Fractal Growth of Zinc Dendrites

Shazia Akbar*, Iftikhar Imam Naqvi†, Mahboob Muhammad† and Erum Zahir
Department of Chemistry, University of Karachi, Karachi, Pakistan
Fax: (92)481901819; E-mail: shaz-chem@hotmail.com; shazchem@gmail.com

An insight into diffusion limited aggregation (DLA) guides the interpretation of cluster designs. The structure and growth pattern of the zinc dendrites are similar to the Witten-Sander DLA model. The fractal dimension of zinc dendrites is 1.669 measured by Box-counting dimension method. This value is quite similar to the two dimensional DLA model (1.666). This fractal analysis suggested that zinc dendrites are two dimensional aggregates , have fractal nature and formed on the basis of DLA model. This study also revealed that zinc dendrites growth pattern is affected by different experimental conditions such as concentration of electrolyte, thickness of electrolyte layer, voltage variation, solvent nature and anion variation.

Key Words: Diffusion limited aggregation, Zinc dendrites, Fractal dimension, Box-counting dimension method.

INTRODUCTION

In many natural settings diffusion and aggregation usually dominate the transport of particles or molecules. Molecules in dense phases collide with each other and invariably stick together to form crystals. These aggregates of crystals having same dimensions and branch like appearances as that of the dendrites of nerve cell, are termed as dendrites. Dendrites are well defined branched tree like structures.

The diffusion-limited aggregation (DLA) has provided a basis for the development of more extensive and realistic models for dendrites growth and solidification[1-5]. Zinc dendrites are grown from a line electrode (carbon cathode) by electrodeposition under diffusion limited condition. This diffusion limited condition is provided by taking solvent which is immiscible with water and pouring that solvent on the top of the aqueous zinc sulfate solution. Zinc sulfate in aqueous medium is dissociated into zinc and sulfate ions. As the current of particular voltage is applied an electric field is generated between cathode and anode .The path followed by zinc ions is governed by Brownian motion due to the electric field. Zinc ions dance or stagger around the central carbon cathode randomly. The zinc ions that hit the cathode are deposited as zinc after receiving two electrons from cathode.

$$Zn^{2+} + 2e^- \longrightarrow Zn$$

---

†H.E.J. Research Institute of Chemistry, International Centre for Chemical and Biological Sceinces, University of Karachi, Karachi, Pakistan.

These ions move in random manner following Brownian path. The randomly moving zinc ions that contact any zinc are also deposited to a growing structure. Growth of zinc dendrites is an interface controlled crystal growth process. Immiscible solvent, which is poured on top of the electrolytic solution produces interface with low interfacial tension and screens the diffusion and aggregation of zinc ions from all sides. Surface tension also has an important role in dendrite formation because it prevents the formation of deformation that's why dendrite grows under well defined path[6]. Zinc ions are more likely to hit the exposed finger rather than protected interior of the dendrites, causing creation of empty spaces or Fjords because it is very difficult for a zinc ion to get inside the Fjords avoiding all the side branches, similar to DLA pattern[7].

This study is undertaken to show that zinc dendrites forms on the basis of DLA model, and have fractal nature. The growth of zinc dendrites with DLA model were compared by using quantitative and qualitative approaches. Fractal geometry of Mandelbrot[8] is used to quantify the zinc dendrites. This quantification is done by measuring the fractal dimension of cluster. Fractal dimension presents a method of measuring complexity of fractals. For quantification of zinc dendrites, Box-counting dimension method was used.

The shape of zinc dendrites is covered by a sheet of graph paper, where the side of each box is size 's'. Instead of finding the exact size of the fractal, the number of boxes were counted that are not empty. Let this number be N. By making the boxes smaller it gave more detail, which is the same as increasing the magnification.

According to this method

$$N_{(s)} = (1/s)^D$$

D = fractal dimension. If we take logarithms of both sides we have

$$D = \log(N_s) / \log(1/s)$$

The dimension was estimated by plotting $\log(N_s)$ against $\log(1/s)$ the slope of which is the fractal dimension. For DLA in two dimensions this quantity is 1.666[9].

Fractal theory also provides a basis for studying various phenomena by modeling and making predictions. A binary fractal tree[10] as shown in Fig. 3 is used to model the growth of zinc dendrites. So far the effects of different experimental conditions on the growth of zinc metal leafs have not been studied. This study reveals that dendritic growth pattern is affected by different experimental conditions such as concentration of electrolyte, thickness of electrolyte layer, voltage variation, solvent nature and anion variation.

EXPERIMENTAL

100 mL of 1 mol/dm^3, 2 mol/dm^3 and 3 mol/dm^3 $ZnSO_4$ solution and 50 mL of $ZnCl_2$ solution were prepared by dissolving specific amount of that reagent in deionized water. $ZnSO_4$, $ZnCl_2$ and other organic solvents like n-hexane, chloroform and methanol were used for this study. These reagents were of analytical grade, supplied by Merck. Deionized water was used whenever needed during the analysis.

