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Computer modeling of electrochemical growth with convection and migration in a rectangular cell

Weiguang Huang* and D. Brynn Hibbert
School of Chemistry, University of New South Wales, Sydney, New South Wales 2052, Australia
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We model the growth of electrodeposits with diffusion, convection, and migration in an electric field in a rectangular cell. From differential equations, we derive the expressions of growth probability, which predict that the direction and speed of convection and the electric field govern the pattern formation of electrochemical growth. These theoretical predictions are demonstrated by computer simulations. Different patterns, diffusion-limited aggregation, dendritic, dense, needle, and treelike, are governed by two parameters: the convection velocity in the direction parallel to the electrodes, and the flow (convection plus migration in an electric field) perpendicular to the electrodes.

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I. INTRODUCTION

We [1–3] have developed a one-dimensional mathematical model of the concentration and current for electrochemical growth in diffusion, convection, and migration in electric fields. By comparison with both Chazalviel's and Fleury's models [4,5], our models are exact solutions of differential equations. Concentration and current are dependent on the applied voltage, and the mathematical treatment is simple.

The diffusion-limited aggregation (DLA) model [6,7] has attracted much attention because of its possible relationship to electrochemical deposition in two-dimensional (2D) thin cells without supporting electrolyte. The DLA model by computer simulation shows that we should expect a fractal pattern with dimension 1.70 when a diffusion field governs the growth of a cluster. It has been reported that in an electrochemical experiment, the cluster was fractal and well described by DLA [8]. However, it was soon discovered that in most experimental conditions of an unsupported binary electrolyte, the clusters are dense or dendritic rather than fractal, and diverge from the DLA model [9,10]. The main weakness of the DLA model is that it is a single field model (i.e., a diffusion field from the concentration gradient) and the actual growth must go beyond a single field. After further consideration of the growth process, Fleury, Chazalviel, and Rosso [11] claimed that the genuine electrochemical aspects of the growth were not relevant to the DLA model, and that electrochemical deposition may not belong at all to the DLA class of structures.

However, we propose in this paper that a modified DLA model is relevant to electrochemical deposition, which does indeed belong to the DLA class of structures. The DLA model is modified by introducing convection and migration in electric fields. Computer modeling of the growth of electrodeposits with diffusion, convection, and migration in the electric field in a rectangular cell will be presented. We will show that in a random walk the particle in the DLA model moves with the equal probability of $\frac{1}{4}$ in four different directions, but the probability is no longer equal in different directions when flow or electric field is turned on. The expressions of growth probability derived from differential equations predicate that the pattern formation is governed not only by the diffusion but also by the convection and migration in the electric field. Furthermore, they indicate that the direction of flow has an effect on the pattern formation. We can produce various patterns (e.g., DLA, dendritic, dense, needle, and treelike patterns) by two parameters: the convection velocity in the direction parallel to the electrodes, and the flow (convection plus migration in electric field) perpendicular to the electrodes. In addition we can control the growth by the deposition time. The effect of convection and electric fields on morphology will be discussed.

*Author to whom correspondence should be addressed.

II. MODEL

We consider the electrochemical deposition in a two-dimensional rectangular thin cell of width W and length L with two parallel linear electrodes (cathode at $y=0$ and anode at $y=L$). Assume that the deposit grows very slowly in a quasi-steady-state, and is governed by diffusion, convection, and migration in the electric field. For a practical value of concentration, the charged layer is very narrow, and the cell would be quasineutral, so the electric field gradient can be ignored (i.e., $\partial E/\partial y=0$). The component of the electric field parallel to the electrodes will stay zero (i.e., the electric field in the x direction $E_x=0$). To simplify the equations, we write E for E_y. The concentration c satisfies the differential equation

$$D\frac{\partial^2 c}{\partial x^2}+D\frac{\partial^2 c}{\partial y^2}-v_x\frac{\partial c}{\partial x}-v_y\frac{\partial c}{\partial y}-\mu E\frac{\partial c}{\partial y}=0\ , \tag{1}$$

where D is the diffusion coefficient, v_x and v_y are the convection velocities in the x and y directions, respectively, μ is the mobility of the ion, and the electric field $E=-U/L$, where U is voltage applied between the electrodes. The first two terms are the diffusion terms in the x and y directions, the third and fourth terms are the convection terms in the x and y directions, and the last term is the migration in the electric field term in the y-direction.

