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Dendritic Fractal Electrodeposits of Zinc from Zinc Acetate and Zinc Sulphate Solution

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ABSTRACT: Electrodeposition of metals from electrolytes result in growth of dendritic patterns exhibiting fractal character under certain cell operating conditions. Electrodeposition of zinc in the form of dendritic patterns exhibiting fractal character is studied in circular cell geometry using zinc acetate and zinc sulphate as electrolyte in circular electrodeposition cell geometry. It is shown that the electrodeposits obtained from the two electrolyte exhibit different character in terms of the branching pattern morphology and complexity of structure. The electrodeposited patterns are analysed for fractal character using box counting technique and the results and findings are presented.

KEYWORDS: Electrodeposition, Fractal dimension, Circular cell geometry, self similarity, scale invarience.

I. INTRODUCTION

The concept of fractal and fractal dimension is a tool, which characterize irregular shapes and patterns, generated from natural and scientific experiments. The characterization of phenomena arising due to random processes is extensively used by fractal geometry. Formation of dendritic patterns or tree like patterns due to electro-deposition in circular cell geometry under the different operating condition shows scaling behavior and fractal characteristics. Diffusion Limited Aggregation (DLA) [1, 2] of ions under a week electric field is the main process-giving rise to such branching patterns. Pattern formation by diffusion-controlled phenomena have been recent topic of interest, amongst them are DLA (Diffusion Limited Aggregation), dendritic crystal growth. Electro-deposition and viscous fingering [3, 4] have received the major attention. The concept of fractal and non-fractal aggregation is applicable in physics especially in dendritic growth, flocculation, coagulation, turbulence [5, 6], polymerization [7, 8] and crystallization. Gelation process also exhibits self-similarity and fractal character in many cases. Fundamental principle of diffusion limited growth processes has its practical importance, which has motivated extensive studies in the past years.

II. RELATEDWORK

Experimental studies of growth of fractals and dendritic patterns are well suited in electro-deposition processes [9-11]. Physicists took keen interest in the study of fractals and related studies after the boom of fractals [12-14], which began in 1980. To explain the complexity of irregular shapes that could not otherwise be quantified was explained by very useful different fractal models. The concept of fractal model is being effectively used for the random events like prices of shares in the share market [15-16] and forecasting. Self-similar patterns [17] and fractal character is also observed in some of solidification processes. Patterns formed by discharge of liquids like water into the soil or flows through coffee grains or materials in the form of fine particles, are described by fractals known as percolation clusters.



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III. EXPERIMENTAL

The circular geometry electro-deposition cell was designed by keeping in view the ease of photography and electrical operation of growth pattern. As the time history of evolution of the growth patterns are important, particularly the branches of growth pattern were of interest; provision for video recording was made. The cell was made from Perspex (Poly methyl metha acrelate) sheets 0.2cm in thickness and 35 cm x 35 cm square in area. Semi-transparent sheet was used from the point of view of photography and illumination contrast. This is allowed for uniform illumination using sources of light at suitable position on the hind side. A fine hole (0.08 cm diameter) was drilled to accommodate the cathode pin at the center of circular collar (about 1 cm width) was fixed in the middle of the Perspex sheet.

The care was taken to see it that there are no scratches on the surface within the cell cavity for proper photography. A carbon electrode was inserted through the hole, to be used as cathode. A cathode of carbon, derived from a central part of pencil was used; though it was found that use of a thin copper pin as cathode also worked well during the deposition of copper dendrites. The outer circular anode was made of carbon and was obtained by turning a carbon slab of 0.5 cm thickness to provide a diameter of 9.0 cm.

Cathode was at the center of the anode ring in the cell. Removable connectors' wires were used behind the cell to connect to the cathode. To ensure uniform two-dimensional growth, leveling arrangement was made for cell to maintain uniform thickness of electrolyte. Minimum thickness of solution for good quality two-dimensional fractal growth care was taken. The pattern of fractal growth tends towards the three dimensional with the thicker electrolytic layer, which is not desirable.



