Determination of a correlation between applied voltage and fractal dimension of an electrodeposited aggregate formed by DLA-based clustering

John Enns

Science One Program

University of British Columia

Vancouver, Canada

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Abstract

The accumulation of solid copper in a 2-dimensional electrolytic cell can be modeled by diffusion limited aggregation of particles undergoing Brownian motion. The resulting aggregate forms an approximate fractal shape. It is hypothesized that the fractal dimension of such aggregates will correspond positively with the voltage applied to the cell. Measurement of the fractal dimension of aggregates formed at voltages of 8 V, 12 V and 16 V are made through use of the box-counting technique, showing statistically significant mean dimensions of 1.28 ± 0.04, 1.51 ± 0.01 and 1.65 ± 0.02 respectively. A conclusion is made supporting the hypothesis.

Introduction

Diffusion limited aggregation (DLA) is a model for the growth of an aggregate by the clustering of individual point particles undergoing random movement in 2 (or more) dimensions due to Brownian motion, which is hypothesized to occur when diffusion is the main form of transport in the system [1]. The result is a branched fractal shape called a Brownian tree, with fractional fractal dimension. Computer simulations involving individual point particles usually result in a dimension of approximately 1.7 [2], but this is variable due to the intrinsically random nature of the clustering.

Approximate diffusion limited aggregation is observed in many physical systems [2], including electrodeposition. In a 2-dimensional electrolytic cell of a copper anode, cathode and electrolyte, a diffusion limited aggregate will form when a voltage is applied to both electrodes. Aqueous copper ions will undergo the reaction

$$Cu^{2+} + 2e^{-} \rightarrow Cu_{(s)} \qquad (1)$$

and be reduced to solid copper at the cathode, forming a fractal aggregate. The reverse of Eq. (1) will occur at the anode, sustaining the current. Qualitatively, lower fractal dimension entails a more dendritic, less branched shape while higher fractal dimension entails a multiply branched structure. Quantitative estimation of the dimension of the fractal is possible through the use of a box-counting technique, which involves the drawing of boxes of different side length ε over a photograph of the fractal. The number of boxes $\mathcal{N}(\varepsilon)$ needed to completely cover the aggregate is theorized [3] to be proportional to the scale factor of the boxes $1/\varepsilon$ in a power law, with the fractal dimension D as the power:

$$\mathcal{N}(\varepsilon) = \left(\frac{1}{\varepsilon}\right)^{D}. \qquad (2)$$

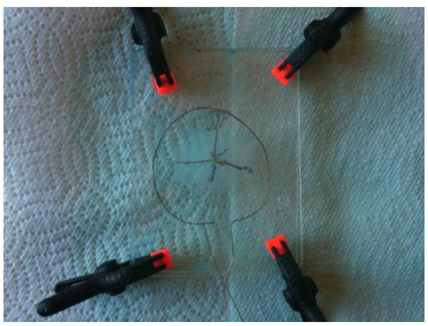
Taking data of $\mathcal{N}(\varepsilon)$ for different ε and plotting in a log-log plot will result in the estimation of D as the slope of the resulting graph:

$$\log \mathcal{N}(\varepsilon) = D \log 1/\varepsilon. \qquad (3)$$

It is by this method that this experiment hopes to measure the fractal dimension of the aggregate formed when different voltages are applied to such an electrolytic cell. The hypothesis is that a higher voltage will correspond to a higher fractal dimension. This prediction is based on the finding that an electodeposited aggregate behaves more like a DLA cluster at high voltages [2]. Thus, I would also expect to find fractal dimensions of ~1.7 at the highest voltages.