In order to write the differential equation in a dimensionless form, we set $C=c/c^0$ for the dimensionless concentration, $V=vL/D$ for the dimensionless convection velocity, $X=x/L$ for the dimensionless distance, and $M=\mu EL/D$ for the dimensionless electric field. By multiplying both sides of Eq. (1) by $L^2/(Dc^0)$, it may be rewritten in a dimensionless form as

$$\frac{\partial^2 C}{\partial X^2}+\frac{\partial^2 C}{\partial Y^2}-V_x\frac{\partial C}{\partial X}-V_Y\frac{\partial C}{\partial Y}-M\frac{\partial C}{\partial Y}=0\ . \tag{2}$$

A. Model for 2D diffusion

Consider a simple diffusion case. In two-dimensional diffusion, Eq. (2) is simplified to the Laplace equation

$$\frac{\partial^2 C}{\partial X^2}+\frac{\partial^2 C}{\partial Y^2}=0\ . \tag{3}$$

By converting the equation into its discrete version and imposing the condition of $\delta X=\delta Y=\Delta$ (the step in the x direction δX is the same as the step in the y direction δY), the differential operators are

$$\frac{\partial C}{\partial X}=(C_{X,Y}-C_{X-1,Y})/\Delta\ , \tag{4}$$

$$\frac{\partial C}{\partial Y}=(C_{X,Y}-C_{X,Y-1})/\Delta\ , \tag{5}$$

$$\frac{\partial^2 C}{\partial X^2}=(C_{X+1,Y}+C_{X-1,Y}-2C_{X,Y})/\Delta^2\ , \tag{6}$$

$$\frac{\partial^2 C}{\partial Y^2}=(C_{X,Y+1}+C_{X,Y-1}-2C_{X,Y})/\Delta^2\ . \tag{7}$$

Substituting Eqs. (6) and (7) into Eq. (3) gives

$$C_{X,Y}=\frac{C_{X+1,Y}+C_{X-1,Y}+C_{X,Y+1}+C_{X,Y-1}}{4}\ . \tag{8}$$

This is the diffusion-limited aggregation (DLA) process following Eq. (3), where the particles undergo random walks in two dimensions.

The concentration contribution from point $(X+1,Y)$ to point (X,Y) is equal to the product of concentration $C_{X+1,Y}$ at point $(X+1,Y)$ and the probability $p_{X+1,Y}$ of a particle moving along the X axis from point $(X+1,Y)$ to point (X,Y), which corresponds to the coefficient of concentration. Therefore from Eq. (7), we get $p_{X+1,Y}=\frac{1}{4}$. The probability $p_{X+1,Y}$ of a particle moving along the X axis from point $(X+1,Y)$ to point (X,Y) is the same as the probability $p_{X,Y}$ of a particle moving from point (X,Y) to point $(X-1,Y)$. In the same way, we get probabilities of the particle moving in the other directions (e.g., the $-X$, Y, and $-Y$ directions):

$$p_{X+1,Y}=p_{X-1,Y}=p_{X,Y+1}=p_{X,Y-1}=\tfrac{1}{4}\ . \tag{9}$$

Note that the sum of all probabilities is 1.

