

Effect of electric field on the dendritic electrodeposits of zinc

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Abstract: Electrodeposition in circular geometry under certain cell operating conditions yield growth of fractal patterns with dendritic patterns. Electrodeposition of zinc from 0.5 M zinc acetate solution at different cell operating voltages in the range of 5 to 14 V DC (5, 7, 9, 12 and 14 V) at room temperature (28°) has done. It was observed that the electrodeposits of zinc are qualitatively different from electrodeposits of copper in that the branches were thin and fragile with slightly leafy structures. It is shown that the electrodeposits of zinc obtained from zinc acetate solution are relatively dense with more branches exhibiting a fractal dimension close to that of DLA. The electrodeposited patterns are analysed for fractal character using box counting technique and the results and findings are presented

Key Words: Electrodeposition, Zinc acetate, fractal, fractal dimension, dendritic pattern, Diffusion Limited aggregation, Box counting.

1. INTRODUCTION:

Electro deposition in circular geometry under certain cell operating conditions yield growth patterns resembling tree structure with dendritic pattern. These dendritic patterns show scaling behaviour and Fractal Characteristics under typical electrodeposition condition. The main process giving rise to such branching patterns is the Diffusion Limited Aggregation (DLA) of ions under a weak electric field. The patterns so obtained are also known as DLA patterns, this phenomenon is found to explain formation of many irregular shapes in nature. Diffusion controlled pattern formation have been recent topic of interest, amongst them the Electro deposition, viscous fingering, dendritic crystal growth, and DLA (Diffusion Limited Aggregation) [1, 2, 3] have received the major attention. The concept of fractal and non fractal aggregation is applicable in physics especially in turbulence [4, 5], polymerization, [6,7]. Flocculation, coagulation, dendritic growth, crystallization. Gelation process also exhibit self-similarity and fractal character in many cases. The practical importance and fundamental principle of Diffusion limited growth processes has motivated extensive studies in the past years. Electro-deposition processes [8, 9] are well suited for experimental studies of growth of fractals and dendritic patterns. The boom Fractals and related studies began in the 1980s and Physicists took keen interest in this area. Different Fractal models were later proposed and were found to be very useful in explaining complexity of irregular shapes that could not otherwise be quantified. For the purpose of forecasting the trends of the random events like prices of shares in the share market, the concept of Fractal model is being effectively used [10, 11]. Circular cell geometry is used with circular outer electrode acting as anode and the middle electrode (at the centre of the circular anode) works as cathode. Cell operating conditions like applied voltage and the concentration of the electrolyte mainly govern the shape of resulting dendritic deposits. It was found that the complexity of the shape of the growth and the branching patterns depend more on the electric field conditions under a given set of conditions. It was also found that the concentration of the solution strongly influences the structure and textures of electro deposition [12]. Few dendritic patterns obtained under different cell operating conditions and their characterization is presented. We also studied the electro deposition using lead acetate solution. It is observed that as the process is governed by random walk like processes [14, 15], there is tendency of self avoiding. As a result, the growth is prominent on the outer side of growth i.e. around the tips of the branches. As a result of this, as the growth proceeds, the thickness of the branched does not appreciably grow as the cluster grows. Results of the study at different cell voltages and at different concentration of electrolyte solution is presented.

2. EXPERIMENTAL:

We studied electrodeposition of zinc from zinc acetate solution in circular cell geometry by changing the cell applied voltage. A circular electrodeposition cell was designed and constructed and a constant regulated potential difference was applied across the electrodeposition cell. Electrodeposition of zinc from 0.5 M zinc acetate solution was studied at different cell operating voltages in the range of 5 to 14 V DC (5, 7, 9, 12 and 14 V) at room temperature (28°C). The Electrodeposition cell was made from acrylic sheet with a cavity for electrolyte and a circular zinc anode at the centre of which a point cathode was placed through a narrow hole drilled in the acrylic sheet.

It was observed that the electrodeposits of zinc are qualitatively different from electrodeposits of copper in that the branches were thin and fragile with slightly leafy structures. Slight movement of ambient air resulted in movement of electrolyte in the Electrodeposition cell and some convection current were also present. This resulted in movement of fragile branches and many of the branches turned on their side or change their position and started developing like curved branches, in fact this is the effect of local movement of the portions of the electrolyte.

