

Electrodeposition of Lead from Lead Acetate and its fractal character



Engineering

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ABSTRACT

Electrodeposition of lead in the form of dendritic patterns is studied using circular cell geometry and the electrolyte used is lead acetate solution. The electrodeposits so obtained have crystalline appearance and the deposits are in the form of wide leaves with secondary and tertiary branches at the characteristic angles in accordance with the crystal structure. The growth of electrodeposits and the shape and branching pattern gets modified as the size of the deposit increase and branches tend to approach outer anode. Characterization of selected dendritic patterns in terms of fractal dimensions is presented. It is shown that electrodeposits of lead obtained from lead acetate solution possess self similarity and scale invariance and have fractal character. Comparison of electrodeposits at two different cell operating voltages and two different electrolyte concentrations is discussed using the concept of fractals and fractal dimension.

Introduction.

Electro deposition in circular cell geometry under certain operating conditions results in formation of dendritic patterns showing scaling behaviour and Fractal Characteristics. 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. Electrodeposition of Lead from Lead Acetate

The growth of electrodeposition of lead from lead acetate solution is studied at different electrolyte concentrations. The electrodeposition of lead in circular cell geometry using 0.5 molar lead acetate solution showed that the growth commences at relatively lower voltages as compared to copper and at higher cell operating voltages the growth becomes in the form of fine strands rapidly growing towards the anode. At lower voltages the growth is in the form of leafy patterns showing branches and sub branches at the characteristic angles. The leafy branches are broad and have a tendency to grow in a direction the growth began and formation of the new secondary and tertiary branches is controlled by the crystalline lattice pattern. This is the reason why all the branches do not grow in the same plane, this gives rise to a problem that when viewed from above, the flat branches are seen as broad and the branches developed in vertical plane appear as fine narrow line. The electrodeposited growth has bright metallic luster and crystalline appearance. While photographing the growing pattern, the surfaces facing the camera reflect more and appear more whitish as compared to the rest of the electrodeposit.

This causes the difference in contrast from point to point in the electrodeposit. A typical electrodeposit obtained using 0.5 molar lead acetate solution is shown in Fig. 1. The presence of secondary and tertiary branches is clearly seen and the different in contrast for different regions of the growth patterns is also visible. As the branches grow in size, at times they tend to fall down because of their weight and thus the branch is bent or turned at some point. Before folding the branch was proceeding in its original direction in straight manner, after it turned it changed the direction as is seen from the vertical folded branch.

The image shown in Fig. 1 was captured after 12 minutes of the commencement of the electrodeposition. The middle part of the electrodeposit is over crowded and branches are coming closer to each other which is different from the self avoiding tendency where the branches tend to avoid each other and growth is promoted in areas with less crowded regions.

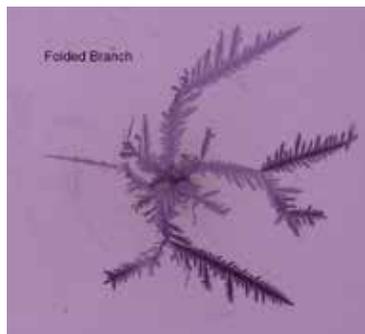


Fig. 1 Electrodeposition of lead using 0.5 M lead acetate solution at a cell operating voltage of 2V in circular cell geometry, the anode diameter was 6 cm.



Fig. 2 Growth of Fig. 1 at a time of 4 minutes showing straight vertical branch.

The same electrodeposit of Fig. 1 at a time of 4 minutes after commencement of the electrodeposition is shown in Fig. 2. The vertical branch is growing straight vertically and the crowding of the branches at the centre is found from early stages. The branch going to the left (shown in Fig. 1) is not yet developed. This branch from Fig. 1 appears to be narrower than the rest of the branches and also the structure is not clearly visible. This is because of the fact that the branch is developing in the vertical plane and the vertical view does not capture the details of sub branches and structure of the leaf.



Fig. 3 Growth of Fig. 1 at a time of 22 minutes.

The developed stage of electrodeposition of Fig. 1 at a time of 22 minutes after the commencement of the electrodeposition is shown in Fig. 3. All the branches have developed in the form of dendritic leaves with secondary and tertiary branches in specific directions making same angle with the main branch. As

the growth becomes larger in size, the space between the actual metallic growth and the outer anode is substantially reduce, this reduction in the distance between the growth attached to the cathode and anode causes substantial increase in the local electric field at the growing tips of the electrodeposit. This excess of electric field modifies further growth pattern. In the high electric field conditions the branching is enhances and growth becomes faster with increased current.



