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. 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. 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:

$$E = \frac{k_e \times q}{r^2} \times \hat{r}$$  \hspace{1cm} (1)$$

$$F = q_1 \times E$$ \hspace{1cm} (3)

[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:

$$\vec{E} = \sum_{i=1}^{n} \frac{k_e \times q_i}{r_{i}^2} \times \hat{r}_i$$ \hspace{1cm} (2)$$

Where $n$ is the total number of point charges and $r_i$ is the distance between the point of interest and the $i$th 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:

[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:

$$\vec{a} = \frac{\vec{F}}{m}$$ \hspace{1cm} (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:

$$\vec{a} = \frac{q \times \sum_{i=1}^{n} \frac{k_e \times q_i}{r_{i}^2} \times \hat{r}_i}{m}$$ \hspace{1cm} (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.

\[ \ddot{x} = \ddot{x}_0 + \ddot{v}_0 t + \frac{1}{2} \dddot{a} t^2 \]  \hspace{1cm} (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.

\[ \ddot{x}_j = \ddot{x}_{j-1} + \ddot{v}_{j-1} \Delta t \]  \hspace{1cm} (7)

Where \( \ddot{x}_j \) is the position at the end of the time interval, \( \ddot{x}_{j-1} \) is the position at the beginning of the time interval, \( \ddot{v}_{j-1} \) is the constant velocity during the time interval, and \( \Delta t \) 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.

\[ \ddot{v}_j = \ddot{v}_{j-1} + \ddot{a}_{j-1} \Delta t \]  \hspace{1cm} (8)

Where \( \ddot{v}_j \) is the velocity at the end of each time interval and \( \ddot{a}_{j-1} \) 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
later evaluation.

Regardless of the shape of the outer electrode, it must be tied together somewhere. The location of the tie, later referred to as the knot, provides a reference point when discussing the location of cluster branches.

To improve the precision of parameters involving the shape and positioning of electrodes, we 3D printed the following pieces.

Figure 5: This piece enabled us to bend the wire into precise square outer electrodes by molding the wire around the piece as such.

Figure 6: The holes in this piece enabled us to precisely place the central electrode either exactly in the center or a known distance off the center of the petri dish. The perimeter of the piece enabled us to precisely form circular outer electrodes.

3 Early Observations

3.1 Simulations

Using the mathematical processes described above, a java-based computer simulation can predict the fractals generated by any electrode shape. Below is the output of the simulation for the circular electrode approximated using 62415 point charges evenly spaced along the outer electrode with 30 copper ions:
Figure 7: Simulated cluster with 30 particles.

3.2 Experiments

Early experiments produced unexpected hair-like strands of copper-colored material near the outer electrode, as shown in Figure 8:

Figure 8: Strands coming off the outer electrode.

In the figure 7, the largest circle is the circular outer electrode. The two concentric circles in the middle represent the inner electrode. The rest of the circles are copper ions that began branch formation. With only 30 particles, the simulation generated an image that appears similar to Figure 2. This is an encouraging sign, but simulations involving more particles (and therefore more computational power) need to be run to further test the accuracy of the simulation.

These hairs formed with every cluster regardless of voltage applied, solution concentration, use of distilled or deionized water, or cleaned copper wire. We eventually tested a positively charged inner ring electrode with a negatively charged outer electrode. This led to no cluster growth and the inner
electrode becoming eventually replaced with the hair-like structures. From this result, we hypothesized that the electric field was pulling copper off of the wire until there is no wire left. When the positive electrode was the outer electrode, there was significantly more wire, so most of it remained intact. When the inner electrode was positive, however, there was not nearly as much copper, so the entire electrode was consumed by this process.

Due to the consistency of the various tests involving the hairs (changing physical parameters doesn't significantly change the amount or positioning of the hairs), we believe that this phenomenon will have minimal impact on our research question. As a result, we began investigating our research question without taking the hairs into account.

4 Data Analysis

To assist with the cluster analysis, a printout of the following image is placed under the petri dish, aligned with the electrode.

![Figure 9: Diagram of petri dish with partition lines]

The lines partition the petri dish into eight regions. The regions are then categorized: regions towards the center of the square and regions toward the corners of the square. Regions of the circular electrode can be categorized as one region containing the knot and seven not containing the knot.
Placing the printout under a circular electrode and tallying the direction of branches as shown below allows classification of circular electrode branches.

Figure 10:

In the above example with a circular electrode, one branch grows towards the knot while two grow away from the knot. Repeating this test with seven clusters yields the following table:

<table>
<thead>
<tr>
<th>Number of Clusters</th>
<th>Branches Toward Knot</th>
<th>Branches Away From Knot</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>1</td>
<td>23</td>
</tr>
<tr>
<td>Per Cluster</td>
<td>Per Cluster</td>
<td>Per Cluster</td>
</tr>
<tr>
<td>1</td>
<td>32</td>
<td>3280</td>
</tr>
<tr>
<td>Percent of Branches</td>
<td>Percent of Branches</td>
<td>Percent of Branches</td>
</tr>
<tr>
<td>N/A</td>
<td>24.83%</td>
<td>85.17%</td>
</tr>
</tbody>
</table>

As shown in the table, approximately 15% of the branches were in the region containing the knot. If the probability density of branches was uniform, approximately $\frac{1}{8}$, or 12.5% of the branches would be in the region containing the knot. This disparity suggests that branches are slightly more likely to move towards the knot than to similar regions without the knot.