At lower cell operating voltages the number of branches formed are fewer and thinner as compared to that at relatively higher cell operating voltages. Typical electrodeposits of zinc obtained from 0.5 M zinc acetate solution at cell operating voltages of 5, 9, 12 and 14 V are shown in Fig.1.1. It is seen that as the cell operating voltage is higher and higher, the electrodeposits exhibit more complex branching patterns and the electrodeposits here deviate from the standard DLA structures exhibiting a fractal dimension of 1.6. From the series of images recorded during the development of branching patterns from Electrodeposition at different voltages fully developed last stages before introduction of abnormalities at the outer most branches were selected for fractal analysis.

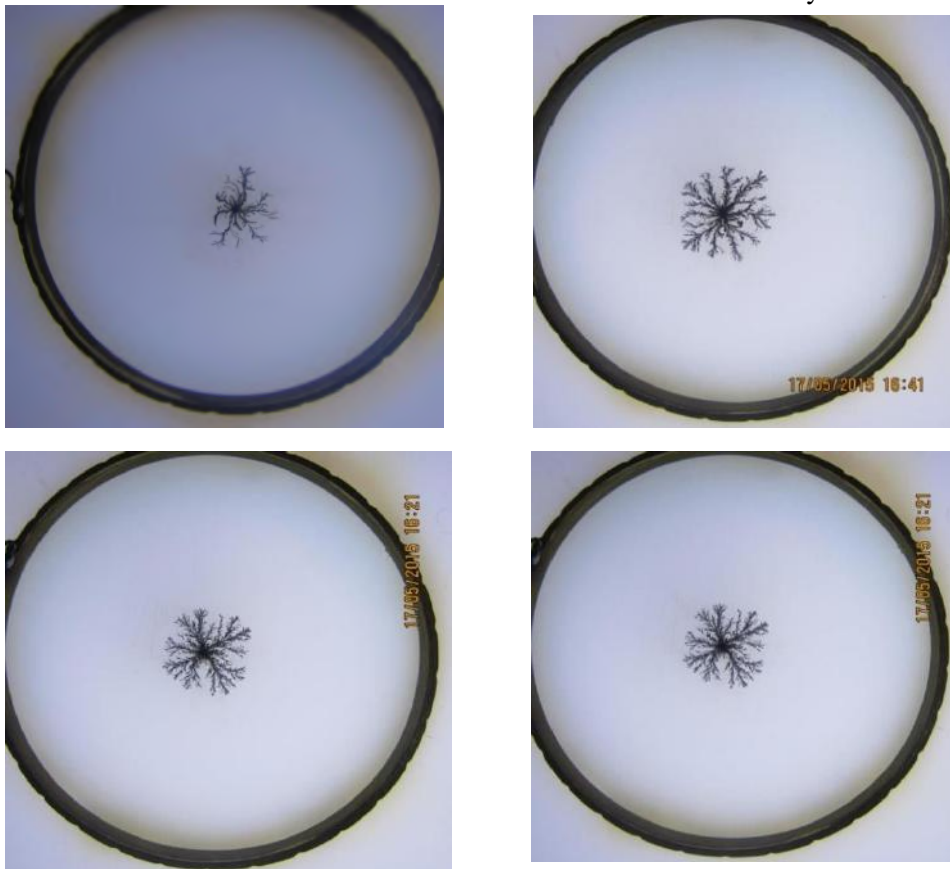
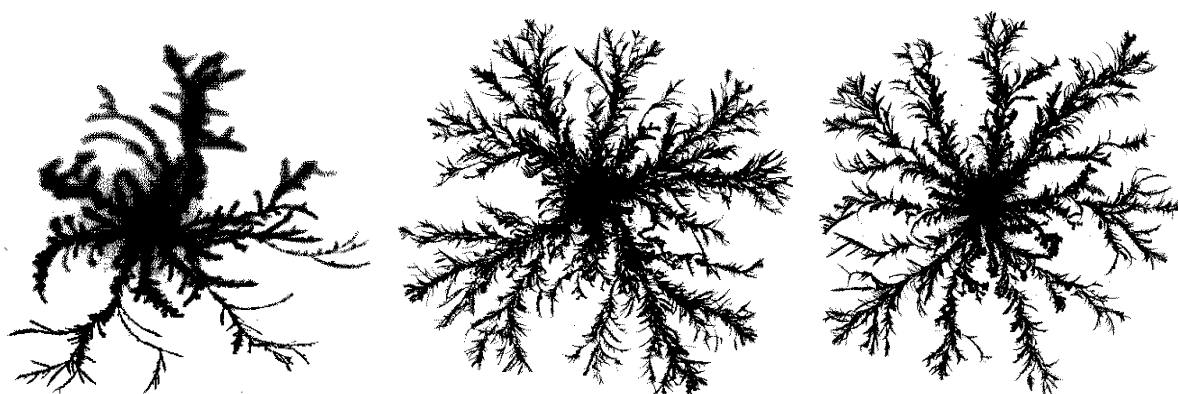


