Research paper
J. Electrochem. Sci. Technol. **5(2)**, 53-57 (2014)

Journal of Electrochemical Science and Technology

Effect of Particles Drift on Dendritic Growth

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ABSTRACT

With the use of diffusion-limited aggregation modeling, we have investigated the effect of particle drift for dendritic growth. It is found that the morphology of dendritic growth is sensitive to the particle drift, i.e., the larger drift effect results in the denser growth of dendrite. From the analysis using the correlation function, we found the fractional dimension of each dendrite increases as the particles drift increases. Furthermore, we showed the height of dendrite significantly decrease for the slight change of particles drift. Finally, we discussed the strategy to reduce dendritic growth by modifying the transport properties of electrolytes.

Keywords: dendrite, diffusion-limited aggregation, fractional dimension, particle drift

Received December 7, 2013 : Accepted December 17, 2013

1. Introduction

The study for morphology of growing surface has been an interesting topic in broad areas of biology such as morphogenesis of living organisms and physical sciences such as metallurgy, combustion, and electrochemistry [1]. The growing surfaces in solid-phase are normally contacted with fluids including their ingredients in gas or liquid phase. Contrary to biological systems, inorganic systems are mainly governed by the condition of thermodynamic equilibrium. However, statistical fluctuations (time-dependent deviation of physical quantities) often affect the morphology of surface significantly. When fluctuations are minor, a surface will grow in the crystalline structure, on the contrary, when fluctuations are dominant, the surface will grow in tree-like shape, i.e. dendritic growth [2,3].

One of representative theory describing dendritic growth is the diffusion-limited aggregation (DLA) which is proposed by Witten and Sander in 1981 [3]. DLA is based on the random work of particles in the fluid, the so-called Brownian motion. In DLA model, when a diffusing particle is located on a site contacting with the part of the cluster (or seed), it becomes a part of cluster and does not move to other direction any more, i.e. growth. It has been known the aggregation generated in DLA model is followed by power-law correlations [3-7], where the fractional power law behavior is related to the self-similarity as in fractals, which means there is no characteristic length scale to define the system.

In experiments, the dendrite has been observed in several areas such as an aggregation of silver atoms on a surface of platinum (epitaxy growth) [8], the growth of succinonitrile dendrite (supercooling of the liquid) [9], and the growth of zinc metal leaves (electrodeposition)

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Open Access **DOI: http://dx.doi.org/10.5229/JECST.2014.5.2.53**

[10]. Especially, the dendrite formation on the lithium metal anode in rechargeable lithium metal, lithium-sulfur, and lithium-air batteries has been observed [11-13] and becomes a serious problem, affecting life time and safety of battery cells due to short-circuit [14-17]. To use a lithium metal anode for achieving high capacity in rechargeable lithium batteries, it is necessary to reduce the dendritic growth on the lithium metal surface. Therefore, the motivation of our study mainly originates from the question ‘How can the dendritic growth be controlled?’. Until now, several effects of adsorption [4], drift [5], concentration [6], anisotropy [18], and surface tension [19] have been suggested as main mechanisms. However, these studies were mainly performed in the radial geometry with a seed in the center as a starting point. Furthermore, even though the study of height of dendrite directly related to short-circuit is important, the relation between the height and those effects are not clear yet.

Here, to study the effect of particle drift for dendritic growth, the DLA simulations have been performed in the two-dimensional geometry with a linear-shaped electrode. We have showed the morphology of dendrite becomes dense by increasing particles drift. We have also analyzed the fractional dimension of dendrites using a correlation function and showed a relationship between the degree of drift and dimensions. Finally, we conclude the height of dendrite, which is an important value for short-circuit, can be changed significantly by increasing the probabilistic weight of particles drift slightly.