Fig. 4 Electrodeposition of lead using 0.5 M lead acetate solution at a cell operating voltage of 2V in circular cell geometry after 42 minutes.

A fully developed electrodeposit (same as that in Fig. 1) after 42 minutes of deposition is shown in Fig. 4. Excess of crowded multiple branching at the outer tips of electrodeposit near the anode ring are visible. The self avoiding tendency of fractal growth is also visible as the branches tend to keep away from each other, however at times, the branches turn on their side and fall in nearby location bringing two branches closer than they actually were. This is an extreme stage where outer periphery of the electrodeposition has developed under different electric field conditions as compared to the inner portions of the electrodeposition. A typical electrodeposit obtained from 1 molar lead acetate solution at a cell operating voltage of 2 V is shown in Fig. 5. Intentionally the growth is allowed to proceed too far from the centre, approaching the outer ring anode to demonstrate the effect of excess branching at the outer tips when the growth approaches the anode.

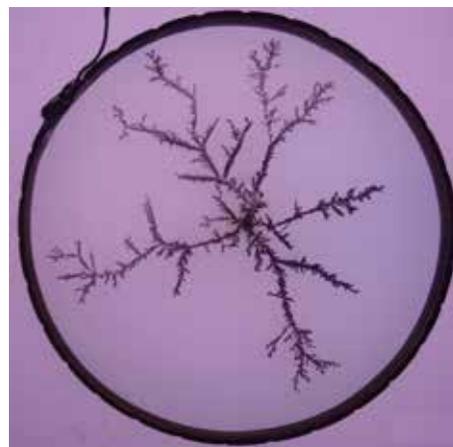


Fig. 5 Typical electrodeposit from 1 M lead acetate solution obtained at a cell operating voltage of 2 V

Similar to Fig. 5, a typical electrodeposit obtained from 1 molar lead acetate solution at a cell operating voltage of 5 V is presented in Fig. 6. In Fig. 5, the growth was allowed to extend

close to anode whereas here, it is terminated when the branches come close to the anode. This deposit differs from that in fig. 1 in that here the branches exhibit leafy appearance with more pronounced crystal structure as is indicated by the secondary branches originating at definite angles determined by the crystal structure of the material.



Fig. 6 Typical electrodeposit from 1 M lead acetate solution obtained at a cell operating voltage of 5 V

Fractal Dimensions: Analysis of Electrodeposits

Irregular shapes can best be characterized using the concept of fractals and fractal geometry, therefore the images of the electro-deposition are subjected to fractal analysis. The images are first converted to gray scale and then to a two colour bitmap image format using suitable threshold. These two colour bitmap images are then analyzed using a computer program specifically developed for this purpose. 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.

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 cover the entire image. The program saves the results in a text file for further use of plotting the log(N) versus log(r) plot. Two typical two colour bitmap images corresponding to Fig. 3 and 4 are shown in Fig. 7 and 8 respectively.



Fig. 7 Typical two colour bitmap image obtained from Fig. 3



Fig. 8 Typical two colour bitmap image obtained from Fig. 4

The results of box counting for the four electrodeposits shown in Fig. 3, 4, 5 and 6 are presented in the form of a graph of log(N) against log(r) are shown in Fig. 9 – 12 respectively.

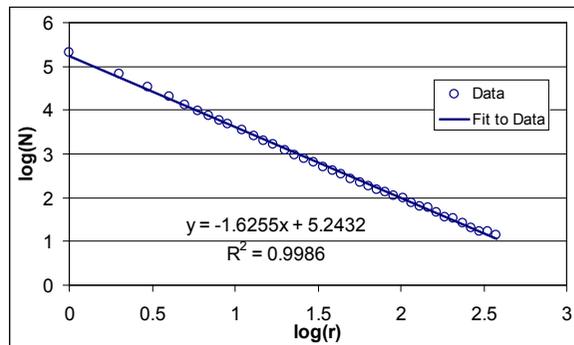


Fig. 9 plot of log(N) versus log(r) for image shown in Fig. 3.

