Aggregation in coupled diffusion fields: a model for electrochemical deposition

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Abstract   The effect of ion concentration on electrochemical deposition is investigated with the use of computer simulations. The model equations are expressed in terms of the coupled diffusion Aelds: one is the concentration field of ions and the other is the electric potential field. Two important dimensionless parameters are introduced to describe concentration of ions and strength of applied voltage. It is found that the aggregate crosses over from DLA fractal to dense aggregate when the concentration of ions is increased. Together with our previous studies which show that the aggregate becomes a compact structure with increasing voltage, the morphology diagram expressed in terms of the two parameters is obtained. It is found that the diagram is close to that obtained by experiments on electrochemical deposition.

1. Introduction

A wide variety of irreversible aggregation phenomenal has recently attracted much attention[1,2]. Examples of such systems including viscous fingering[3], dielectric breakdown[4], and electrochemical deposition[5,10] are all governed by the Laplace equation. The developement of this new field was triggered by a diffusion-limited aggregation model introduced by Witten and Sander[11]. The experimental realization of two-dimensional diffusion-limited deposition was firstly obtained by Matsushita et al.[5]. A crossover phenomenon from DLA fractal to dense aggregation in electrochemical deposition was recognized experimentally by Sawada et al[6],

Grier et al.[7,8], and Hibbert et al.[9,10] with varying applied voltage and concentration of electrolytes. This phenomenon was investigated numerically by Meakin[12] and Nagatani[13] with biased random walker simulation. Voss[14] and Uwaha et al.[15] with the use of multi-particles Monte Carlo method. However, a generalized DLA model has not been presented to allow for describing both effects. In our previous paper[16], we investigated the effect of applied voltage on electrochemical deposition. The mechanism of aggregation presented in it was more realistic in the light of the comparison with the experimental situation rather than usual drift-DLA, because the drift force was proportional to the gradient of the electric field.

In this paper, we propose a new model which allows for describing both the effect of voltage and concentration. In this model, two diffusion fields are introduced, one is the concentration field of ions and the other is the electrostatic potential field. This is a generalization of the DLA process governed by the ordinary Laplace field[4,17]. The dependence of electrolyte concentration on the dielectric constant is introduced to allow us to describe that effect in our generalized model. In the dimensionless form of the coupled diffusion equations, there exist two important dimensionless parameters representing concentration of ions and applied voltage. The distinct morphology is developed with the increase of each parameter, which is similar to that obtained by experiment.

2. Basic equations and model

In this section, we present model equations to describe the effect of both concentration of electrolytes and applied voltage on the electrochemical deposition. In the electrodeposition of Zn or Cu, from acqueous $ZnSO_4$ or $CuSo_4$ solutions, we have at least three relevant field to take into account. They are $Zn^{2}+$ concentration, which we call C, $= C, (x,t)$, SO_4^{2-} concentration, $C_2 = C_2(x,t)$, and the electrostatic potential, $\Phi = \Phi(x,t)$, whose gradient is the electric field in the electrolyte. We consider the system in which these fields are governed by the following diffusion and Poisson's equations,

$$\frac{\partial C_i}{\partial t} = V \cdot (z_i \mu_i C_i \nabla \Phi + D_i \nabla C_i) \tag{1}$$

$$\nabla \cdot (\epsilon \nabla \Phi) = \sum z_i C_i \quad , \tag{2}$$

where D's, μ's, z's, and ϵ are the diffusion constant, mobility, charge of the species, and dielectric constant, respectively. The charge neutrality condition $z_1 C_1 + z_2 C_2 = 0$ is reasonable outside the interfacial region. Hence it is enough to consider either the positive ion or negative ion and hereafter we only consider the concentration field of the positive ion C_1 and omit the subscript. The right hand side of eq.(2) equals zero. Next, we assume that the dielectric constant would be of the following form,

$$\epsilon = \epsilon_0 + \gamma C(x) \quad , \tag{3}$$

where ϵ_0 is the constant part of the dielectric constant and γ is the coefficient of the concentration-dependent part. Since the dielectric constant is sensitive to the existence of Zn^2 (or Cu^{2+}) and SO_4^{2-} ions, this assumption is reasonable. Now in the quasi-static approximation we can write

