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Dendritic Electroless Deposits of Lead From Lead Acetate Solution

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Abstract: *Electroless deposition of lead from lead acetate is studied in a planar cell geometry. Dendritic patterns are grown using electroless deposition in planar cell geometry. Electroless deposition cell is designed and constructed and the depositions obtained are analysed for self similarity and fractal characterization. Details and findings are presented*
Keywords: *Electroless deposition, Self-similarity, Fractal Dimension, Scale-invariance.*

I. Introduction

The process of electroless deposition is not much different from the electrodeposition in that the ionic movement in the electrolyte is governed by applied electric field in electrodeposition where as in electroless deposition, the metallic electrode is so chosen that it generates its own potential in the electrolyte that in turn makes the ions move [1, 2]. The potential difference required by the ions to migrate toward negative electrode (the cathode) causing deposition of metal ions at the cathode comes from the electrode potential developed based on the the position of the metal ion in electrochemical series. Metals at the top of the electrochemical series are good at giving away electrons and thus are good reducing agents. The reducing ability of the metal increases as one goes up in the electrochemical series. Metal ions at the bottom of the electrochemical series are good at picking up electrons and thus they are good oxidizing agents. The oxidizing ability of the metal ions increases as one goes down the electrochemical series. The list of ions arranged in sequence in electrochemical series is given in Table – 1. Electro deposition has been employed in many technical applications, nano structure and nano wires are also developed using electroless deposition technique[3]. Nano wires of Palladium were grown by Zhongliang Shi et.al[4], they demonstrated that such nano-wires can be developed by electroless this technique in a time of less than two minutes.

Table 1: Position of selected elements in Electrochemical series

Sr. No.	Element / Ion	Result of Reaction	Electrode Potential V
Silver	$Ag^+ + e^-$	= Ag	0.7996
Copper	$Cu^+ + e^-$	= Cu	0.521
Copper	$Cu^{2+} + 2e^-$	= Cu	0.3419
Iron	$Fe^{3+} + 3e^-$	= Fe	-0.037
Lead	$Pb^{2+} + 2e-$	= Pb	-0.130
Nickel	$Ni^{2+} + 2e-$	= Ni	-0.25
Zinc	$Zn^{2+} + 2e-$	= Zn	-0.76
Aluminum	$Al^{3+} + 3e^-$	= Al	-1.662
Magnesium	$Mg^{2+} + 2e^-$	= Mg	-2.372
Magnesium	$Mg^+ + e^-$	= Mg	-2.7
Calcium	$Ca^+ + e^-$	= Ca	-3.8

Concepcion et.al. [5] used the electroless deposition technique for deposition of metals on paper and on polymer sheets like those used for OHP transparencies, they deposited Gold films on paper using line pattern technique. The main interest in such experiments is to deposit small masses having a desired configuration in the form of tiny nano particles or nano wires. The major hurdle in this approach of deposition of very small structures using electroless deposition technique is that the electroless deposition relies on depositions using drying left to itself where exercising control on the depositing conditions becomes a challenge. Commonly used Electroless deposition technique is the one used by Patil A.G [6-8] with the electrolyte solution in an Electroless deposition cell with aluminum (or other electronegative) plate that is used to support the substrate as one of the electrode. The electrode potential developed between the Aluminium plate and lead ions is 1.532 V and this is responsible for the growth of the dendritic patterns.

This potential difference provides the driving force for the ions to move towards the Aluminium plate. Also at room temperature there is lot of zigzag Brownian motion present in the ions of the solution. The presence of linear motion of attraction of the positive ions towards the negative electrode (Aluminium plate acting like a cathode) and the zigzag random motion due to Brownian motion at that temperature results in migration of ions

towards the cathode that is influenced by random motion. Such a process is called as Diffusion Limited Aggregation (DLA). Under such conditions in a small cavity where the deposition is governed by DLA like processes and the deposited structures very much resemble the DLA patterns.
Electroless deposition cell in planar geometry consists of two glass plates between which a porous material like paper is sandwiched and the paper is moistened with a electrolyte solution. The cross section of a typical electroless deposition cell like the one used in our studies is shown in Fig. 1. In this figure a white printing paper with lead acetate solution as an electrolyte is sandwiched

