FRACTAL STABILIZATION AND STOCHASTIC MODELING OF ZINC ELECTRODEPOSITION STRUCTURES IN THIN PLATES

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ABSTRACT

Thin-layer electrodeposition has been studied to involve complex branched morphologies, useful for different industrial processes. In this work, it was studied the electrodeposition of Zinc for a constant Zn^{2+} concentration and two currents, 3mA and 10.3mA. The electrodeposition test was carried out in a thin circular layer, analyzing the variation of the mass-radius fractal dimension over time and the different radius of the deposits formed. The study was focused on the fractal dimension stabilization analysis and the mathematical modeling of this parameter through the stochastic methodology. It was found that the fractal dimension stabilizes depending on the radius studied and becomes constant over time. The stochastic model proposed involves the radius of the deposit and the electrodeposition time. The model predicts the fractal dimension value with a correlation of 61.43% for the highest current value, which is an indication that the faster deposition velocity produces a more stable fill-up effect of the spaces in the deposition surface.

KEYWORDS: Branched Electrodeposition; Fractal Electroplate, Zinc Reduction

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INTRODUCTION

In the last decades, electrochemical processes have found several industrial applications [1-6]. Since the 1980s, it was started the study of Zinc (Zn) deposition morphology, determining that the Zn electrodeposition process is sensible for the experimental conditions [7-11]. For example, in a circular anode/tip cathode arrangement, where the cathode tip is centered in the anode surface, the ramifications start from the tip following the dendritival DLA mechanism (diffusion-limited aggregation) [2-7,12,13]. However, this dendritival growth is not fully explained though DLA [14]. Besides, some other structures or deposits can be found [11]: Compact (deposition with no specific structure/ramification); Homogeneous (dense ramifications with a parallel growing to cathode); Open (disordered and faltered ramifications); Assorted (dendritival/other ramifications); Needle-shaped growths without lateral ramifications.

The structures can also be modified according to the electrodeposition rate of the Zn^{2+} ions, which is tuned by the electric current, which in turn is lesser for a long distance between the electrodes and vice versa [14]. Some other experimental conditions can be set under constant potential or constant current, high Zn^{2+} concentrations and high potentials (more open structures), Zn^{2+} concentrations from 0.03 to 0.1 M (usual dendritival growths like DLA) [15], electric potential ramps (uncontrolled growth) [10], and voltage oscillations [10,13]. Electrodeposition structures are ideal models for the general processes of fractal growth, and they are similar to other fractal morphology on solids [16]. Some studies focus on the time-changing fractal dimension of electrodeposition. For 0.1 mm diameter electrodes, with a separation of 50 mm and under constant potential (12 V), it was found a fractal

dimension of 1.66 ± 0.08 , and it was established that the morphologies were self-similar [8].

MATERIALS AND METHODS

To study the temporal variation of the fractal dimension was studied under two constant current values of 3 mA and 10.3 mA at 25 °C, with a ZnSO_4 0.1026 M (Merck, Mexico). The Zn growth was studied every 10 min for 30 s with a polarization microscope (BA310POL, Motic) at 10-40x in circular plates of acrylic crystal. The anode was annular with 44 mm of radius, and the anode was set up to 0.44 mm diameter, both electrodes were made of Pt [2,3]. The voltage/time variation was measured with a digital multimeter (MUL-5000, Steren). The images obtained were contrasted in black and white through the ImageJ software as in [17-19], and the diameter of the structures was measured in pixels with the Fractalyse software [18]. The fractal dimension was determined with Harfa software [19] for two cases: the final image and concentric 100 pixels thick rings. The content of Zn in the ZnSO_4 solution was followed by titration with EDTA to determine the final concentration.

This work considers as a hypothesis that the fractal dimension is a result of the random deposition processes and the chemical reactions at the microscopic level. Thereby, the stochastic modeling of the fluctuations and the fractal geometry bases were used to estimate the fractal dimension and the system size over time. The final surface of the system is quantified from the fractal structure radius.

RESULTS AND DISCUSSIONS

Figure 1 shows the images obtained for the experiments at 3 and 10.3 mA. For 3 mA tests, in most of the cases, the fractal dimension decreases per unit of time, and it is diminished while the diameter is more significant. This behavior is a result of the Zn random electrodeposition; thus, the empty spaces on the surface are filled with crystals reducing the ramifications at the initial stage while ramification grows 30 seconds later. The temporal growth of the mass-radius fractal dimension seems reasonable due to as the Zn is deposited, the area of study is increased. This behavior is also observed for the 10.3 mA tests, where the growth is faster. Figure 2 shows the maximum radius of the crystal growth for six samples. As it was expected, the Zn decay in the solution was linear, which favors the formation of H_2 (g). The high potential experiments were modified to be measured up to 10 min to avoid surface modification due to gas release.