$$V \cdot (z\mu C \nabla \Phi + DVC) = 0 , \tag{4.1}$$

$$V \cdot [(\epsilon_0 + \gamma C)\nabla \Phi] = 0 . \tag{4.2}$$

The boundary conditions are given by $\Phi = 0$, $C = 0$ on the aggregate and $\Phi = \Phi_\infty$, $C = C$, at the outer boundary. To cast these equations in dimensionless form, we scale each variable with characteristic units as follows:

$$x \rightarrow \hat{x} = x/L \text{ , (L: system size of the simulation)} \tag{5.1}$$

$$(\nabla \rightarrow \hat{\nabla}),$$

$$C \rightarrow \hat{C} = C/C_\infty \quad , \tag{5.2}$$

$$\Phi \rightarrow \hat{\Phi} = \Phi/\Phi_\infty \quad , \tag{5.3}$$

$$\epsilon \rightarrow \hat{\epsilon} = \frac{\epsilon}{\epsilon_0} = 1 + \frac{\gamma}{\epsilon_0} C_\infty \hat{C} \tag{5.4}$$

Then eqs. **(4.1)** and (4.2) **become**

$$\hat{\nabla} \cdot (\alpha \hat{C} \nabla \hat{\Phi} + \hat{\nabla} \hat{C}) = 0 \tag{6.1}$$

$$\hat{\nabla} \cdot [(1 + \beta \hat{C}) \hat{\nabla} \hat{\Phi}] = 0 \tag{6.2}$$

Careted variables are **all** dimensionless. We find two important dimensionless parameters: $\mathbf{a} = z\mu\Phi_\infty/D$ and $\beta = \gamma C_\infty/\epsilon_0$ representing the strength of applied **voltage** and concentration of ions respectively.

The algorithm of the growth process in our numerical simulation is similar to that of our previous study[16]. However, for the sake of consistency and clarity of this article, we think that it is better to explain it again here. The aggregation starts from the point seed settled at the center. The concentration field of ions and the electrostatic potential field are calculated step by step by solving eqs. **(6.1)** and **(6.2).** The growth probability $\mathbf{P}i$ at the i-th perimeter on the surface **is** proportional to the current of ions at the i-th **site**

$$J_i = \left(\alpha \hat{C} \frac{\partial \hat{\Phi}}{\partial \hat{x}_i} + \frac{\partial \hat{C}}{\partial \hat{x}_i} \right)$$

So the normalized growth probability at the ith **site is** given by

$$Pi = \frac{|j_i|}{\sum_k |j_k|}$$

where the summation runs over **all** perimeter sites on the surface of the aggregate. Once the calculation of grotwh probability **has** been completed, then the next **site** is added to the aggregate. Thus aggregation process of one particle **has** ended, and the same procedure continues until the **size** of the aggregate is adequately large. The **outer** boundary is diamond-shaped, of which the diagonal line is **400** latice units.

3. Results and Discussion

In our previous paper, we investigated the effect of applied **voltage** in the same system. So we **fix** the parameter a and study the **dependence** on the parameter β. This corresponds to seeing how the aggregate changes its pattern

when concentration of electrolytes is varied. Fig. 1(a) shows the result obtained for the parameter a = 10; $\beta = 0$. The cluster looks like a DLA fractal as the Witten-Sander-model[11] in which particles are assumed to follow Brownian trajectories. Fig. 2(b) and 2(c) show the results obtained for the parameters (b): a = 10; $\beta = 20$, (c): $\alpha = 10$; $\beta = 80$. The crossover from DLA fractal to dense aggregation is found with increasing parameter β. This observation is consistent with the fact that a trend from open growth to dense aggregation with increasing concentration of electrolytes is found in the experiment of electro-chemical deposition. The statistics of each cluster are shown in fig. 2, which indicates the dependence of cluster density on distance from the origin in the form of log-log plots. At small distances, the slope of curves being close to -1/3 which gives fractal dimension, $D_f \sim \frac{5}{3}$. At large distances, however, the slope of curves deviates, from -1/3 and changes to keep plateau levels. We define the crossover length at the crossing point of extrapolation of these two lines as shown in fig. 2. Thus we obtain the crossover lengths ξ_1 and ξ_2 for the case of $\beta = 20$ and $\beta = 80$, respectively. Observation of decreasing crossover length were made with increasing concentration.