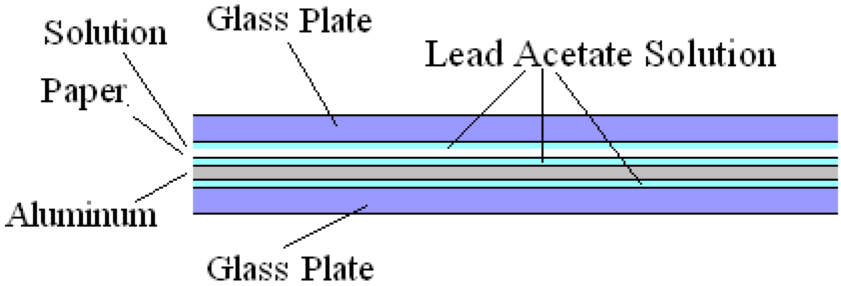
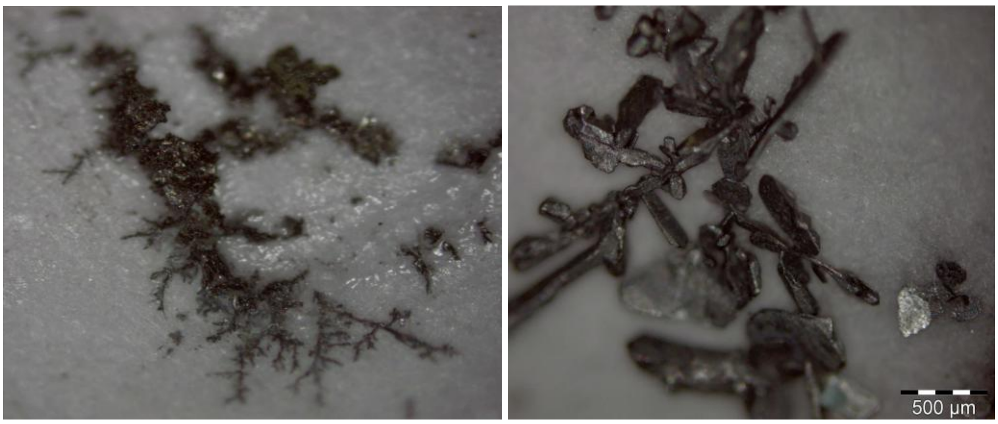


Fig.1 Electroless deposition cell, cross section showing aluminum plate and electrolyte with paper.

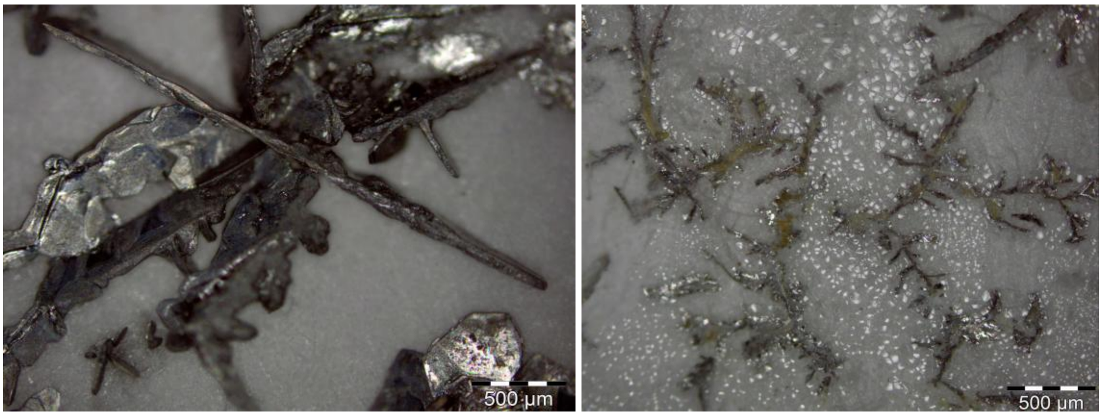
Between two glass plates and kept on the aluminum plate shown in gray. The aluminum plate acts as a cathode and The electrolyte like lead acetate solution spreads along the entire surface of the plate and paper and at times flows below the aluminum plate. The electrolyte having direct or indirect contact with the plate develops necessary driving force for the ions to move towards the aluminum plate and get deposited there. All the material that is deposited directly on the aluminum plate appears like a crude deposit and that part is not of our interest.
Our interest in the present study is related to that part of ionic movement that is taking place in the narrow cavity between the paper placed on the Aluminium plate and the glass plate. As this cavity is narrow, in the presence of weak electrostatic force creates conditions that very much resemble the DLA like situation. As the paper is porous, the porosity allows for electrical contact between the two. This results in deposition of dendritic patterns in regions where DLA like conditions prevail. In most of the cases such depositions are initiated near discontinuities. In a rectangular electrodeposition cell of size 3” × 4” the dendritic patters are develop all around the boundary of the plates where there is discontinuity, additionally nucleation commences at selected site where electrical contact is established.