The relationship between concentration and probability of a particle moving is

$$C_{X,Y}=p_{X+1,Y}C_{X+1,Y}+p_{X-1,Y}C_{X-1,Y}+p_{X,Y+1}C_{X,Y+1}+p_{X,Y-1}C_{X,Y-1}\ . \tag{10}$$

B. Model for 2D diffusion, convection, and electromigration

We take account of diffusion, convection, and migration in an electric field in two dimensions, using Eq. (2). By substituting Eqs. (4)–(7) into Eq. (2), we obtain

$$C_{x,y}=\frac{C_{X+1,Y}}{4+(V_X+V_Y+M)\Delta}+\frac{(1+V_X\Delta)C_{X-1,Y}}{4+(V_X+V_Y+M)\Delta}+\frac{C_{X,Y+1}}{4+(V_X+V_Y+M)\Delta}+\frac{(1+V_Y\Delta+M\Delta)C_{X,Y-1}}{4+(V_X+V_Y+M)\Delta}. \tag{11}$$

For our diffusion $V_X=0$, $V_Y=0$, and $M=0$, this equation is simplified to Eq. (8).

In the similar way to the case of 2D diffusion, from Eq. (11), the probabilities of the particle moving in four directions are

$$p_{X+1,Y}=\frac{1}{4+(V_X+V_Y+M)\Delta}\ , \tag{12}$$

$$p_{X-1,Y}=\frac{1+V_X\Delta}{4+(V_X+V_Y+M)\Delta}\ , \tag{13}$$

$$p_{X,Y+1}=\frac{1}{4+(V_X+V_Y+M)\Delta}\ , \tag{14}$$

$$p_{X,Y-1}=\frac{1+(V_Y+M)\Delta}{4+(V_X+V_Y+M)\Delta}\ . \tag{15}$$

Because the value of probability is non-negative, we take the absolute value of each parameter to warrant $p\geq 0$. As above, the sum of all probabilities p is 1 and each indi-

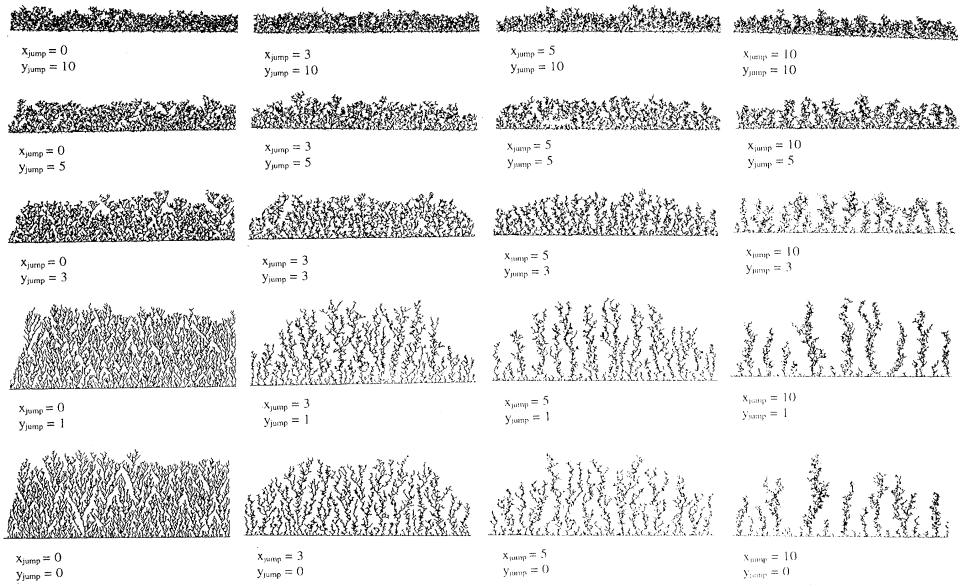

FIG. 1. Growth patterns produced by computer simulations.

vidual $p \leq 1$. For pure diffusion $V_X=0$, $V_Y=0$, and $M=0$, Equations (12)–(15) are simplified to Eq. (9). Notice that Eq. (10) is still valid for this case of 2D diffusion, convection, and migration in the electric field.