Fig. 1 Schematic and actual Electrodeposition cell in circular geometry

IV. ELECTRODEPOSITION UNDER DIFFERENT CONDITIONS

Electrodeposition of metal ions from electrolyte in circular cell geometry in most of the cases is governed by DLA or DLA like processes and DLA stands for Diffusion Limited Aggregation. In the present study the electrodeposition cell consisted of a circular anode at the centre of which a point cathode was situated. Constant voltage was applied between the anode and cathode and the space between the anode and cathode was filled by a thin layer of electrolyte under study. Care was taken to see to it that the electrolyte thickness remains as small as possible so as to allow a near two dimensional growth of the electrodeposit. The electric field at the central cathode being strong the growth is initially fast and usually in the form of a small lump, thereafter small branches start growing around this lumpy structure. Once a branch begins to grow, the size of the branch tends to grow outwards. It is a tendency exhibited by most of the DLA like processes that the growing branches continue to grow further and there is very limited or no growth in the region between the two branches. Fig.2 shows a typical electrodeposit obtained from 1 M zinc acetate solution as an



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electrolyte at a cell operating voltage of 5 V. For fractal analysis the image was converted to two colour bitmap image after converting the actual image to gray scale and applying suitable threshold.



Fig. 2 Electrodeposit form 1M zinc acetate solution at cell voltage of 5 V and the same image after converting to two colour bitmap.

Table – 1 shows the results of box counting applied to two colour bitmap image of Fig. 2 in the form of table of r, N, log(r) and log (N).

r	N	log(r)	log(N)	r	N	log(r)	log(N)
1	43189	0	4.6354	39	233	1.5911	2.3674
2	14839	0.3010	4.1714	44	197	1.6435	2.2945
3	8478	0.4771	3.9283	50	162	1.6990	2.2095
4	5352	0.6021	3.7285	57	131	1.7559	2.1173
5	3810	0.6990	3.5809	64	112	1.8062	2.0492
6	3091	0.7782	3.4901	72	96	1.8573	1.9823
7	2460	0.8451	3.3909	81	85	1.9085	1.9294
8	2046	0.9031	3.3109	91	72	1.9590	1.8573
9	1741	0.9542	3.2408	103	59	2.0128	1.7709
11	1306	1.0414	3.1159	116	54	2.0645	1.7324
13	1039	1.1139	3.0166	131	48	2.1173	1.6812
15	843	1.1761	2.9258	147	38	2.1673	1.5798
17	720	1.2304	2.8573	165	29	2.2175	1.4624
20	516	1.3010	2.7126	186	30	2.2695	1.4771
23	460	1.3617	2.6628	209	24	2.3201	1.3802
26	399	1.4150	2.6010	235	22	2.3711	1.3424
30	319	1.4771	2.5038	264	18	2.4216	1.2553
34	275	1.5315	2.4393	297	16	2.4728	1.2041

Table – 1 Results of box counting for Fig. 2

The two colour bitmap image of the electrodeposit was subjected to box counting using computer program. The computer program selects different sizes of squares and scans the entire image to find out the total number of square



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boxes required to completely cover the entire image. The program records the size of box (r) and the number of boxes required to cover the image (N) and makes a table of r, N, log(r) and log (N) and saves in a computer file for further processing.

The data from Table -1 was plotted using log (N) on the y – axis and log(r) on the x – axis. The resulting plot is shown in Fig. 3. The points plotted are the actual data from Table -1 and the straight line joining these points is the best fitting straight line to this data.



Fig. 3 log (N) versus log(r) plot for electrodeposit of Fig.2 whose box counting results are shown in Table - 1.

It is clearly seen that all the points lie well along a straight line indicating that power law holds good for the electrodeposited pattern analysed and confirms the presence of self similarity and scale invariance. The fractal dimension of the electrodeposit as obtained from power law exponent and the slope of the straight line of Fig. 2 is 1.3762 that is much lower than the standard DLA fractal dimension.