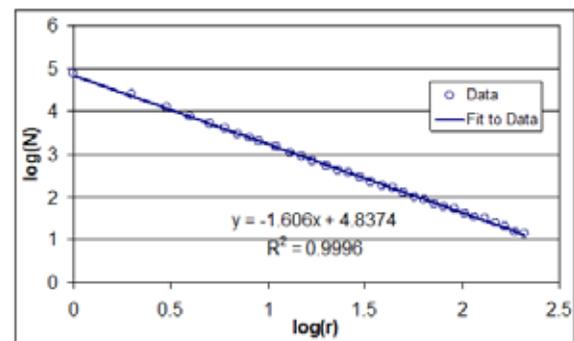


Fig. 10 plot of log(N) versus log(r) for image shown in Fig. 4.

The points plotted are actual data from the results of box counting and the straight line joining these points is the best fitting straight line (least square fit) to the actual data. The equation shown in the inset is the equation of this fitting straight line, the value of R² is also indicated.

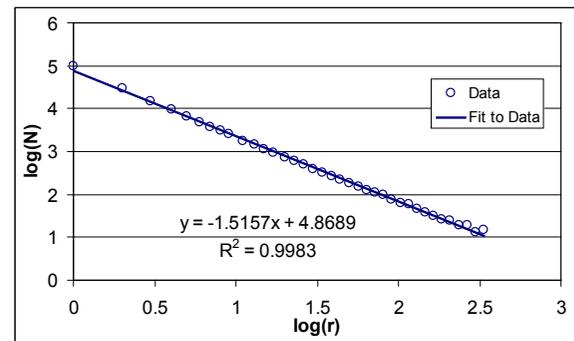


Fig. 11 plot of log(N) versus log(r) for image shown in Fig. 5.

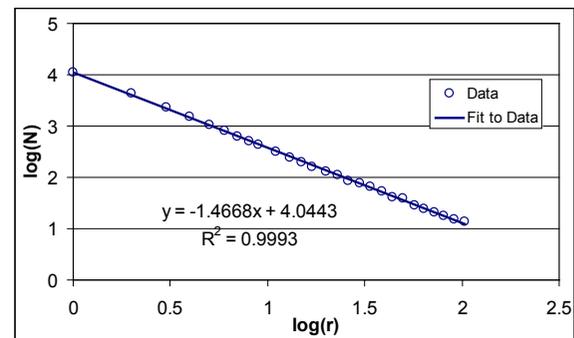


Fig. 12 plot of log(N) versus log(r) for image shown in Fig. 6.

It is clearly seen from all the $\log(N)$ versus $\log(r)$ plots of Fig. 9 – 12 that all the data point lie well along a straight line indicating that the power law holds good which is also indicated by the value of R^2 that is close to unity in all the cases. This confirms that the images analyzed exhibit fractal character and obey scaling law and possess self similarity and scale invariance and the fractal dimension can be obtained from the slope of the straight line fitting the data. The fractal dimensions obtained for the four patterns shown in Fig. 3 – 6 are tabulated in Table – 1.

Figure	Slope	Fractal Dimension
Fig. 3	-1.6255	1.6255
Fig. 4	-1.6060	1.6060
Fig. 5	-1.5157	1.5157
Fig. 6	-1.4668	1.4668

The difference between Fig. 3 and 4 is that of growth time, Fig. 3 is a stage of growth at 22 minutes and Fig. 4 corresponds to a time of 42 minutes. It is seen from the images and corresponding graphs that as time increased there was more of branching with addition of secondary and tertiary branches resulting in slight reduction in fractal dimension. This indicates that overall complexity of shape in terms of structure has slightly reduced.

Images shown in Fig. 4 and 5 are fully grown electrodeposits of lead from lead acetate solution of 0.5M and 1 M respectively. Comparison of the fractal dimensions for the two i.e. 1.6060 and 1.5157 shows that the fractal dimensions obtained for the electrodeposits at higher molarity with same cell operating voltage are on the lower side indicating lower amount of structure to the electrodeposit. This is because of the fact that the branches or leaves in Fig. 4 are broader than those in Fig. 5 and the thickness of the branch or leaves contribute to the fractal dimension and its complexity of shape.

Results and Discussion

It is successfully demonstrated that the electrodeposits of lead obtained from lead acetate solution under conditions discussed possess self similarity and scale invariance and exhibit fractal character. It is also shown that the irregular shapes like the dendritic patterns shown in Fig. 3 – 6 can be characterized by using fractal geometry and the fractal dimension that describes the complexity of shape associated with the pattern analyzed. The fractal dimension is an index to the complexity of shape associated with the structure and texture of the irregular shape.

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