II. Electroless Deposition Of Lead

For the study of electroless deposition of lead from Lead Acetate solution we used one molar lead acetate solution in the electroless deposition in planar geometry as discussed earlier. The cell was arranged with the Aluminium plate sandwich between two glass plates with a paper on the Aluminium plate. The paper on the aluminum plate was moistened with the 1 M lead acetate solution and cell was softly clamped and was left to itself for drying for six hours. If the conditions are not suitable for DLA like patterns, formation of lumps takes place, in some cases fine branches are formed along with the lumps as shown in Fig. 2 a. Fig. 2 b and c show the electroless depositions obtained from lead acetate solution and the branches prefer to develop at preferred sites and angles. Also the growing branches continue to grow forming needle shapes structures. Fig. 2 d shows a typical electroless deposit obtained using 0.5 M lead acetate solution where fine branching is seen.



a) b)



c) d)

Fig. 2 Electroless deposition of Lead a, b and c from 1 M and d from 0.5 M solution.

We analysed two selected patterns from Fig. 2 i.e. Fig. 2 c and d for power law and fractal dimensions using box counting technique. The results of box counting are electroless deposit of Fig. 9 b is shown in Table – 5 and the log(N) versus log (r) plots for the data from Table – 2 are shown in Fig. 3.

Table 2 Results of box counting for electroless deposit of Fig. 2 b.

r	N	log(r)	log(N)		r	N	log(r)	Log(N)
1	136592	0	5.135		30	319	1.477	2.504
2	45252	0.301	4.656		34	257	1.532	2.410
3	21194	0.477	4.326		39	210	1.591	2.322
4	12401	0.602	4.094		44	169	1.644	2.228
5	8195	0.699	3.914		50	138	1.699	2.140
6	5845	0.778	3.767		57	113	1.756	2.053
7	4411	0.845	3.645		64	85	1.806	1.929
8	3442	0.903	3.537		72	70	1.857	1.845
9	2783	0.954	3.445		81	60	1.909	1.778
11	1912	1.041	3.282		91	50	1.959	1.699
13	1411	1.114	3.150		103	42	2.013	1.623
15	1096	1.176	3.040		116	32	2.065	1.505
17	878	1.230	2.944		131	28	2.117	1.447
20	655	1.301	2.816		147	22	2.167	1.342
23	515	1.362	2.712		165	19	2.218	1.279

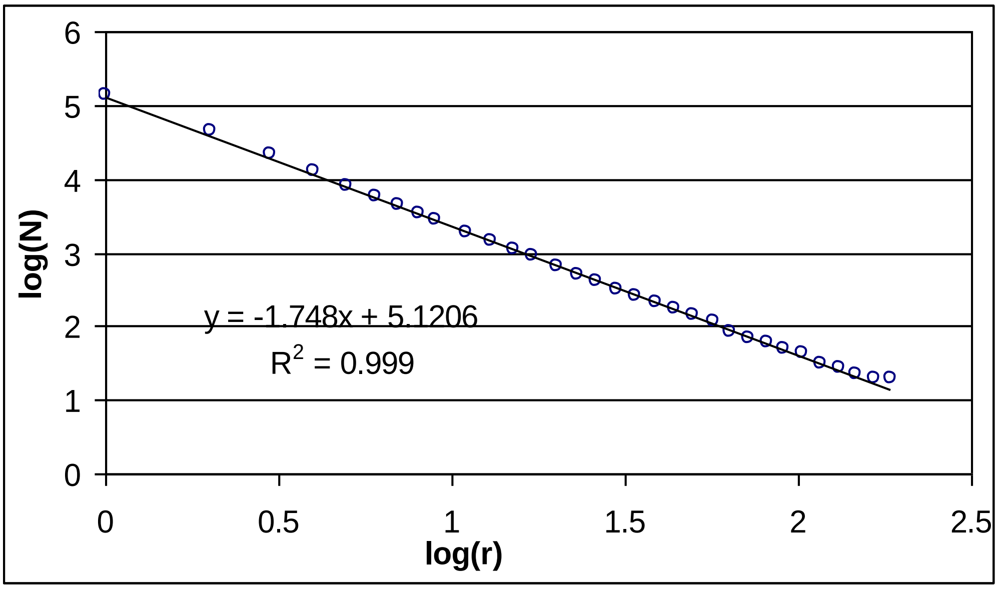


Fig.3 log (N) versus log(r) plot for data from Table – 2 and Fig. 2 b.