The process can be repeated with square electrodes as shown in Figure 12:
In this example, no branches are towards the center, two are towards corners, one is towards the knot, and two intersect partition lines. After doing this for all 16 clusters (eight square clusters with the knot at the midpoint of a side and 8 with the knot at a corner), the probability of a particular branch approaching the electrode within a certain regional category (towards the midpoint or towards the corner) can be calculated. This is done in the following table:

Figure 13: Data in this table was collected from eight clusters generated from each type of square electrode and seven clusters generated form the circular electrode. Note: Branches towards the knot were counted twice: once as either towards the center or towards the corner and once as towards the knot.

<table>
<thead>
<tr>
<th>Electrode Type</th>
<th>Branches Toward Center</th>
<th>Branches Toward Corner</th>
<th>Branches on Line</th>
<th>Percent of Branches</th>
<th>Percent of Branches</th>
<th>Percent of Branches</th>
<th>Percent of Branches</th>
</tr>
</thead>
<tbody>
<tr>
<td>Center Tie</td>
<td>15</td>
<td>12</td>
<td>10</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Corner Tie</td>
<td>11</td>
<td>9</td>
<td>8</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Center Tie</td>
<td>1.875</td>
<td>1.68</td>
<td>1.25</td>
<td>.625</td>
<td>4.125</td>
<td>4.125</td>
<td>4.125</td>
</tr>
<tr>
<td>Corner Tie</td>
<td>1.875</td>
<td>1.875</td>
<td>1.25</td>
<td>3</td>
<td>3.875</td>
<td>3.875</td>
<td>3.875</td>
</tr>
<tr>
<td>Center Tie</td>
<td>35.333</td>
<td>36.526</td>
<td>30.101</td>
<td>13.153</td>
<td>80</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Corner Tie</td>
<td>35.684</td>
<td>32.258</td>
<td>32.258</td>
<td>12.903</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Each regional category (towards the midpoint and towards the corner) consists of four regions. As a result, the number of branches in a region should be a quarter of the number of branches in its category. However, for both electrode types the region containing the knot has more than a third of the number of branches in its category. This supports the observation from the circular electrode.

There does not appear to be a strong correlation between regional category and probability of a branch ending in that region. This suggests that the probability of a branch growing towards the midpoint of an edge is the same as the probability of a branch growing towards a corner. However, branches cross the partition lines about a third of the time. Rotating the printout so that a partition line is a particular angle from the corner of the square and tallying the resulting number of branches that intersect the partition can reveal information about the probability density of branch direction. A similar process can be done with the circular electrode measuring angles relative to the direction of
the knot. The data collected by doing this is put into the following table and graph:

<table>
<thead>
<tr>
<th>Angle</th>
<th>Circle Electrode Intersections</th>
<th>Center Tip Intersections</th>
<th>Corner Tip Intersections</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>12</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>17</td>
<td>17</td>
<td>16</td>
</tr>
<tr>
<td>10</td>
<td>12</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>15</td>
<td>11</td>
<td>13</td>
<td>9</td>
</tr>
<tr>
<td>20.5</td>
<td>11</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

**Figure 14:**

For the circular electrode (the blue curve), the number of intersections between cluster branches and partition lines varies minimally between 11 and 13. This confirms our initial suspicion that branches are approximately uniformly distributed for circular outer electrodes. Intersections between cluster branches and partition lines varies significantly more between 10 and 17 for both square electrode configurations. There are significantly more branches intersecting partition lines when a partition line is within five degrees of the corner of the square electrode. This suggests that branches are more likely to form in the red regions in the image below:

**Figure 15:**

Figure 15 shows that regions near the midpoints of the sides are approximately as likely to contain branches as regions near the corners. This means that the red regions containing the midpoints exhibit similar behavior as the red regions containing the corners.
5 Significance and Applications

Electrochemical deposition has applications in many high-tech fields including microelectronics and nanobiotechnology. Many small-scale semiconductors are manufactured using electrochemical deposition and related processes. Use of electrochemical deposition has also enabled transistor size to decrease while increasing component efficiency and keeping manufacturing cost low. [8] Electrochemical deposition is also used to make materials for use in the field of nanobiotechnology. A key property of electrochemical deposition in this field is the precise symmetries that can arise from it. [9]

6 Future Research

This research can be expanded on in a few areas. The Java code described earlier in this paper can be adapted to run on a supercomputer. After several runs of the simulation, results on the computer can be compared to results in the lab to determine the accuracy of the mathematics described in the theory section.

In the lab, the composition and formation of the hair-like strands can be investigated. Different electrode shapes, such as a regular pentagon or a regular hexagon, can also be tested. These tests can determine if the pattern of increased probability density near midpoints and corners continues for all regular polygons.

7 Conclusion

The goal of this research is to determine how the shape of the outer electrode impacts the shape of the cluster growths. We initially hypothesized that regular polygon electrodes would cause branches to be biased towards the corners of the electrode and away from the midpoints of the electrode’s sides. We
believed this because the increased length of wire in that region causes a stronger electric field there, which we thought would cause an increased force on the copper ions. We then decided to test this hypothesis experimentally.

We then optimized the precision of the experiment using the 3D printed pieces. With the optimized experiment, we were able to generate clusters for seven circular electrodes, eight square electrodes with a knot in the corner, and eight square electrodes with a knot in the center. Next, we analyzed the clusters that we grew.

We ran three tests on the clusters, each described in the analysis section. The test of the circular electrode indicates that branches are slightly more attracted to the knot than they are to other areas of the outer electrode. The first test with the square electrodes shows that branches are equally attracted to midpoints and corners of square electrodes. The second square electrode test showed that branches are more attracted to these areas than to other areas.

These results do not align with the initial hypothesis, but do show that the electrode shape has an impact on the shape of cluster growth.

References