Figure 1: B/W Crystal growth for Zn at a) 3 and b) 10.3 mA.

Figure 2: Maximum diameter values for 3 and 10.3 mA.

Figures 3 and 4 show the fractal dimension variation on time. It can be seen that this parameter rises but reaches a stable point, and this stabilization is achieved faster for the 10.3 mA experiments. For the first rings, it is observed a higher value of the fractal dimension due to a faster filling effect of the surface, a result mainly linked to nucleation (with a fractal dimension of 2). The value of the fractal dimension will be reduced as the ramifications are more significant, and the diameter of the circles is increased.

By applying this methodology, it is observed that for smaller diameters, this problem will always be present. If the diameter analysis rises as seen in figures 3 and 4, the fractal dimension is reduced. If the circle analyzed presents a big diameter (approximately 900 pixels), the mass-radius fractal dimension (MRFd) would be diminished because of the space inside the crystal (space between ramifications). Therefore, the MRFd shows an apparent stabilization of the fractal dimension for the analysis of the concentric rings over time. For the final image, Figure 5 shows the fractal dimension results, which indicates an average value of 1.71 as DLA growth for both cases, 3.0 and 10.3mA.

Figure 3: Fractal dimension (D) of concentric rings at 3 mA. Numbers in column (right) correspond to the radius in pixels.

Figure 4: Accumulative fractal dimension (D) of concentric rings at 10.3 mA. Numbers in column (right) correspond to the radius in pixels

Figure 5: Fractal dimension over time for 10.3mA (blue) and 3.0 (red) ($V=10$ mL, $C_i=0.1026$ mol/L, and $r=44$ mm)

3.1. MRFd Stabilization Model

The mass of a compound deposited (m) is determined for the equation (1):

$$m = kIt \quad (1)$$

I is the current (A), t is time (s), and k is an adjustment constant. In the same way, it is easy to determine the mass of the deposit if its density (ρ), radius (R), and fractal dimension D are known:

$$m = \rho(R)^D \quad (2)$$

From equation (1), it can be obtained the variation of mass over time:

$$\frac{dm}{dt} = \rho(R)^D \left[\frac{DdR}{Rdt} + \left(\frac{dD}{dt} \right) \ln R \right] \quad (3)$$

By combining equations (1) and (3), it can be deduced the variation of the fractal dimension over time:

$$\frac{dD}{dt} = \left[\frac{kI}{\rho(R)^D} - \frac{DdR}{Rdt} \right] \frac{1}{\ln R} \quad (4)$$

From equation (4), it can be obtained:

$$\lim_{R \rightarrow \infty} \frac{dD}{dt} = \lim_{R \rightarrow \infty} \left[\frac{kI}{\rho(R)^D} - \frac{DdR}{Rdt} \right] \frac{1}{\ln R} \quad (5)$$

For $R \rightarrow \infty$, $dR/dt \rightarrow 0$, and $D/R \rightarrow 0$, therefore:

$$\lim_{R \rightarrow \infty} \frac{dD}{dt} = \lim_{R \rightarrow \infty} \left[\frac{kI}{\rho(R)^D} \right] \frac{1}{\ln R} \quad (6)$$

If $D > I$, then $R^D \rightarrow \infty$, and $I/R^D \rightarrow 0$. For case $D < I$, $R^D \rightarrow I$, and $I/R^D \rightarrow I$. But in any case, if $R \rightarrow \infty$ then $\ln R \rightarrow \infty$. Then, for $D > I$:

$$\lim_{R \rightarrow \infty} \frac{dD}{dt} = 0 \quad (7)$$

Then, in equation (7), while the radius R grows up, the value of MRFd is going to be stable. This result is in concordance with the experimental behavior observed for 3 and 10.3 mA.

