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Honors Thesis

An Honors Thesis Titled

How Modifying Electrode Shapes Impacts the Fractals Formed During Electrochemical Deposition

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by

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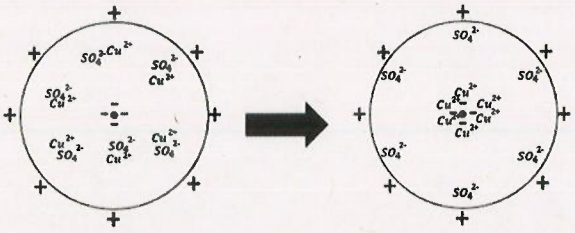
Abstract

Electrochemical deposition is a process by which ions migrate to a specific location, solidify, and form clusters. Clusters formed by copper ions during electrochemical deposition can be influenced by the electric field between the electrodes. This electric field can be modified by changing the shape of the outer electrode. The influence of this change can be quantified by determining the relative probabilities that a branch will form towards particular regions. This paper will discuss the impact of the electrode shape on the directional probabilities of individual branches as well as expected cluster growth patterns.

1 Introduction

Electrochemical deposition is a process by which positively charged copper ions migrate towards a negatively charged terminal, as shown in Figure 1.

Figure 1: A standard setup.



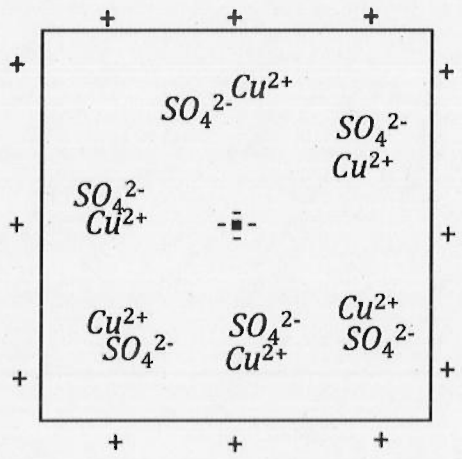
Once the copper ions reach the negative electrode, they solidify and stick to the electrode. Eventually, the number of copper ions that stick to the negative electrode becomes large enough that a distinct fractal pattern becomes visible. [1]

Figure 2: A copper cluster formed by Electrochemical Deposition

The goal of this research is to determine how changing the shape of the outer electrode changes the fractal pattern formed. For ex-

ample, what does the fractal look like if the outer circle from Figure 1 is changed to a square?

Figure 3: Hypothetical Setup with a Square Electrode



Electrochemical deposition is commonly modeled using Diffusion Limited Aggregation (DLA). DLA is a process by which simulated particles move in a series of random linear paths until they reach one of a series of acceptable ending conditions. In the case of electrochemical deposition, the walk of a particle ends once it either meets the cluster or gets too far away from the cluster.[2] However, these models can be improved by biasing the random walks in favor of the direction of the electric field. In other words, the model can be improved by making the particle more likely to go in the direction of the electric field than in other directions.[3] This can be taken a step further by modeling electrochemical deposition as a deterministic system with high sensitivity to random initial conditions.

2 Methods

2.1 Theory and Simulations

The migration of the copper ions towards the negative electrode is caused by the electric field emanating from the positive electrode. This electric field can be expressed as a sum of the electric fields emanating from a large number of point charges evenly distributed along the perimeter of the outer electrode. For example, in Figure 3, the outer electrode has 12 point charges, three on each

side. Each point charge has an associated electric field in accordance with the equation:

$$\vec{E} = \frac{k_e * q}{r^2} * \hat{r} \quad (1)$$

[4] Where k_e is the electrostatic constant, q is the amount of charge associated with the point charge, r is the distance between the point charge and the point of interest, and $\hat{r}$ indicates the direction associated with r.

