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ELECTRO-DEPOSITION OF METAL FROM DIFFERENT ELECTROLYTE AND THEIR FRACTAL CHARACTERISTICS

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ABSTRACT

Electro-deposition of metal from different electrolyte solutions are studied in the form of dendritic patterns using circular cell geometry. Characterization of selected dendritic patterns in terms of fractal dimensions is presented. It is shown that electro-deposits of different metal obtained from their electrolyte solution possess self similarity and scale invariance and have fractal character. Comparison of different electrodeposits at same cell operating voltages with same electrolyte concentrations is discussed using the concept of fractals and fractal dimension.

KEYWORDS: Electro-Deposition, DLA, Fractal, Fractal Dimension, Self-Similarity, Dendritic Pattern

INTRODUCTION

The concept of fractal and fractal dimension characterizes 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 behaviour 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. 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 [18, 19].

The study of growth patterns by electro deposition of different electrolyte solution under different sets of working conditions is discussed in this paper. Circular cell geometry is used that consist of central cathode and circular outer electrode acting as anode. Cell operating conditions like the concentration of the electrolyte and applied cell voltage mainly govern the shape of resulting dendritic deposition. It was found that the branching patterns and complexity of the shape of the growth depend more on the electric field conditions under a given set of conditions. It was also found that the structure and textures of electro-deposition are strongly influences by concentration of the solution and cell applied voltage. Many dendritic patterns obtained under different cell operating conditions and their characterization is presented. Typical fully developed electro-deposit of the fractal patterns grown by electro-deposition using different electrolyte solutions has been studied. It is observed that there is tendency of self-avoiding, as the process is governed by random walk like processes [20]. On the outer side of growth i.e. around the tips of the branches the growth is prominent. As a result of this, during the growth, the thickness of the branches does not appreciably grow as the cluster grows. Results of the study of different electrolyte solution with same concentarion at same cell applied voltages are presented.

ELECTRO-DEPOSITION OF METAL FROM DIFFERENT ELECTROLYTE SOLUTIONS

The comparison of the characteristics of the growth of electro-deposition of copper, lead and zinc has been studied from the Copper Sulphate, Lead Acetate and Zinc Acetate electrolyte solutions at the concentration of 0.5 molar with cell applied voltage of 7V.

A typical fully developed electro-deposit of copper from copper sulphate electrolyte solution after 12.28 minutes of deposition is shown in Figure 1-a. It is observed that the dendritic pattern obtained at 7V applied voltage with 0.5 molar concentration, there are very thick primary, secondary and tertiary branches of irregular pattern are seen, however many prominent main primary branches could be identified. The self avoiding tendency of fractal growth is also visible as the branches tend to keep away from each other.

(a) (b) (c)

Figure 1: Original Images of 0.5 Molar a) Copper Sulphate ($CuSo_4$) b) Lead Acetate Pb ($C_2H_3O_2$)$_2$ c) Zinc Acetate Zn (O_2CCH_3)$_2$ Under Cell Applied Voltage 7V

Similar typical fully developed electro-deposit of Lead and Zinc from Lead Acetate and Zinc Acetate electrolyte solution were observed after 4.55 minutes and 7.22 minutes of deposition are shown in Figure 1-b and c respectively. It is observed from the Figure 1-b that growth was thicker with dense branches, secondary and tertiary branches are also seen from the growth. The self avoiding tendency of fractal growth is also visible as the branches tend to keep away from each other. It is also observed from the Figure 1-c that the fully grown pattern has dense and more prominent primary, secondary and tertiary branches than Figure 1-b but less than Figure 1-a. They are also have self avoiding tendency to keep away each other.

ANALYSIS OF ELECTRO-DEPOSIT

Concept of fractals and fractal geometry can be used to characterized irregular shapes; therefore the images of the electro-deposition are subjected to fractal analysis. After taking the photograph, it is edited to remove the outer anode in the form circular shape removed for the further analysis of the image then the images were converted to 2 bit black and white images, selecting suitable threshold. The final images after processing are shown below in Figure 2a,b & c. Computer program which are specifically developed for this purpose has been used to analyze the two colour bitmap images. The program reads in the image and converts the image to a matrix with ‘0’ and ‘1’ where ‘0’ indicates unoccupied regions and ‘1’ represents the regions occupied by the image.

(a) (b) (c)

Figure 2: Two Color Bit Images of 0.5 Molar a) Copper Sulphate ($CuSo_4$) b) Lead Acetate Pb ($(C_2H_3O_2)_2$) c) Zinc Acetate Zn ($(O_2CCH_3)_2$) under Cell Applied Voltage 7V

The program makes use of boxes of different size (r) and scans the entire image to find out the total number of boxes (N) required to completely covering the entire image. The program saves the results in a text file for further use of plotting the log (N) versus log(r) plot.