Similarly, using 1 M solution of zinc acetate electrodeposition was studied at a cell operating voltage of 7 V in the same electrodeposition set up with the same cell in circular geometry. The electrodeposits obtained at cell operating voltage of 7 V are shown in Fig. 4.



Fig. 4 Electrodeposit form 1M zinc acetate solution at cell voltage of 7 V and the same image after converting to two colour bitmap.



(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 8, August 2017

The electrodepositions shown in Fig. 4, corresponding to cell operating voltage of 7 V are different from those shown in Fig. 2 (Cell operating voltage = 5 V) in that the branches are crowded with secondary and tertiary branches and the deposit appears to have more complexity of structure. This is due to the increased cell operating voltage as the component of radial force acting on the ions is increased. Two colour bitmap image of the electrodeposit obtained from 1 M zinc acetate solution at a cell operating voltage of 7 V shown in Fig. 4 was subjected to box counting using computer program. The results of box counting applied to the image shown in Fig. 4 are presented in Table – 2 as size or square box (r), the number of boxes required to cover the image (N), $\log(r)$ and $\log(N)$.

		1 401	c = 2 Results c	1 002	x counting	101 1 15. 4		
r	Ν	log(r)	log(N)		r	Ν	Log(r)	log(N)
1	88658	0	4.9477		39	221	1.5911	2.3444
2	28078	0.3010	4.4484		44	189	1.6435	2.2765
3	14123	0.4771	4.1499		50	141	1.6990	2.1492
4	8761	0.6021	3.9426		57	118	1.7559	2.0719
5	6057	0.6990	3.7823		64	100	1.8062	2.0000
6	4492	0.7782	3.6524		72	82	1.8573	1.9138
7	3485	0.8451	3.5422		81	72	1.9085	1.8573
8	2792	0.9031	3.4459		91	60	1.9590	1.7782
9	2284	0.9542	3.3587		103	49	2.0128	1.6902
11	1659	1.0414	3.2198		116	42	2.0645	1.6232
13	1285	1.1139	3.1089		131	35	2.1173	1.5441
15	1012	1.1761	3.0052		147	28	2.1673	1.4472
17	828	1.2304	2.9180		165	26	2.2175	1.4150
20	636	1.3010	2.8035		186	20	2.2695	1.3010
23	506	1.3617	2.7042		209	19	2.3201	1.2788
26	410	1.4150	2.6128		235	15	2.3711	1.1761
30	337	1.4771	2.5276		264	15	2.4216	1.1761
34	271	1.5315	2.4330		297	12	2.4728	1.0792

Table - 2 Results of box counting for Fig. 4

The two electrodeposits shown in Fig. 2 and 4 look very much different in terms of structure and branching pattern. To explore the morphological differences between the two electrodeposits the fractal dimensions can be compared. To determine the fractal dimension of the electrodeposited pattern shown in Fig. 5 a graph is plotted using the corresponding results from box counting shown in Table – 2. Log (N) is plotted on the y – axis and log (r) on the x – axis, the points plotted represent actual data taken from Table – 2 and the straight line joining these points is the best fitting straight line to this data obtained using methods of least squares. The equation of the best fitting straight line is also shown in the inset. It is evident from the graph that all the data points nicely fit to a straight line. This confirms existence of self similarity and scale invariance and that the shape of image shown in Fig. 4 is a fractal. The fractal dimension as obtained from the power law exponent or the slope of the straight line is 1.5707.



Fig. 5 log (N) versus log(r) plot for electrodeposit of Fig.4 whose box counting results are shown in Table - 2.



