activation energies values comes from cyclic voltammetry experiments. Apparent activation energies were calculated on several potentials between -0.39 V and -0.27 V, using the current values of the voltammetries done at different temperatures. For higher potential values, near to 50 kJ/mol were obtained, and with the reduction in the applied potential, the energy steadily decreased, reaching values close to 20 kJ/mol. This lines up with the values calculated from the quasiperiodic oscillation frequencies, providing reliability to the values reported.

## Conclusions

It is reported the quasiperiodic behavior in the electrodeposition of Cu/Sn multilayers. Using two different techniques, namely analysis of frequency of oscillations in the time series and cyclic voltammetry, it was possible to isolate two main apparent activation energies, of magnitudes 50 kJ/mol and 20 kJ/mol, which might be related to activation and diffusional processes, respectively, contributing with the understanding of the electrochemical mechanism in play.

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