The results of box counting for the electroless deposition of fig 2 c are shown in Table – 3 and the log(N) versus log (r) for the data from Table – 3 for Fig. 2 c are shown in Fig. 4.

Table 3 Results of box counting for electroless deposit of Fig. 2 c.

r	N	log(r)	log(N)		r	N	log(r)	Log(N)
1	101888	0	5.008		30	232	1.477	2.366
2	33365	0.301	4.523		34	179	1.532	2.253
3	15490	0.477	4.190		39	148	1.591	2.170
4	9020	0.602	3.955		44	119	1.644	2.076
5	5953	0.699	3.775		50	96	1.699	1.982
6	4206	0.778	3.624		57	76	1.756	1.881
7	3147	0.845	3.498		64	60	1.806	1.778
8	2467	0.903	3.392		72	48	1.857	1.681
9	1980	0.954	3.297		81	44	1.909	1.644
11	1383	1.041	3.141		91	36	1.959	1.556
13	1022	1.114	3.010		103	29	2.013	1.462
15	794	1.176	2.900		116	23	2.065	1.362
17	624	1.230	2.795		131	20	2.117	1.301
20	469	1.301	2.671		147	15	2.167	1.176
23	361	1.362	2.558		165	14	2.218	1.146
26	298	1.415	2.474		186	14	2.270	1.146

Fig. 3 and 4 show that power law is obeyed for both the electroless depositions for Fig. 2 b and c as all the points lie well along a straight line which is also seen from the value of R^2 obtained from least square fitting and the equation shown in the inset.

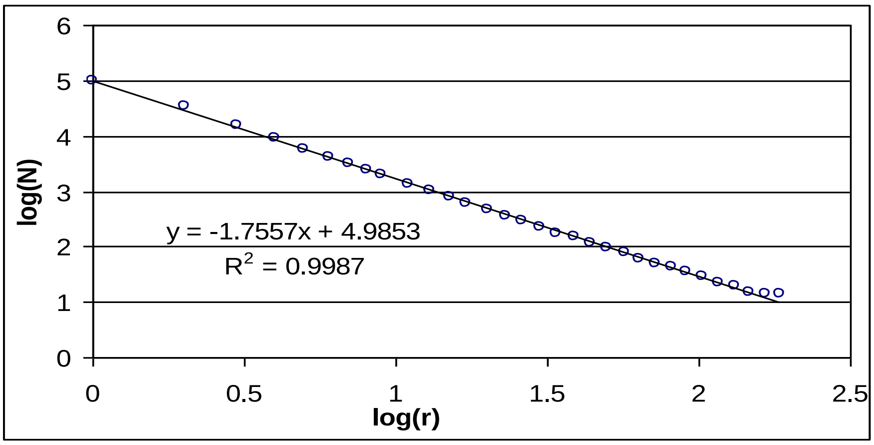


Fig. 4 log (N) versus log(r) plot for data from Table – 3 and Fig. 2 c.

The power law exponent for the two patterns analysed are –1.748 and –1.7557 therefore the resulting fractal dimensions are 1.748 and 1.7557. It is seen that the two power law exponents and hence the fractal dimensions are close to each other indicating that the two electroless deposited patterns are very much identical in terms of morphological structure. R^2

III. Results And Discussions

Electroless deposition in planar cell geometry is studied and the required electroless deposition cell was designed and constructed as shown in Fig. 1. The electrolyte solutions used was Lead acetate. Selected electroless deposit from lead acetate was analysed for fractal dimension to explore the degree of complexity associated with the electroless deposited patterns. The electroless deposits exhibit distinct branching patterns with metallic luster and the two patterns analysed showed fractal dimension of 1.748 and 1.7557 and a higher fractal dimension represents higher degree of complexity of the pattern.

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