2. Computational Method

The DLA clustering was simulated in the two-dimensional square lattice with $(N_x, N_y) = (200,6000)$, where N_x and N_y are the number of grid in x and y directions, respectively. 5,000 particles were used for all simulations. Bottom lines in Fig. 1 represent an initially flat anode surface. To realize the random work describing Brownian motion, random numbers were generated to decide the direction of particles move-

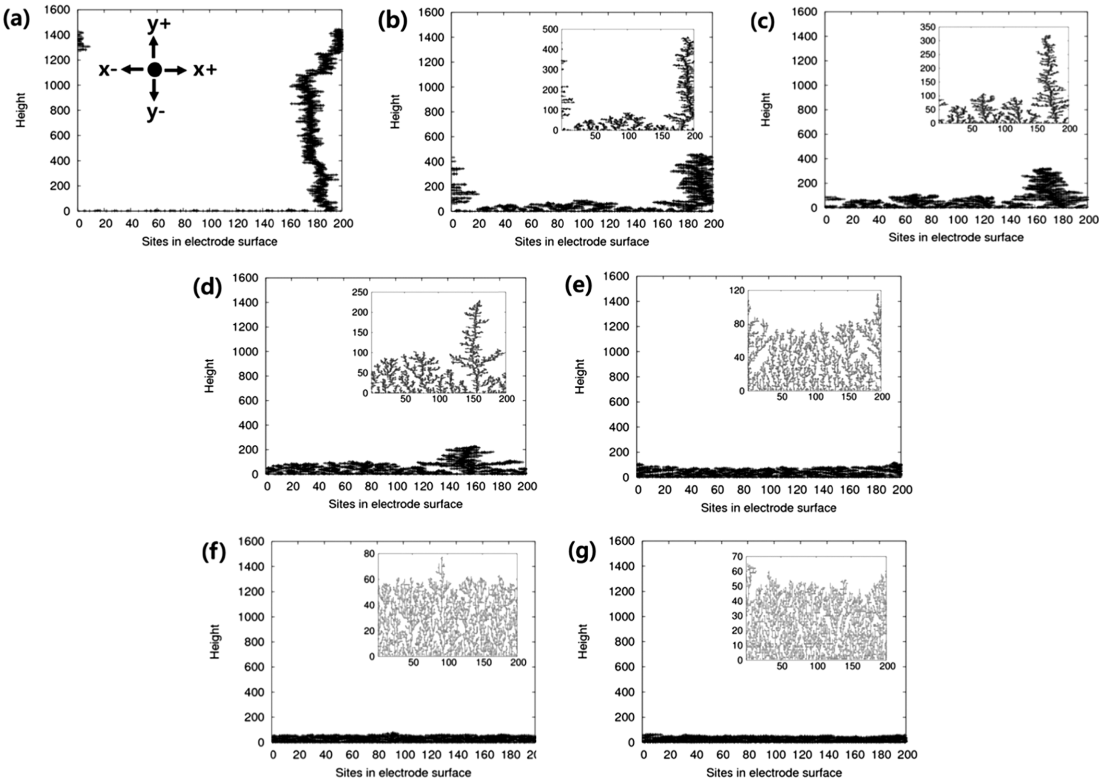

Fig. 1. Morphologies of dendritic growth depending on the particle drift (P_{y-}) of (a) 0.25, (b) 0.27, (c) 0.28, (d) 0.31, (e) 0.4, (f) 0.7, (g) 1.0; (insets) (a) moving directions of particles, (b)-(g) enlargement of each dendritic growth.

ment each time. For the random work without drift, moving probabilities (P) for four directions, (P_{x+}, P_{x-}, P_{y+}, P_{y-}), were given by (0.25, 0.25, 0.25, 0.25). The four directions were shown in the inset of Fig. 1a. The degree of drift was changed by the change of moving probability in 'y-' direction, in which other probabilities were given by equal amounts of (1-P_{y-})/3. When diffusing particles meet the bottom line or the part of aggregated cluster, they do not move any more, i.e. attached to the cluster. The periodic boundary condition was also used in the boundaries of x = 1 and 200.