III. COMPUTER PROGRAM

A computer program for simulation of pattern formation of electrochemical growth was written in Borland Pascal, and implemented on an IBM PC. The diffusion field is simulated by a DLA random walker, and both the convection and migration in an electric field are simulated by the superimposed drifts. The user can produce various patterns (e.g., DLA, dendritic, dense, needle, and treelike patterns) by two parameters: $x_{\text{jump}}=V_X$ (the convection velocity in the direction parallel to the electrodes) and $y_{\text{jump}}=V_Y+M$ (convection plus migration in electric field perpendicular to the electrodes). In addition the user can control the growth by the deposition time (t). The parameters V_X and V_Y (the dimensionless convection velocities) and M (the dimensionless electric field) change the pattern while the parameter t changes the size of growth.

Particles start one at a time at randomly chosen positions 20 points away from the deposit tip. This restriction saves a lot of computation time. The particle continues to move until it either reaches the lower electrode (i.e., a point adjacent to a site already occupied by a particle), or it moves outside the rectangular cell. When the particle hits a point adjacent to a site already occupied by a particle, it sticks on the aggregate. When the particle goes outside the rectangular cell, it is finished.

The pattern can be saved in a file for later redisplay and measurement of its fractal dimension. Further information and the program are available from the authors upon request.

IV. RESULTS AND DISCUSSION

The growth probability in the DLA model for pure diffusion given by Eq. (8) shows that in a random walk the particle moves with the equal probability of $\frac{1}{4}$ in the four different directions. Equations (12)–(15) predict that the probability is no longer equal in different directions when convection and migration are turned on. These equations show that the pattern formation is governed not only by the diffusion field but also by the convection field and the electromigration field. Furthermore, they predict that both magnitude and direction of flow governs the pattern formation.

Figure 1 shows simulations for different values of the parameters in the x and y directions. For $x_{\text{jump}}=0$ and $y_{\text{jump}}=0$ without convection and migration, the pattern is the DLA fractal. For pure horizontal convection without vertical flow, as the value of x_{jump} increases, the pattern changes from DLA to treelike, becoming a less ramified structure, then to separate trees or needles. The introduction of horizontal convection has a strong effect upon the structure of the cluster, inducing a strong screening which prevents particles going into the inner part of the deposit. The deposit grows mainly at the tips of the cluster. The screening effect increases with raising horizontal flow. Under low vertical flow (convection and/or voltage) with increasing horizontal flow, the pattern of the deposit changes from DLA into the columnar morphology, decreasing the width and the number of columns. But under high vertical flow, patterns are dense, regardless of the value of horizontal convection.

For a pure vertical flow, as the value of y_{jump} increases, the pattern changes from fractal to dendritic, then to dense. These pattern changes are different from those with a change of the horizontal convection velocity. For a combination of both horizontal and vertical flows, we change the vertical flow under the condition of constant horizontal convection. The pattern under low horizontal drift (e.g., $x_{\text{jump}}=3$) changes from dendritic into dense growth with increasing vertical flow. But under high horizontal convection with increasing vertical drift, e.g., $x_{\text{jump}}=10$, patterns change from needles into dense growth.

All of these patterns can be found in electrochemical experiments, and similar morphological transitions are seen in the growth of metal electrodeposits (e.g., copper from $CuSO_4$) as the voltage changes [12,13]. At low voltage, DLA-like trees grow. As voltage increases, a transition from open branches structures of deposition to dentritic structures is reported. Using this approach, it is possible to model the vortices seen by Fleury, Kaufman, and Hibbert [14] at the growing tips.

V. CONCLUSION

From differential equations, we derive the expressions of growth probability which predict that direction and speed of convection, and electric field govern the pattern formation of electrochemical growth. These theoretical predictions have been demonstrated by computer simulations. Both the magnitude and direction of imposed flows have great effects on morphology. It is possible to simulate a range of experimentally observed patterns by this model.

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