Methods

The electrolytic cell was constructed in the following manner (see Figure 1): Two plastic plates (11.6 cm by 8.6 cm) were sandwiched together. Two small holes of diameter 1 mm (the diameter of the copper wire to be used) were drilled through both plates at their centers. One strand of copper wire was threaded through the holes, and then connected to the negative terminal of a power supply providing a variable voltage. This wire was the cathode, at which copper ions were reduced. A second copper wire, connected to the positive terminal, was bent into a rough circular shape of diameter large enough to be just contained within the boundaries of the plastic plates, and then placed in between the two plates, surrounding the negative terminal. It was made certain that the positive loop of copper wire did not self-intersect at any point. This wire was the anode at which solid copper was oxidized into solution. The electrolytic solution of 0.5 M $CuSO_4$ was also placed in between the two plates such that it touched the cathode and the anode at all points. It is important that all parts of the copper wires touching the electrolyte were uninsulated. After the solution was placed, clamps were placed at all four corners of the two plates, leaving the space between them equal to the diameter of the copper wire used (around 1 mm), thus approximating a 2-dimensional space in which to grow the aggregate.



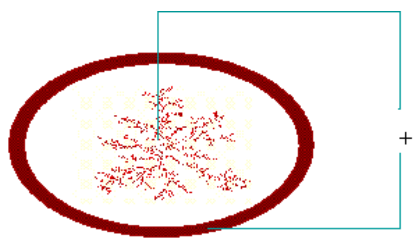


Figure 1. *Photograph and schematic of electrolytic cell, showing cathode and anode wires, along with a small aggregate. Schematic reproduced without permission from [4].*

The accumulation of solid copper around the anode by Eq. (1) and its reverse is driven by the application of a potential difference between the positive and negative terminals of the electrolytic cell, causing a current to run through the cell. The resulting aggregates grew to full size over a period of 20 to 30 minutes. The current was stopped at the point where the aggregate was on the verge of touching the anode, to prevent a short circuit. It was observed that allowing a short circuit to occur lead to destruction of the aggregate. The majority of the final fractal structures analyzed were in the range of diameter 4 cm at their widest. Photos of the aggregates were taken using a 3.0 Megapixel iPhone camera at close range. Photos were uploaded into a computer and treated with Windows Picture Editor in order to increase brightness and contrast, making the fractal shape stand out. Finally, the photos were printed and then cut into a square shape (of approximately 15 cm side length) to allow for box-counting analysis.

Box-counting dimension of the fractal shapes were determined by hand-drawing boxes over the edited photos. Data with uncertainty was taken of the box side length ε (relative to $\varepsilon = 1$, the original side length of the photo) and $\mathcal{N}(\varepsilon)$, the number of boxes needed to completely cover the image of the fractal structure. Uncertainty in these two figures was due to inaccuracy in measuring where to subdivide lines for the boxes and uncertainty in whether a box covered the structure or not (due to blurriness, pixellation, etc.), respectively. These data, with Eqs. (2) and (3) in mind, were transformed into $1/\varepsilon$, $\log(1/\varepsilon)$, and $\log(\mathcal{N}(\varepsilon))$, keeping uncertainties using the relation

$$\delta\big(f(y)\big) = f^{'}(y)\delta y, \qquad (4)$$

where $f(y)$ represents a function applied to the data point y and δ represents an uncertainty. The linear relationship of $\log(1/\varepsilon)$ and $\log(\mathcal{N}(\varepsilon))$ had a slope D (as in Eq. (3)), where D was the box-counting dimension of the original aggregate, determined using the "Trend Line" function in Microsoft Excel 2007. Uncertainty in the slope of the regression line (the dimension) was determined using:

$$\sigma_D = \sqrt{\frac{\frac{1}{n-2}\sum_i^n (y_i - \hat{y}_i)^2}{\sum_i^n (x_i - \bar{x})^2}}, \qquad (5)$$

with σ_D the uncertainty in D, n the number of data points, $\bar{x}$ the average x-value and $\hat{y}$ the y-value predicted by the regression line. In this way, the box-counting dimension with uncertainty was determined for aggregates grown in the electrolytic cell at different voltages.

Results & Discussion

It was observed that immediately after turning on the power, copper ions would begin to form the aggregate. After about 5 seconds, initial branching was visible, at a diameter of about half a centimeter. Aggregates at all voltages underwent the same initial macroscopic branching process. At a time of about 4 – 5 minutes, aggregates at lower voltages began to grow one branch more than the rest, leading to a more dendritic shape. For the higher voltage aggregate, branching was fairly constant throughout the process. Branches would begin to grow at any point and stop at any time, although with the lower voltages, there seemed to be a preference for only growing at the tips of already existing branches. The growth process, visible during the early stages, became slower as the aggregate grew larger. Initial current started at about 50 mA and rose throughout the process, going as high as 400 mA. This was observed in all trials. Upon examination of the anode after 20 minutes, slivers of copper wire had broken off, as the wire underwent the reverse reaction of Eq. (1).