Fig. 1.1 Electrodeposits of zinc obtained from zinc acetate solution in circular Electrodeposition cell at different cell voltages of 5, 9, 12 and 14 V respectively.

The colored images of electrodeposits were processed for color correction and boundaries of cell and outer anode structure was removed and after cropping it was converted to suitable size and then converted to gray scale image from which two color bitmap images were extracted using a suitable threshold from the actual image.



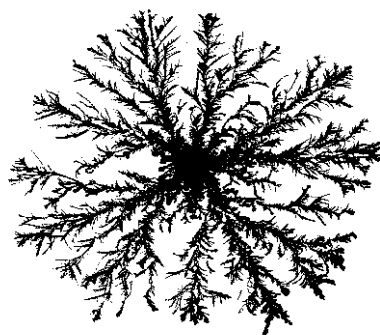


Fig. 1.2 Images obtained after cropping the images shown in Fig.1.1, the branching pattern is more clearly visible.

The image of electrodeposit obtained at 7 V being not much different is not included for brevity. These two color bitmap images were subjected for box counting using computer program developed for this purpose.

The computer program uses the two color bitmap images and converts it in to a matrix of pixels. The program uses different sizes (r) of square boxes and scans the entire image to count the total number (N) of such boxes of size 'r' required to cover the entire image. The computer program makes a table of r, N, log(r) and log(N) which is used for further processing by plotting a graph of log(N) versus log(r). A typical table of r, N, log(r) and log (N) for the electrodeposit obtained at cell operating voltage of 5 V shown in Fig. 1.1 is presented in Table – 1.1.Using the data of log(r) and log(N) a graph is plotted using the values of log(r) on the x axis and log(N) on the axis of y as shown in Fig. 1.3.

Table – 1.1: table of r, N, log(r) and log (N) for the electrodeposit at 5 V

r	N	log(r)	log(N)	r	N	log(r)	log(N)
1	60682	0	4.7831	30	206	1.4771	2.3139
2	20917	0.301	4.3205	34	166	1.5315	2.2201
3	9907	0.4771	3.9959	39	134	1.5911	2.1271
4	6012	0.6021	3.779	44	110	1.6435	2.0414
5	4021	0.699	3.6043	50	91	1.699	1.959
6	2946	0.7782	3.4692	57	76	1.7559	1.8808
7	2253	0.8451	3.3528	64	64	1.8062	1.8062
8	1809	0.9031	3.2574	72	51	1.8573	1.7076
9	1478	0.9542	3.1697	81	46	1.9085	1.6628
11	1050	1.0414	3.0212	91	33	1.959	1.5185
13	807	1.1139	2.9069	103	33	2.0128	1.5185
15	637	1.1761	2.8041	116	24	2.0645	1.3802
17	516	1.2304	2.7127	131	22	2.1173	1.3424
20	401	1.301	2.6031	147	17	2.1673	1.2305
23	311	1.3617	2.4928	165	16	2.2175	1.2041
26	262	1.415	2.4183	-	-	-	-