An electric circuit was designed by using an AC-DC adapter of 1-12 volt and rating 500 mA, Digital multimeter rating 300 mA, Analog voltmeter, pot-potentiometer upto 100 ohm and rating 0.5 mA.

A petri dish of 1.7 cm deep, 8.3 cm diameter was used. Carbon rod was taken from pencil cell. It has been 4.5 cm long having 3.5 mm diameter and was used as a cathode. Zinc plate of 4.5 cm long and 7 mm width, 2 mm thickness was used as anode.

Procedure for zinc dendrites formation: In a typical procedure, solution of zinc sulfate ($ZnSO_4$) of concentration 2 mol/dm^3 was placed in a petri dish and thickness of solution was maintained upto 5 mm[11]. A few millimeters thick layer of *n*-haxane solvent was poured on the top of the zinc sulfate solution to make an interface. A carbon rod (as a negative electrode) was placed in the center of the dish so that the end of the rod just touched the interface, while the zinc plate was placed at the edge of dish 5 volt potential difference was maintained by power supply. Consequently the pattern of dendrites formation was followed (Fig. 1). Fig. 1 represents the zinc aggregate pattern at 2 M conc. of zinc sulfate, 5 mm thickness of electrolyte, 5 volt potential and by using *n*-hexane solvent. Growth started after 2 min and got completed up to 35 min.

Fig. 1. Zinc dendrites growth pattern

Same procedure was applied for 10 experiments by changing 5 parameters *i.e.* concentration (2 M), voltage (5 v), thickness of electrolyte (5 mm), solvent (*n*-hexane), anion (sulfate) one by one and the effects of these parameters on the pattern of zinc dendrites were recorded.

RESULTS AND DISCUSSION

Results of zinc dendrites formation can be concluded by using qualitative and quantitative approach (Table-1).

Qualitative approach: It is observed that zinc dendrite growth patterns are affected by different experimental conditions. By increasing voltage, thickness of electrolyte layer and concentration of electrolyte the thickness of zinc dendrite branches get increased, further to that different solvents and anions affect the patterns of zinc dendrite growth.

TABLE-1
DIFFERENT PARAMETERS UTILIZED IN THE STUDY OF
ZINC DENDRITES FORMATION

Variation of Concentration of electrolyte, while other four parameters were kept the same				
Concentration of electrolyte (mol/dm^3)	Thickness of electrolyte layer (mm)	Voltage (volt)	Non-aqueous solvent	Anion
1	5	5	n-Hexane	SO_4^{2-}
3	5	5	n-Hexane	SO_4^{2-}
Variation of thickness of electrolyte layer, while other four parameters were kept the same				
Thickness of electrolyte layer (mm)	Concentration of electrolyte (mol/dm^3)	Voltage (volt)	Non-aqueous solvent	Anion
1	2	5	n-Hexane	SO_4^{2-}
8	2	5	n-Hexane	SO_4^{2-}
Variation of voltage while other four parameters were kept the same				
Voltage (volt)	Concentration of electrolyte (mol/dm^3)	Thickness of electrolyte layer (mm)	Non-aqueous solvent	Anion
8	2	5	n-Hexane	SO_4^{2-}
11	2	5	n-Hexane	SO_4^{2-}
12	2	5	n-Hexane	SO_4^{2-}
Variation of non aqueous solvent while other four parameters were kept the same				
Non-aqueous solvent	Concentration of electrolyte (mol/dm^3)	Thickness of electrolyte layer (mm)	Voltage (volt)	Anion
Chloroform	2	5	5	SO_4^{2-}
Methanol	2	5	5	SO_4^{2-}
Variation of anion while other four parameters were kept the same				
Anion	Concentration of electrolyte (mol/dm^3)	Thickness of electrolyte layer (mm)	Voltage (volt)	Non-aqueous solvent
Cl^-	2	5	5	n-Hexane

Variation of concentration and thickness of electrolyte layer: It is noted that by increasing the concentration of electrolyte or thickness of electrolyte layer the thickness of zinc dendrite branches increased (Fig. 2). It is due to the fact that by an increase in the concentration of electrolyte or thickness of electrolyte the number of random walker *i.e.* zinc ions get increases (Fig. 3). Since there is very low probability of wandering of zinc ions without sticking to a branch as a result the thickness of branches increases.