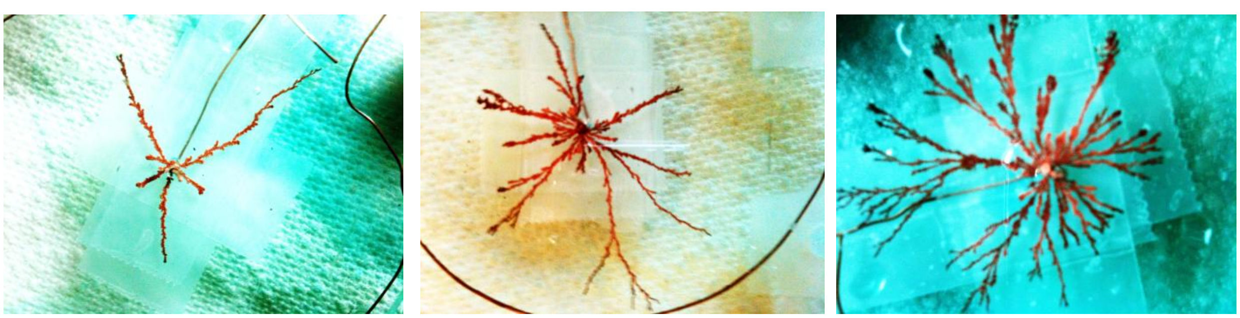


Figure 2. *False-colour photographs of aggregates grown at 8V, 12V and 16V respectively.*

Overall, data was taken for three different voltages (8 V, 12 V, and 16V). Each trial was repeated three times, for a total of 9 measures of box-counting dimension (see Appendix A). Three samples of the aggregate formed at each of the different voltages are visible in Figure 2 (above). It is immediately apparent that the higher voltage aggregates are more branched than the lower voltage aggregates, implying a higher dimension, which is in accordance with the hypothesis. The results of box-counting analysis done on the 3 aggregates in Figure 2 are visible in the plots of $\log(1/\varepsilon)$ vs. $\log(\mathcal{N}(\varepsilon))$ seen in Figure 3 (below):

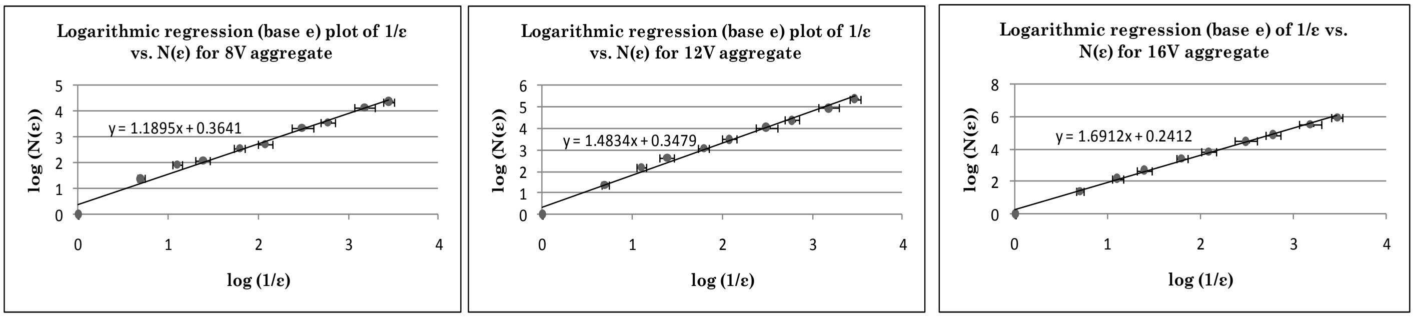


Figure 3. *Graphed box-counting data from the aggregates in the previous figure, showing respective dimensions of 1.19, 1.48 and 1.69. Vertical error bars in $\mathcal{N}(\varepsilon)$ too small to be visible.*