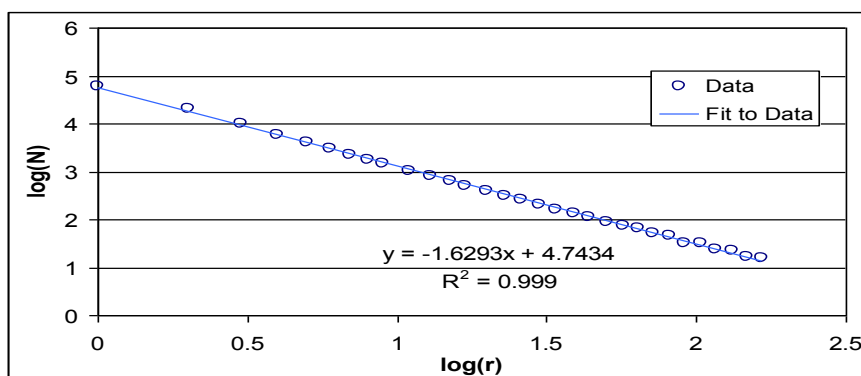


Fig.1.3 Log (N) versus log(r) plot for data from Table – 1.1 corresponding to the electrodeposit of 5 V.

The points plotted represent actual data from Table – 1 and the straight line joining these points is the best fitting straight line to this data obtained using the method of least square fitting. Equation of the best fitting line to this data is also shown in the inset. It is seen from the plot shown in Fig.1.3 that all the points lie well along the straight line confirming the presence of self similarity and scale invariance and thus the image analysed possesses fractal character. Similarly using the same procedure for the rest of the electrodeposits at different voltages log (N) versus log(r) plots were obtained as shown in Fig1.4, 1.5 and 1. 6 for electrodeposits at 9, 12 and 14 V respectively.

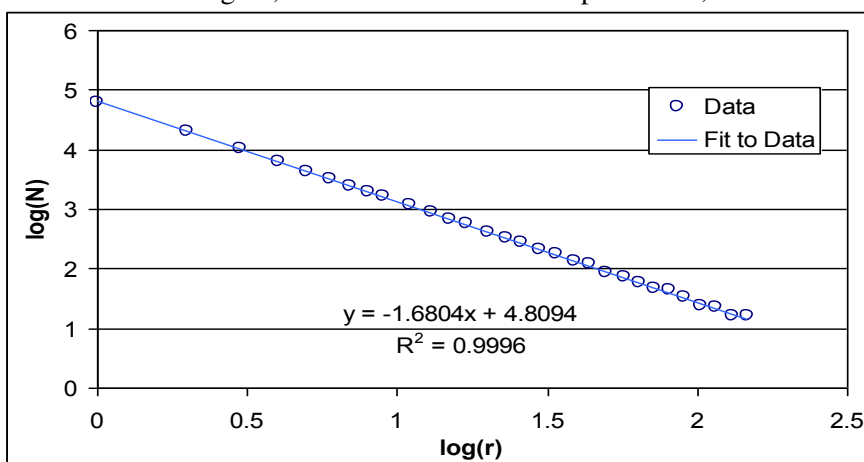


Fig. 1.4 log (N) versus log(r) plot for electrodeposits of zinc at 9 V using circular cell.

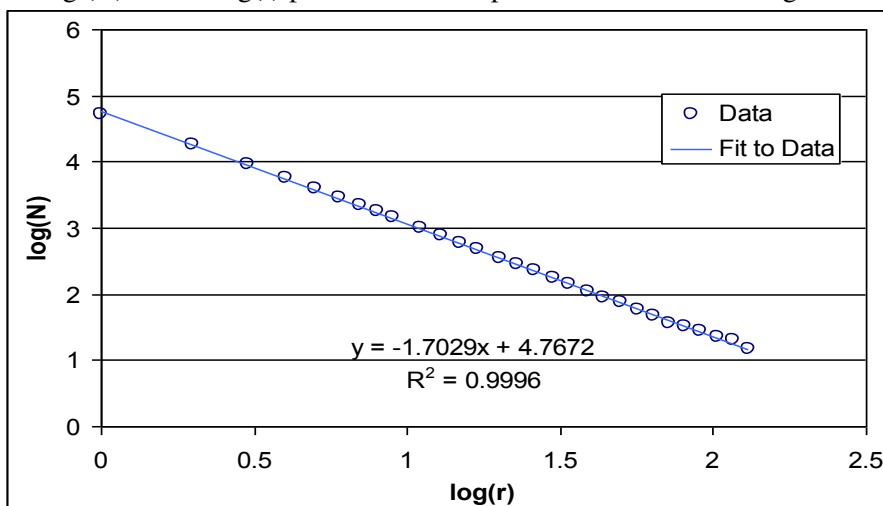


Fig.1.5 log (N) versus log(r) plot for electrodeposits of zinc at 12 V using circular cell.