3. Results and Discussion

Fig. 1(a) shows a dendritic growth based on random work of particles with directional moving probability of (0.25, 0.25, 0.25, 0.25). The height of single big dendrite is 1,445 grids and the width is around 10 grids. This height is very large compared to 25 grids, calculated from 5,000 particles/200 sites, in close-packing of all particles. Therefore, in the random motion of particles, it can hardly keep the surface flat, then short-circuit may occur in short time. This case may correspond to the movement of Li ion in electrolyte without drift. Hence the supply of Li ions to the surface of Li metal anode will be a very slow process. Therefore, particles have a large chance to contact with cluster before reaching the bottom electrode line and the morphology of aggregation becomes more dendritic as in Fig. 1(a). By slightly increasing the probability of P_{y-} from 0.25 to 0.27, i.e., from (P_{x+}, P_{x-}, P_{y+}, P_{y-}) = (0.25, 0.25, 0.25, 0.25) to (0.243, 0.243, 0.243, 0.27), the height of dendrite is significantly reduced as in Fig. 1(b). Its height is 462 grids and width is around 25 grids. However, most particles are still attached in one large branch of dendrite. As seen in Fig. 1(c) and 1(d) with P_{y-} of 0.28 and 0.31, respectively, there is still one large dendrite distinguished from other dendrites. Even though the height of the large dendrite continually decreases with increasing P_{y-}, its width does not increase any more. Instead, other smaller dendrites grow more.

In Fig. 1(e) with P_{y-} of 0.4, the morphology of dendrite is drastically changed. The upper front of dendrites is flat compared with Fig. 1(a)-(d). From the inset in Fig. 1(e), the dendrite with notable size is not found. The height is only 116 grids. By increasing P_{y-} more, denser dendrites are obtained as in Fig. 1(f) with P_{y-} of 0.7 and Fig. 1(g) with P_{y-} of 1.0. The heights of dendrites become lower, 77 and 64 grids for P_{y-} = 0.7 and 1.0, respectively. Especially, we can find an interesting point in the case with P_{y-} = 1.0. Even though all 5,000 particles have moving possibility toward the electrode only, its height is not 25 grids as in closed packing but 64 grids. Why does this happen? All particles always move to the bottom electrode straightly, but initial positions of particles are randomly generated, therefore, some particles can exist in second layer before the first layer is completely filled. Normally, this prohibits particles from filling the first layer perfectly, since moving particles can be attached to the particles in second layer before reaching empty sites in bottom electrode. Without the consideration of thermodynamic diffusion of particles on the layers, it is impossible to make perfect packing of particles.

How can we measure the relation between the probabilistic weight of particles drift represented by P_{y-} and the fractional dimension of dendrites? To quantify this relation, we now introduce the correlation function [3],

$$C(r) = N^{-1}\Sigma_{r'}\rho(r')\rho(r'+r) \tag{1}$$

where r' and r are the sites(positions) of particles and their neighboring particles, respectively. $\rho(r)$ is the local density having a value of 0(empty) or 1(occupied) in site r and N is the number of particles. It has been known the correlation function shows a power-law behavior in DLA model [1,3].

$$C(r) \sim r^{-\alpha} \tag{2}$$

where α is an exponent of the correlation function. Furthermore, the α is also related to the fractional dimension of dendrite, which is given by [1,3]

$$D = d - \alpha \tag{2}$$

where D is the fractional dimension of dendrite and d is the dimension of space, specifically 2 in our case. We obtained the results of correlation functions for each P_{y-} in Fig. 2. The correlation function is plotted in log-log scale, so the slope of each case corresponds to the exponent. In the analysis of correlation function, the slope of two-dimensional case have zero ($\alpha = 0$), since all neighboring sites of a specific particle are completely occupied which gives the relation of $N(R) = \pi R^2$ ($D = 2$), i.e. the area of circle. If the slope

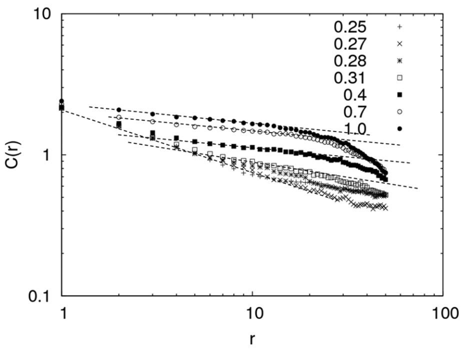

Fig. 2. Analysis of the fractional dimension of dendritic growth for each number of particles drift (P_{y-} = 0.25−1.0) by using correlation functions. The dashed lines show the slope of some correlation functions in log-log scale, which corresponds to the exponents (α) of correlation function in Equation (2).