In total, the following dimension and uncertainty were recorded for each of the 9 aggregates grown:

Table 1. *Fractal dimension and uncertainty of each of 9 copper aggregates grown in the electrolytic cell at different voltages.*

Voltage	Measured box-counting dimension (uncertainty from Eq. (5))		
	Trial #1	Trial #2	Trial #3
8 V	1.19 ± 0.06	1.33 ± 0.04	1.31 ± 0.07
12 V	1.48 ± 0.05	1.53 ± 0.06	1.51 ± 0.06
16 V	1.69 ± 0.04	1.64 ± 0.03	1.61 ± 0.06

We can, from this data, infer a positive correlation between the voltage applied to the electrolytic cell and the box-counting fractal dimension of the resulting aggregate. Figure 4 (below) shows the overall result of this series of measurements, including 95% confidence intervals estimated by the formula $\bar{x} \pm 1.96\frac{s}{\sqrt{n}}$ with s being the standard deviation of the set of points and n being the number of points (in this case, 3).

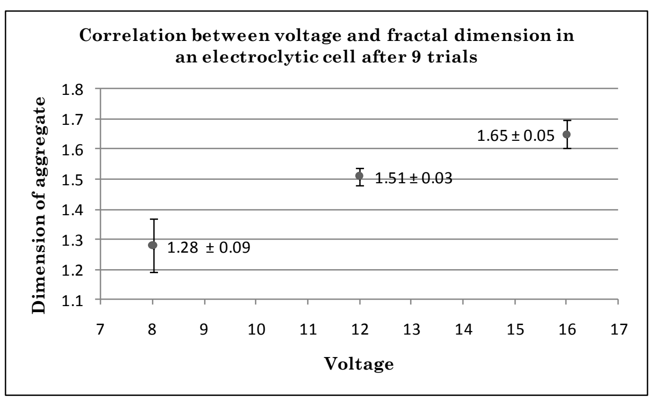


Figure 4. *Mean fractal dimension for all trials graphed with 95% confidence intervals, showing no overlap.*

Despite the low number of repeated measurements, Figure 4 supports by non-overlap of confidence intervals a correlation of higher dimension with higher voltage. Why this should be so remains unknown. A possible beginning of an explanation resides in the fact that a higher voltage causes a higher current, and thus more electrons moving through the aggregate at any given time. This could possibly result in a higher probability that any given electron should undergo Eq. (1) with Cu^{2+} ions in solution at any given point, thus causing more branches. However, this tentative heuristic explanation does little to explain why at lower voltages the electrons tend to react only at the tips of already-growing branches, or why some branches stop growing early or late during the process, or a number of other observations outlined above. This remains an important question that could be illuminated by more measurements.

Error remains an important discussion topic for these measurements. Initial uncertainty was due to the thickness of the pen lines drawn on the photographs, as well as fuzziness or pixellation after printing. This error was quite small, as can be seen from Table 1, on the order of hundredths of a unit. However, the initial recorded error in data taking does not correspond to the amount of variation seen in the final recorded dimensions (Table 1). This suggests some form of systematic error in the data-taking method. Dimension is independent of either size or orientation, so neither the side length of the photograph nor its orientation should have played a noticeable part in such an error. Similarly, the size of the boxes drawn should not affect the measured dimension. A noticeable trend in the data is that the dimensions for Trial 2 and Trial 3 are quite close at all three voltage levels, while that of Trial 1 is further off (either higher or lower), and in the case of the 8 V and 16 V aggregates, quite far off. While otherwise I attempted to keep the experimental set-up constant, I did in fact have to change power supplies between Trial 1 and Trial 2. This could explain the wide gap between those two trials. While there should have been no noticeable difference between the two, it is possible that one had a warped voltage dial, although neither of the power supplies were in any way out of date or visibly damaged. This does not inhibit my conclusion, however, as both power supplies saw the same correlation between dimension and voltage. It is also certain that some variation is due simply to the fact that the method of formation of these aggregates is governed by stochastic processes, and as such no two aggregates will ever be exactly the same.