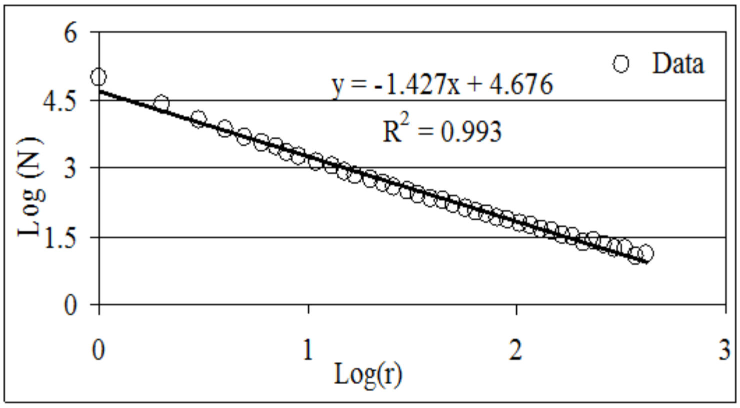

Figure 3: Plots of Log (N) Against Log(r) of Figure 1-a

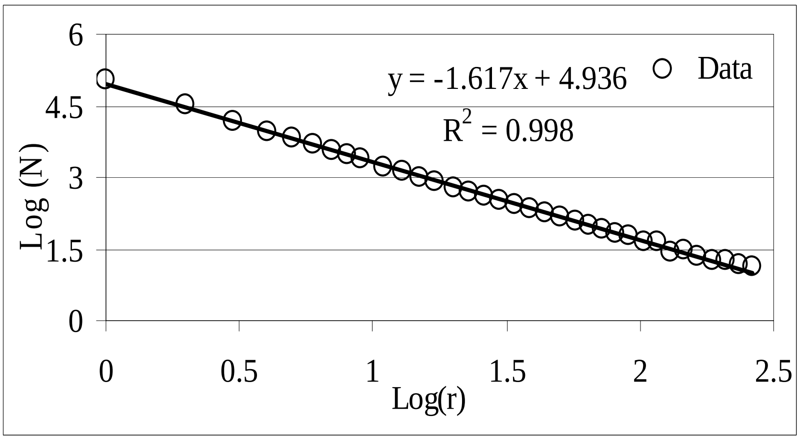

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Figure 4: Plots of Log (N) Against Log(r) of Figure 1-b

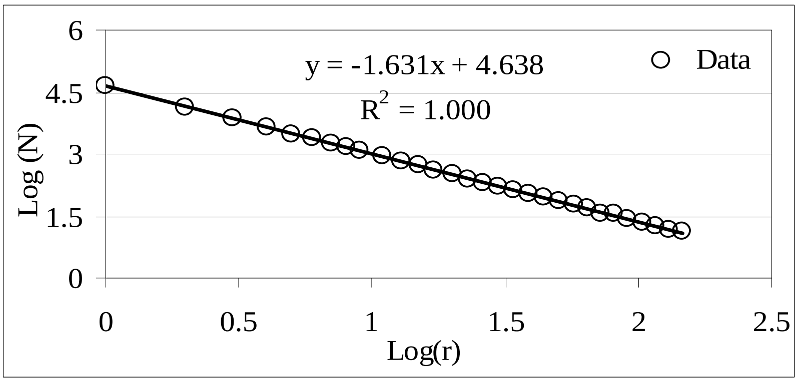

Figure 5: Plots of Log (N) Against Log(r) of Figure 1-c

Two typical two colour bitmap images corresponding to Figure 1-a, b, and c are shown in Figure 2-a, b and c respectively. The box counting technique was used to analyze these files using different sizes of the box (r) and the number of boxes needed to cover the pattern was recorded as N. By taking log (N) on the y-axis and log (r) on the axis of x, a graph was then plotted. Final plots are shown in Figure 3-5.

The plot of Log (N) against Log (r) are shown in Figure 3-6 is a straight line. The plotted points are actual data from box counting [21-26] and the joining line of the points is the least square fit applied confirming that the power law holds good the deposit has fractal character. It is observed that all the data points lie near to a straight line, which is shown by the corresponding value of R^2 for all the cases.

Table 1: Showing Fractal Dimension of 0.5 Molar of Copper Sulphate ($CuSo_4$), Lead Acetate Pb ($C_2H_3O_2)_2$ & Zinc Acetate Zn ($O_2CCH_3)_2$ under Cell Applied Voltage 7V Respectively

Fig. No.	Time (min)	Dimension	R^2 Value
1-a	12.28	1.427	0.993
1-b	4.55	1.617	0.998
1-c	7.22	1.631	1.000

Apart from the different electrolyte solutions with same concentration of 0.5 molar and cell applied voltage of 7V in the Figure 1a, b and c is that of growth time, Figure 1-a is a final stage of growth at 12.28 minutes of copper, Figure 1-b is a final stage of growth at 4.55 minutes of Lead and Figure 1-c is final stage of growth at 7.22 minutes as shown in the

Table 1. Due to DLA process, it is seem from the images and corresponding graphs in Figure 3-5 and Table 1 that the particles in case of copper are don't come in contact with each other and the structure grows one particle at a time and takes more time to grow while in case of Lead and Zinc particles are comes in contact in the form of chunks and takes less time to grow. It is also observed from the Figure 1a,b and that there was more of branching with addition of secondary and tertiary branches in case of Lead and Zinc compare to copper which affect the fractal dimension of the growth. Comparison of the fractal dimensions for the three i.e. 1.427, 1.617 and 1.631 shows that the fractal dimensions obtained for the electro-deposits at 0.5 molar with same cell operating voltage are on the higher side indicating higher amount of structure to the electro-deposit. This is because of the fact that the branches are in the form of leafs shown in Figure 1-b and c while Figure 1-a very fine primary, secondary and tertiary branches are observed which indicates that the thickness of the branch or leaves contribute to the fractal dimension and its complexity of shape.

CONCLUSIONS

It is successfully demonstrated that the electrodeposits of copper, lead and zinc obtained from copper sulphate, lead acetate and zinc acetate solutions under conditions discussed possess self similarity and scale invariance and exhibit fractal character. The various irregular shapes like dendritic pattern are analyzed and classified from the viewpoint of fractal nature, characterized by the box-count fractal dimension which is shown in Figure 1-a,b and c. It is also shown that the complexity of shape associated with the pattern was analyzed by fractal dimension. The fractal dimension is an key to the complexity of shape related with the structure and texture of the irregular shape.

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