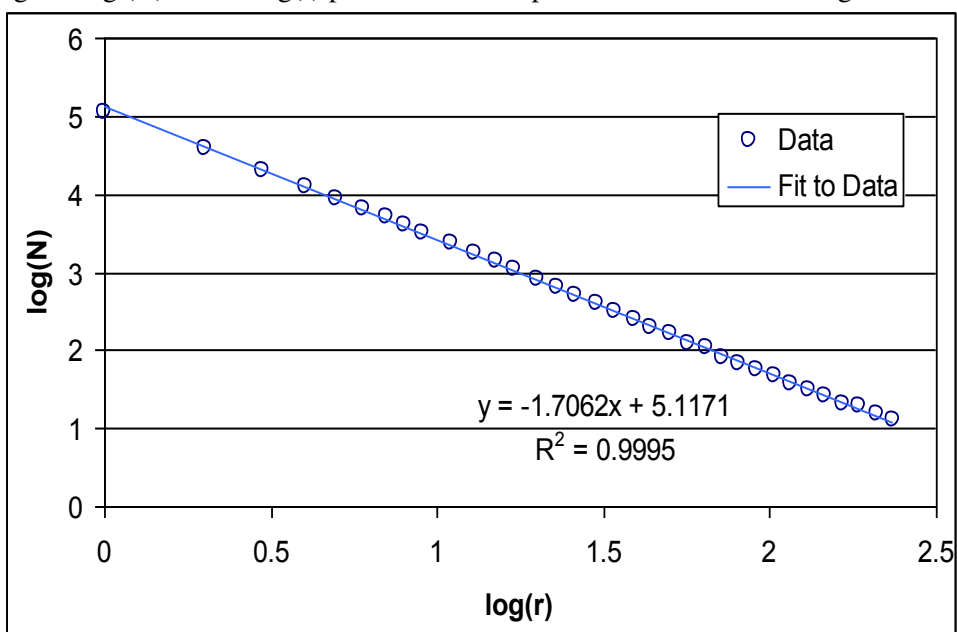


Fig.1.6 log (N) versus log(r) plot for electrodeposits of zinc at 14 V using circular cell.

All the $\log(N)$ versus $\log(r)$ plots shown in Fig. 1.3,1.4, 1.5 and 1.6 show that all the data points representing $\log(N)$ and $\log(r)$ values lie well along a straight line and thus confirm the presence of self similarity and scale invariance in all the electrodeposits of Fig.1.1. The complexity of shape associated with the shape of the electrodeposit is characterized by the fractal dimension of the pattern. Higher the fractal dimension more is the complexity.

3. CONCLUSION:

The results obtained in terms of fractal dimensions of the five electrodeposits shown in Fig. 1.1 are presented in Table –1.2. The electrodeposit at 7 V was not much different so the details of analysis are not included for brevity however the associated complexity being different the associated fractal dimension is included in the table –1.2.

Table –1. 2 Slope of straight line, fractal dimension and value of R^2 for the five images shown in Fig. 1.1.

S. No.	Cell Voltage	Slope	Fractal Dimension	R^2
1	5 V	-1.6293	1.6293	0.999
2	7 V	-1.6544	1.6544	0.9997
3	9 V	-1.6804	1.6804	0.9996
4	12 V	-1.7029	1.7029	0.9996
5	14 V	-1.7062	1.7062	0.9995

It is seen from Table – 1.2 that all the electrodeposited patterns analysed (shown in Fig. 1.1) do possess fractal character and exhibit self similarity and scale invariance because of the fact that the $\log(N)$, $\log(r)$ data is best represented by a straight line as is seen from the value of R^2 which is close to unity and the value of R^2 is greater than 0.999 indicating that the fitting to the straight line is excellent and this confirms that the scaling law hold good. It is also seen that at higher cell operating voltages the electrodeposits of zinc obtained from zinc acetate solution are relatively dense with more branches exhibiting a fractal dimension close to that of DLA.

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