In any case, I would recommend that more measurements of this type be done to give a better idea of the true mean dimension at each voltage, and also to determine the *type* of correlation between voltage and dimension, which at the moment is unanswerable with 3 data points.

Conclusion

There was found to be a statistically significant positive correlation between the voltage applied to a copper electrolytic cell and the fractal dimension of the resulting aggregate. This is in accordance with the hypothesis and the literature and is consistent with the diffusion limited aggregation model of crystal growth. Also consistent with DLA growth is the finding of mean dimension of 1.65 ± 0.02 at 16 V, which is close to the dimension of ~1.7 predicted by DLA. Further experiments could improve on this result by measuring the dimensions of aggregates at a wider range of voltages to give an idea of the precise relationship between those two quantities, something at which we can only speculate using the results of this experiment.

References

[1]. Witten, T., and Sander, L. Diffusion-limited aggregation. *Physical Review B* **27**, 5686-5697 (1983).

[2]. Akbar, S. *et al.* Fractal Growth of Zinc Dendrites. *Asian Journal of Chemistry* **21**, 4190-4198 (2009).

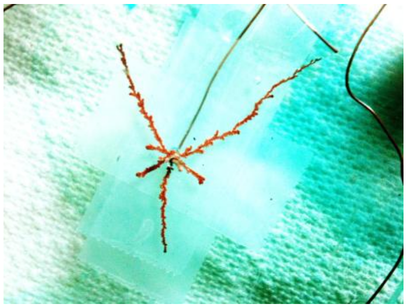
[3]. Mandelbrot, B. The Fractal Geometry of Nature. W.H Freeman and Company. 1983.

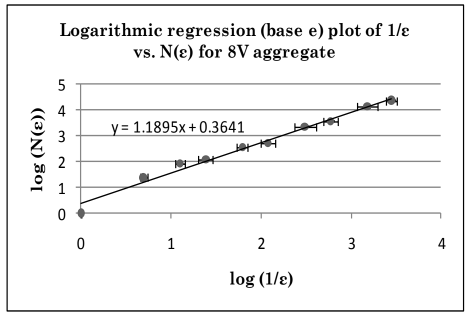
[4]. Hibbert, B. http://www.chem.unsw.edu.au/staff/Hibbert/HibbFrac/fractal.html [website] (2008). Accessed 5 March 2010.

Appendix A

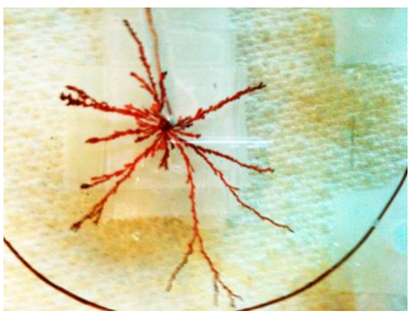
This appendix contains photos of all nine aggregates along with their corresponding logarithmic regression graphs.

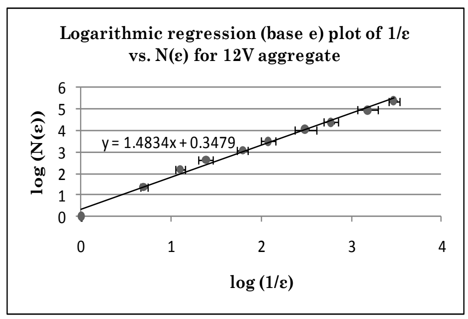
Trial 1 – 8 V aggregate - $D \cong 1.19$