(An ISO 3297: 2007 Certified Organization) Website: <u>www.ijirset.com</u> Vol. 6, Issue 8, August 2017

Comparison of the two electrodeposits shown in Fig. 2 and 4 obtained from 1 M lead acetate solution at 5 and 7 volts respectively reveals that the electrodeposit obtained at cell operating voltage of 7 V is having crowded branches as compared to that obtained at 5 volts. Electrodeposit shown in Fig. 4 is having relatively dense growth with more of branching adding complexity to the structure which in turns results in a higher fractal dimension of 1.5707 where as for the electrodeposit at a lower voltage (5V) shown in Fig.2, the branching is relatively thin and the structure is not dense with limited branching at preferred angles. The electrodeposit shown in Fig. 2 also obeys the scaling laws and exhibits self similarity and has a fractal dimension of 1.3762 which is much less than 1.5707 the fractal dimension of Fig. 4

The study of growth of electrodeposits using 1 M zinc acetate at two different cell operating voltages indicated formation of branches in preferred directions, the structures had self similarity this suggested study of electrodeposition under similar condition using a different electrolyte solution. Thus electrodeposition of zinc from 1 M zinc sulphate solution was studied at cell operating voltage of 7 V in circular cell geometry. The electrodeposit so obtained is shown in Fig. 6 along with its black and white two colour bitmap image of the same electrodeposit.



Fig. 6 Electrodeposit form 1 M zinc sulphate solution at cell voltage of 7 V and the same image after converting to two colour bitmap.

The electrodeposit of Fig. 6 posses fewer branches and very limited secondary and tertiary branches. Also the overall shape of the electrodeposits in Fig. 2 and 4 has complex structures with crowded branching patterns where as here the branches appear to be more or less straight and have tendency to grow in one direction. The tendency of self avoidance is also visible and growth continues at the tip of growing branches rather than uniform growth. The morphology of the electrodeposit shown in Fig. 6 appears to be altogether different from that of the rest of the two electrodeposits discussed (Fig. 2 and 4). The two colour bitmap image of the electrodeposit obtained form 1 M zinc sulphate solution at a cell operating voltage of 7 V using the same cell operating conditions was subjected to box counting using computer program and the results of box counting are presented in the form of graph of values of log(r) and log (N) as shown in Fig 7. The points plotted represent actual data of log (N) and log(r) from box counting and the straight line joining these points is the best fitting straight line to this data obtained by using the method of least square fitting. The equation of the best fitting straight line is also given in the inset. From the equation of the straight line the slope can be found as the coefficient of 'x' which also represent the power law exponent.



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Fig. 7 log (N) versus log(r) plot for electrodeposit of Fig.6.

The straight line graph confirms that there is self similarity and scale invariance to the image analysed and the image in Fig. 6 is a fractal with fractal dimension of -1.4041. The fractal dimension is a measure of complexity of shape, structure and texture, a higher fractal dimension indicates a higher degree of complexity of structure and texture associated with the image of electrodeposit.

V. CONCLUSIONS

It is observed that the Electrodeposition of zinc from zinc sulphate and zinc acetate exhibit different tendencies of developing dendritic patterns in electrodeposition using circular cell geometry. The electrodeposited dendritic patterns from 1 M zinc acetate solution show increasing complexity of structure to the branching pattern of the electrodeposit which is also seen from increase in fractal dimension of the pattern as shown in Table – 3. The fractal dimension of the electrodeposit at 5 V is 1.3762 where as that at a cell operating voltage of 7 V is 1.5707, at higher cell operating voltages the fractal dimension of the electrodeposit approaches the DLA fractal dimension of 1.66.

S.No	Electrolyte	Molarit y	Cell Voltage	FD	\mathbb{R}^2
1	Zinc Acetate	1M	5	1.3762	0.9991
2	Zinc Acetate	1M	7	1.5707	0.9987
3	Zinc Sulphate	1M	7	1.4041	0.9963

Table – 3 Fractal dimension for electrodeposition under different conditions.

The last two rows of the Table -3 give comparison of the fractal dimension of the electrodeposit obtained at the same cell operating voltage for two different electrolytes i.e. 1 M zinc acetate an 1 M zinc sulphate solution. The growth of the electrodeposit using zinc sulphate is poor and the branching pattern is also reduced which is seen from the decrease in fractal dimension from 1.5707 to 1.4041.

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(An ISO 3297: 2007 Certified Organization)

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Vol. 6, Issue 8, August 2017

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