Together with our previom studies, which show that the aggregate becomes a compact structure with increasing applied voltage, we could draw the morphology diagram as shown in fig. 3. This diagram is similar to that obtained by Grier et al[7,8]. Hibbert and Melrose did not present a morphology diagram such as fig. 3, however, they found a trend from open growth to dense radial growth with increasing concentration of electrolytes and applied voltage. This observation is consistent with fig. 3. Sampling points in the 2-dimensional space of α and β are not enough to draw a clear crossover line which distinguishes the variation of structures. However. we show that the morphology of the aggregate changes from DLA-like open structure to dense aggregate along the arrow as shown in fig. 3, and point out that the variation of structure could be qualitatively described as decreasing of the crossover length. It could be said that Grier et al.'s work[7,8] is the remarkable pionerring work, however, the meaning of the crossover line in their morphology diagram is not clear. We would Iike to state that in a narrow sense

(a) $\begin{bmatrix} \alpha = 10 \\ \\ \beta = 0 \end{bmatrix}$

(b) $\begin{bmatrix} \alpha = 10 \\ \\ \beta = 20 \end{bmatrix}$

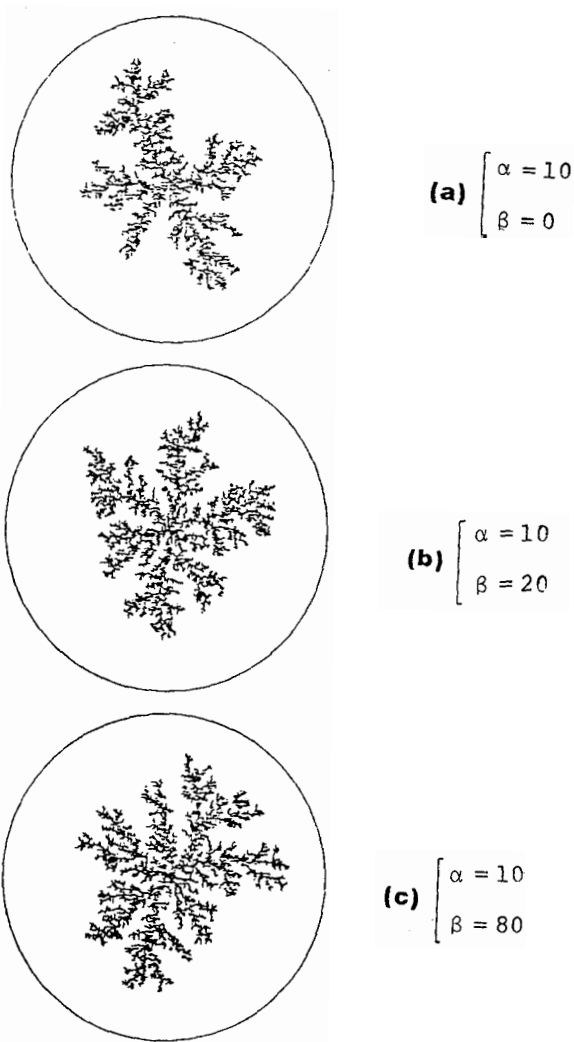(c) $\begin{bmatrix} \alpha = 10 \\ \\ \beta = 80 \end{bmatrix}$