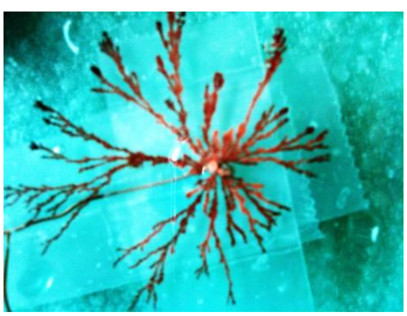


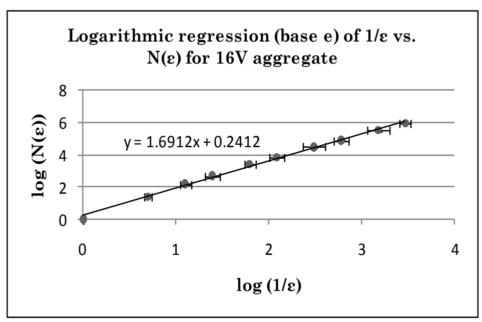
12 V aggregate - $D \cong 1.48$



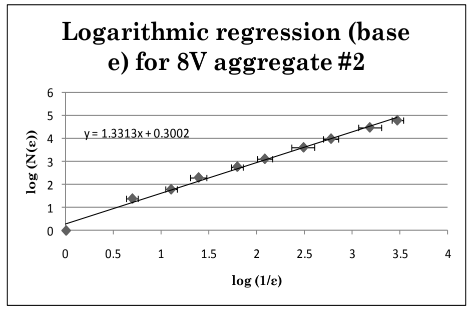


16 V aggregate - $D \cong 1.69$

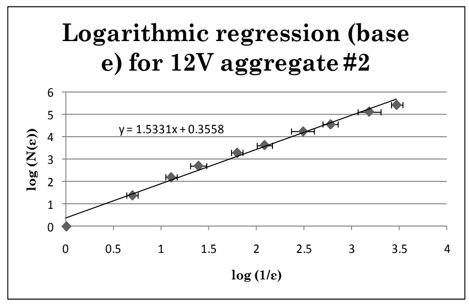




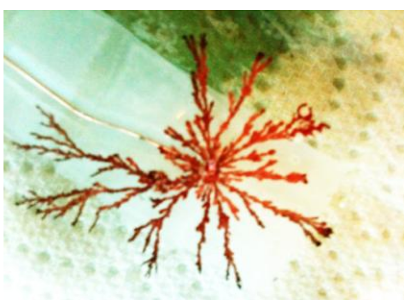
Trial 2 – 8 V aggregate - $D \cong 1.33$

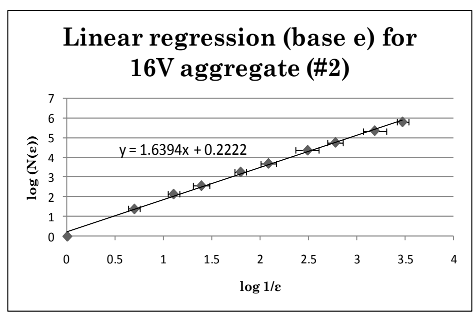


12 V aggregate - $D \cong 1.53$

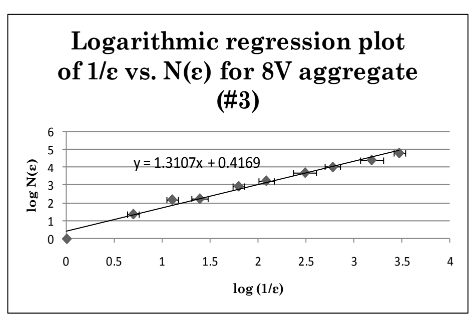


16 V aggregate - $D \cong 1.64$

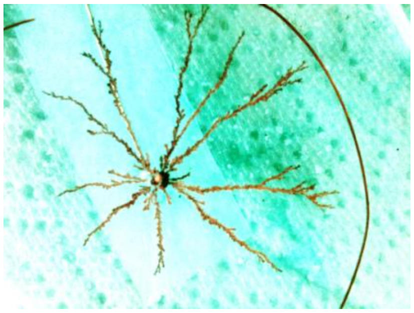


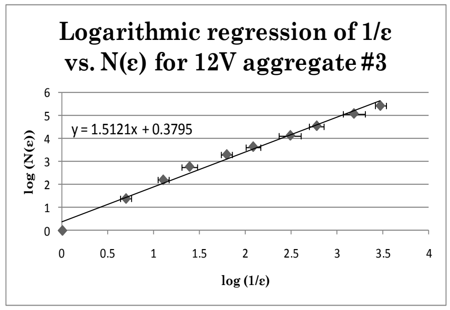


Trial 3 – 8 V aggregate - $D \cong 1.31$



12 V aggregate - $D \cong 1.51$





16 V aggregate - $D \cong 1.61$