So, the total electric field caused by the outer electrode is the sum of the individual electric fields:

$$\vec{E} = \sum_{i=1}^{n} \frac{k_e * q}{r_i^2} * \hat{r_i} \quad (2)$$

Where n is the total number of point charges and r_i is the distance between the point of interest and the ith point charge. For example, r_3 is the distance between the copper ion and the third point charge on the electrode. Once the electric field is calculated, the force exerted on each copper ion can be calculated using the equation:

$$\vec{F} = q_1 * \vec{E} \quad (3)$$

[4] Where q_1 is the charge of an individual copper ion. From here, the acceleration each copper ion undergoes can be calculated using the equation:

$$\vec{a} = \frac{\vec{F}}{m} \quad (4)$$

[5] Where m is the mass of the copper ion. So, the equation for the acceleration of an individual copper ion is given by the equation:

$$\vec{a} = \frac{q * \sum_{i=1}^{n} \frac{k_e * q}{r_i^2} * \hat{r_i}}{m} \quad (5)$$

This equation shows that the acceleration is dependent on the distance between the copper ion and the point charges. So, the acceleration must be dependent on the position of the copper ion. This means that as a copper ion moves through the electric field, the acceleration will change. As a result, equation

6, which is only valid for a constant acceleration, will not work.

$$\vec{x} = \vec{x_0} + \vec{v_0}t + \frac{1}{2}\vec{a}t^2 \quad (6)$$

[6] Where x is the final position of the particle, x_0 is the initial position, v_0 is the initial velocity, and t is the time elapsed. However, if only small intervals of time are considered, the velocity will be approximately constant over those intervals of time, so the acceleration will be zero, and Equation 7 can be used to calculate the position at the end of each time interval.

$$\vec{x}_j = \vec{x}_{j-1} + \vec{v}_{j-1}\Delta t \quad (7)$$

Where $\vec{x}_j$ is the position at the end of the time interval, $\vec{x}_{j-1}$ is the position at the beginning of the time interval, $\vec{v}_{j-1}$ is the constant velocity during the time interval, and Δt is the time interval. By letting the end of one time interval be the beginning of the next, this equation can be used in conjunction with Equation 8 to determine the position after a large number of time intervals given only information at the beginning of the first time interval.

$$\vec{v}_j = \vec{v}_{j-1} + \vec{a}_{j-1}\Delta t \quad (8)$$

Where $\vec{v}_j$ is the velocity at the end of each time interval and $\vec{a}_{j-1}$ is the acceleration at the beginning of each time interval. So, the only information that is needed to determine the final position of a copper ion is the initial position of the ion, the initial velocity of the ion, and the electric field in the region between the two electrodes. The electric field can be determined from Equation 2, the initial position can be generated randomly anywhere between the two electrodes, and the initial velocity can be generated randomly using the probability distribution of velocities of solutions at 20° C.

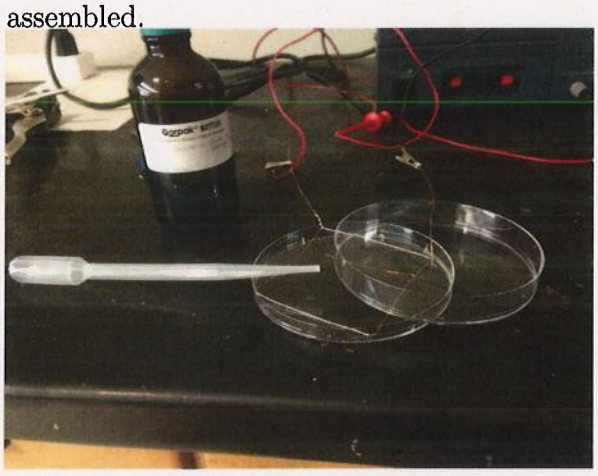
Like the DLA model, this model uses

a series of linear paths. In this model, however, only the first linear path is random. All of the subsequent paths are determined by the mathematics described above. This is done to focus the simulation on the electric field's impact on the physical phenomenon.

2.2 Data Collection

The clusters were grown by applying a voltage to a solution of copper sulfate through two electrodes. The setup was contained within a petri dish, using the lid upside down as the base and the bottom nested inside the lid. The outer electrode was molded into a shape and positioned between the two pieces. The inner electrode was heated up with a soldering iron and pushed through the bottom piece, melting away the plastic. A 0.5 molarity solution of copper sulfate in deionized water was pipetted between the two pieces, filling up the space between the electrodes. The setup was then pressed together and taped on the sides to enhance stability and create an approximate two-dimensional environment. The electrodes were then connected to a voltage source producing 6.0 volts, with the positive terminal on the outer electrode and the negative terminal on the inner electrode.

Figure 4: This is how the setup would be assembled.



The trials were then run at room temperature under these parameters with the shape of the outer electrode as the sole variable. Once the clusters were nearing the outer electrode, the voltage source was removed and the setup was put aside for