Fig.1 - Typical cluster grown in the coupled diffusion fields for the parameters (a) $\alpha = 10$; $\beta = 0$, (b) $\alpha = 10$; $\beta = 20$, (c) $a = 10$; $\beta = 80$. The aggregate crosses over from DLA fractal to dense aggregation with the increase of parameter β which represents concentration of electrolytes.
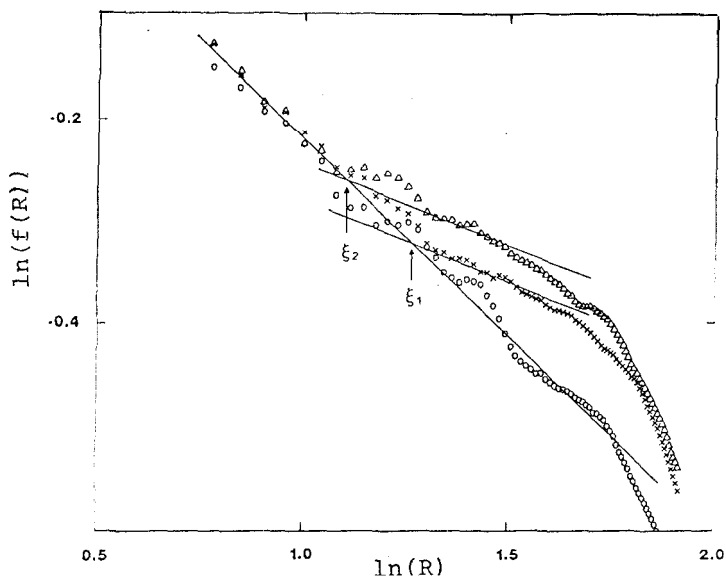
Fig.2 - Dependence of cluster density on distance from the origin in the form of log-log plots with the use of different parameters β. (o) a $= 10; \beta = 0,$ (x) a: $= 10; \beta = 20,$ (A) a: $= 10; \beta = 80.$ At small distances the slope of curves is close to -1/3. At large distance the slope of curves deviates from -1/3 at the crossover length ξ_1 for $\beta = 20, \xi_2$ for $\beta = 80.$

DLA has self similar properties in the scale of infinity (or the system size under consideration), and it has no characteristic length. Therefore a 'DLA' region might exist as the point in the dilute limit of the electrolyte and zero limit of applied voltage. When either of these is increasing a characteristic length appears in the statistics of the aggregate, such as ξ_1 and ξ_2 as shown in fig. 2. Accordingly, a phase diagram should be drawn in terms of a contour map of crossover length as a function of applied voltage and concentration of electrolytes.
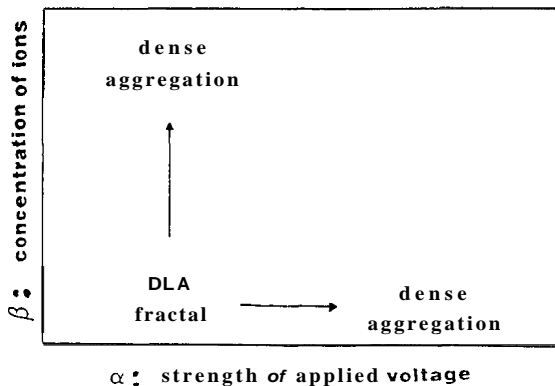
Fig.3 - **The morphology diagram for electrochemical deposition in a schematic form. The DLA fractal crosses over to the dense aggregate with the increase of the parameter α and β. Or more correctly, crossover length is decreased when these parameters are increased.**

4. Concluding remarks

In this paper, we have proposed a new model which allows for describing both effects of voltage and concentration concerning the aggregate in electrochemical deposition. It has been shown that one possible explanation for variation of structure lies in the concentration-dependent dielectric constant. Computer simulations have been performed upon this model and a crossover phenomenon from the DLA fractal to dense aggregate has been found with increase of concentration of electrolytes. The morphology diagram has been described in terms of two dimension less parameters which correspond to concentration and voltage. We have found that this diagram is similar to that obtained experimentally by Grier et al.[7,8], and the variation of structure has been discussed qualitatively with the use of crossover length.

numerical calculations were performed by a HITAC-S820 computer at the Institute for Molecular Science computer center.

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Resumo

O efeito da concentração iônica sobre o fenômeno de deposição eletroquímica 6 investigado com o auxílio de simulações computacionais. As equações do modelo se expressam em termos dos campos de difusão acoplados, os quais são: a concentração iônica e o potencial elétrico. Dois parâmetros adimensionais importantes são introduzidos para descrever a concentração de íons e a intensidade da voltagem aplicada. Obtém-se que o agregado cruza de um comportamento tipo fractal de DLA para o de agregado denso, à medida que a concentração de íons é aumentada. Lançando mão de nossos resultados prévios, que mostram que o agregado se torna uma estrutura compacta com o aumento da voltagem, o diagrama morfológico em termos dos dois parâmetros 6 obtido. Verifica-se que este diagrama é semelhante àquele obtido por experimentos em deposição eletroquímica.