Fig. 2a. Zinc aggregate pattern at 1M conc. of zinc sulfate. Growth started after 1 min and got completed up to 45 min

Fig. 2b. Zinc aggregate pattern at 3M conc. of zinc sulfate solution. Growth started within 1 min and got completed up to 15 min

Fig.3a. Zinc aggregate pattern at 1 mm thickness of zinc sulfate solution in Petri dish. Growth started after 2 min and got completed up to 30 min

Fig. 3b. Zinc aggregate pattern at 8 mm thickness of zinc sulfate solution. Growth started after few seconds and got completed up to 20 min

Variation of voltage: It is appeared that by increasing voltage the thickness of zinc dendrite branches gets increased (Fig. 4). It is due to the fact that as the voltage increases the electric field between carbon cathode and zinc anode increases. Because the path followed by zinc ions is governed by Brownian motion under the electric field so an increase in electric field strength increases the random motion of zinc ion. Higher voltage attracts the zinc ions more quickly, so there is a lower probability of wandering through the Fjords without sticking to a branch, resulting into a thick pattern of zinc dendrite.

Variation of non-aqueous solvent: It is noted that the form of the dendrite pattern is also affected by different solvents (Fig. 5). Fig. 1 shows that *n*-hexane gave compact and crystalline form of zinc aggregates, Fig. 5a represents that the chloroform gave crystalline but loose form of aggregates, while methanol gave loose and porous form of zinc aggregates (Fig. 5b).

Fig. 4a.   Zinc aggregate pattern at 8 volt potential. Growth started immediately and got completed within 30-60 s

Fig. 4b.   Zinc aggregate pattern at 11 volt potential. Growth immediately completed within 1-2 s

Fig. 4c. Zinc aggregate pattern at 12 volt potential. Growth immediately completed within 1-2 s

Fig. 5a.   Zinc aggregate pattern by using chloroform solvent. Growth started immediately and got completed after 60 s

Fig. 5b. Zinc aggregate pattern by using methanol solvent. Growth started after 2 minutes and got completed up to 15 min

Polarity of solvent increases going from *n*-hexane to chloroform and chloro-form to methanol. Zinc dendrite is formed under diffusion-limited condition. Such a condition is provided by pouring immiscible solvent on top of the electrolytic solution. Since *n*-hexane is less polar and highly immiscible with electrolytic solution, it gives a stable interface causing compact and crystalline form of aggregates. The immiscibility of solvent decreases by increasing its polarity that's why chloroform and methanol provide unstable interface resulting loose, porous form of zinc aggregates (Fig. 5a and 5b).

Anion variation: Growth pattern of zinc dendrite was affected by the change in anion. Zinc sulphate electrolyte gave tree like growth pattern of zinc aggregates whereas zinc chloride electrolyte gave tree like but zig zag growth pattern of zinc aggregates (Fig. 6).

Fig. 6.   Zinc aggregate pattern by using zinc chloride as an electrolyte. Growth started after few minutes and got completed up to 20 min

From experiments it is found that zinc dendrites have fractal structure. The cluster's fractal structure arises because the zinc ions that hit the cathode are deposited as zinc. Other zinc ions which come into contact to any already deposited zinc also get deposited forming growing structure. Like DLA cluster zinc dendrite cluster also exhibit multifractility, a property of the growth probability on the surface of the cluster[12]. The probability of growth of a zinc dendrite is found to be inhomogeneous. Tips of the cluster are much more likely to grow than points inside the fords. Growth probability is defined clearly by subtracting two zinc dendrite growth patterns at different time scales like Fig. 7c from Fig. 7b. Only tips are obtained as a resulting pattern. Thus the tips tends to screen the fords and this process of aggregation of zinc ions occurred on all length scale, suggesting that zinc dendrite cluster have fractal property. A noticeable feature during the growth of zinc dendrite was the way that branches screened one another, simultaneously on a variety of length scale. Splitting of tip of zinc leaves results in two daughter leaves. Due to the competition between two daughter leaves one daughter wins totally screening the other. The

death of branches as they are screened by their neighbour is balanced by the creation of new branches *via* microscopic tip splitting process as noticed by Halsey and Leigbig for the growth of DLA cluster[13].

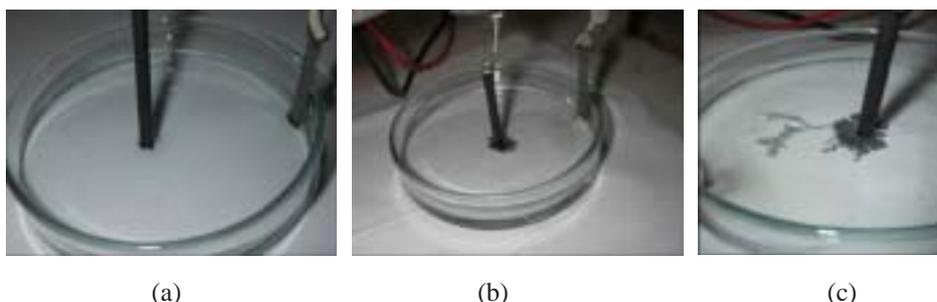| (a) | (b) | (c) |

Fig. 7 (a) When current was not applied, (b) Growth after 1 min (c) Growth after 15 min