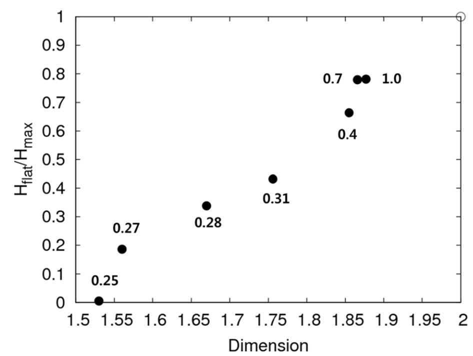

Fig. 3. Distribution of heights ratio of dendrites depending on fractional dimensions and particles drift (P_{y-} = 0.25−1.0). The heights ratio is given by dividing the height obtained from flat dendrites (H_{flat}) by the maximum height obtained from single largest dendrite (H_{max}). Open circle at 2 in dimension-axis represents the height ratio of close packing in two-dimension.

Table 1. Relationship between particles drifts (P_{y-}), exponents from correlation functions, dimensions and heights in dendritic growth.

Weight of Drift (P_{y-})	Exponent (α)	Dimension (D)	Height
0.25	0.47	1.53	1445
0.27	0.44	1.56	462
0.28	0.33	1.67	320
0.31	0.24	1.76	229
0.4	0.14	1.86	116
0.7	0.13	1.87	77
1.0	0.12	1.88	64
-	-	2	25

of calculated correlation function is close to zero, it means a fractional dimension is close to two dimension. In our case, P_{y-} = 1.0 shows the smallest slope, so it is closest to the two-dimensional close-packing among all cases of drift. This is already confirmed in the discussions regarding Fig. 1. The calculated α and D are listed in Table 1. As the P_{y-} increases from 0.25 to 1.0, the D also increases from 1.53 to 1.88. It is reconfirmed the dimensionality of P_{y-} = 1.0 is different from that of perfect close-packing (D = 2).

Finally, we have plotted the heights ratio of dendrites, which can be compared with experimental measurements, depending on dimensions for each P_{y-} in Fig. 3. The heights ratio is obtained by dividing the height of flat dendrites by the maximum height of single large dendrite. We found the rapid increase of heights ratio for the slight increase of dimension of dendrite from P_{y-} = 0.25 to 0.27. After that, the heights ratio increases linearly up to P_{y-} = 0.4. The change of P_{y-} from 0.25 to 0.4 results in dominant change for the heights ratio and dimension of dendrites. However, the range of P_{y-} between 0.7 and 1.0 shows only small change of heights ratio and dimension of dendrites. The degree of drift given by P_{y-} is proportional to the drift velocity of particles. The drift velocity is also proportional to the external force such as electric field and mobility of particles.[20] Therefore, in the same electric field, the higher mobility of particles may improve the drift velocity. From the Stokes-Einstein relation [21], this mobility is proportional to the diffusion coefficient of particles and inversely proportional to the viscosity of the medium. Hence, the effect of particles drift can be enhanced by using electrolytes with lower viscosity which reduces the frictional drag of Li ions induced by surrounding solvent molecules or higher diffusion coefficient. Therefore, it can be a good strategy to modify electrolytes in the direction of lowering viscosity and raising diffusion coefficient, in order to mitigate dendritic growth.

4. Conclusions

We have studied the morphology, dimension, height of dendritic growth depending on the particles drift by using diffusion-limited aggregation method. The morphology of dendrite is intrinsically changed at P_{y-} = 0.4, where the front of dendrite becomes almost flat. The fractional dimension of dendrite, analyzed by the correlation function, is almost saturated around 1.88 in the range of P_{y-} = 0.7 and 1.0, i.e., it shows no significant change in morphology after the drift of P_{y-} = 0.7. In addition, the height of dendrite significantly decreases by the slight change of drift and is saturated near P_{y-} = 0.7. Based on these results, the P_{y-} = 0.7 in drift effect may be a critical point showing the saturation of morphology, dimension, height in dendritic growth. Finally, it is concluded that the improved transport properties of lithium ions in electrolytes can be effective to enhance the cyclability of the lithium metal battery.

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