It was found that zinc dendrites have tree like growth pattern which is self similar to fractal tree (Fig. 8). This comparison of zinc dendrites growth pattern with fractal tree confirmed the fractal nature of zinc dendrite.
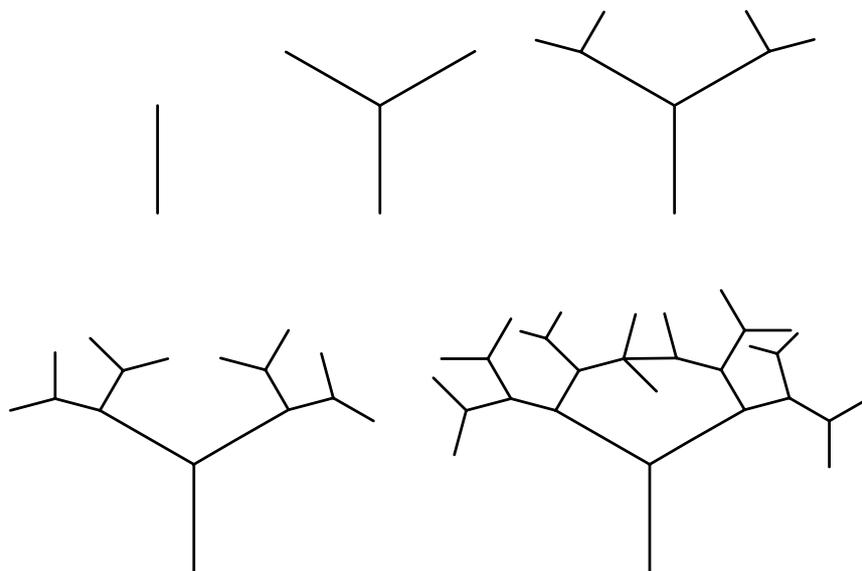

Fig. 8. Fractal tree

Quantitative approach: Fractal dimension of zinc dendrite cluster was measured by box counting method. The value of this fractal dimension is 1.669 which is in excellent agreement with that of the two-dimentional DLA model. This value also suggests that zinc dendrites are two dimensional aggregates and have fractal nature (Table-2).

TABLE-2
BOX COUNTING METHOD FOR DETERMINATION OF
FRACTAL DIMENSION OF ZINC DENDRITES

$N_{(s)}$	s (mm)	log $N_{(s)}$	log (1/s)
483	2.5	2.684	-0.398
146	5.0	2.164	-0.699
75	7.5	1.875	-0.875
46	10.0	1.663	-1.000
33	12.5	1.518	-1.097
27	15.0	1.431	-1.176
17	17.5	1.230	-1.243
15	20.0	1.176	-1.301
10	25.0	1.000	-1.398

REFERENCES

1. J. Nittmann and H.E. Stanley, *Nature*, **321**, 663 (1986).
2. J. Nittmann and H.E. Stanley, *J. Phys. A*, **20**, 1185 (1987).
3. F. Family, D.E. Platt and T. Vicsek (unpublished).
4. S. Liang, *Phys. Rev. A*, **33**, 2663 (1986).
5. J.D. Chen and D. Wilkinson, *Phys. Rev. Lett.*, **55**, 1892 (1985).
6. J.S. Langer and H. Muller-Krumbhaar, *Acta Metall.*, **26**, 1681 (1978).
7. T.A. Witten and L.M. Sander, *Phys. Rev. B*, **27**, 5686 (1983).
8. B.B. Mandelbrot, The Fractal Geometry of Nature, W.H. Freeman, San Francisco (1982).
9. M. Matsushita, M. Sano, Y. Hayakawa, H. Hanjo and Y. Sawada, *Phys. Rev. Lett.*, **53**, 286 (1984).
10. B.B. Mandelbrot and M. Frame, *Mathematical Intelligencer*, **21**, 18 (1999).
11. M. Matsushita, *J. Phys. Soc. (Japan)*, **54**, 857 (1985).
12. T.C. Halsey, M.H. Jensen, L.P. Kadanoff, I. Procaccia and B.I. Shraiman, *Phys. Rev. A*, **33**, 1141 (1986); Y. Hayakawa, S. Sato and M. Matsushita, *Phys. Rev. A*, **36**, 1963 (1987); R.C. Ball and O. Rath Spivack, *J. Phys. A*, **23**, 5295 (1990).
13. T.C. Halsey and M. Leibig, *Phys. Rev. A*, **46**, 7793 (1992); T. Halsey, *Phys. Rev. Lett.*, **72**, 1228 (1994).