3. 2. Fractal Dimension Predictive Model

The model was obtained under the next considerations: i) the microscopic entities describing the system are the molecular aggregates on the 2D structure with an annular geometry of radius R ; ii) the microscopic variable is the number n of entities, for which the transition probabilities overtime for the increment $n+1$ and the decrement $n-1$ are:

$$W_{n+1/n} = k_1 N_0 \quad (8)$$

$$W_{n-1/n} = k_2 n$$

k_1 and k_2 are the velocity constants of the processes, and N_0 represents the total ions in the solution that in this case is considered constant; iii) the occupied space ϕ represents the system evolution for n over the perimetral border l of the total aggregate:

$$\phi = \frac{nl}{R} \quad (9)$$

The changes in a microscopic entity for an individual process can be considered null compared with its total number; thus, n is a continuous variable. Therefore, the Fokker-Planck equation (FPE) for the transition probability of ϕ is written as:

$$\frac{\partial P(\phi; t)}{\partial t} = -\frac{\partial}{\partial \phi} \left(\frac{lk_1 N_0}{R} - k_2 \phi \right) P(\phi; t) + \frac{1}{2} \frac{1}{\Omega} \frac{\partial^2}{\partial \phi^2} \left(\frac{lk_1 N_0}{R} - k_2 \phi \right) P(\phi; t) \quad (10)$$

$$P(\phi_0; 0) = 1$$

Where $1/\Omega = l/R$. FPE is linear for the transition probabilities per unit of time; then, its solution is a gaussian function where the temporal behavior of the expected value $\Phi = \langle \phi \rangle$ and the variance $\sigma = \langle (\phi - \langle \phi \rangle)^2 \rangle$ of the intern fluctuations are described through the differential equations (11) and (12):

$$\frac{d\Phi}{dt} = \frac{lk_1 N_0}{R} - k_2 \Phi \quad (11)$$

$$\Phi(0) = 0$$

$$\frac{d\sigma}{dt} = -2k_2 \sigma + \frac{1}{\Omega} \left(\frac{lk_1 N_0}{R} + k_2 \Phi \right) \quad (12)$$

$$\sigma(0) = 0$$

The exact analytical solutions of equations (11) and (12) are:

$$\Phi(t) = \alpha(1 - e^{-tk_2}) \quad (13)$$

$$\sigma(t) = \frac{\alpha}{\Omega}(1 - e^{-tk_2}) \quad (14)$$

$$\alpha = \frac{lN_0 k_1}{Rk_2} \quad (15)$$

α is the condition of the steady-state. The system is studied in a quasi-stationary state, and σ is expressed as a function of Φ :

$$\sigma = \frac{1}{2\Omega}(\Phi + \alpha_{qs}) \quad (16)$$

Where α_{qs} is the expected value in a time t . For an ergodic process, the average temporal mid-processes are considered equal to the average of the bulk. Thus, the probability expected value is expressed in terms of density (C is a proportionality constant):

$$\rho = \langle P(\phi) \rangle = \frac{C}{(\sigma)^{\frac{1}{2}}} \quad (17)$$

Besides, the variance σ can be expressed as a potential function of Φ :

$$\sigma = \Phi^\mu \quad (18)$$

$$\mu = \lim_{\Phi \rightarrow 1} \left[\left(\frac{d \ln \left(\frac{1}{2\Omega} (\Phi + \alpha_{qs}) \right)}{d\Phi} \right) \left(\frac{d \ln \Phi}{d\Phi} \right)^{-1} \right] = \frac{1}{\alpha_{qs} + 1} \quad (19)$$

From the fractal dimension concept, the total quantity of substance ε within a surface $\pi\Phi^2$ is:

$$\varepsilon = C\Phi^D = \rho(\pi\Phi^2) \quad (20)$$

After mathematical treatment and substituting equation (13) for the expected value of Φ in a time t :

$$D = 2 - \frac{1}{\alpha(1 - e^{-tk_2}) + 1} \quad (21)$$

Equation (15) is adjusted as:

$$\alpha = \frac{\beta}{R} \quad (22)$$

Where β depends on the ions concentration and the dynamic parameters that determine the system evolution:

$$\beta = \ln N_0 \frac{k_1}{k_2} \quad (23)$$

Thereby, for a given system, the fractal dimension D depends on the system expansion over time, in such a way that:

$$D = \frac{R + 2\beta - 2\beta e^{-tk_2}}{R + \beta - \beta e^{-tk_2}} \quad (24)$$

Figure 6 shows the predicted values according to equation (24). Equation (24) can be simplified to adjust the experimental data. In this case, the first four terms of the potential series for t are presented in equation (25):

$$D = 1 + A_1 \frac{t}{R} - A_2 \left(\frac{t}{R} \right)^2 - A_3 \frac{t^2}{R} \quad (25)$$

In equation (25), the A_j constants are obtained for the statistical analysis of the experimental data. The models for the experimental conditions were adjusted through the Marquardt non-linear regression method with the Statgraphics software and are shown in Table 1. Figure 7 is a comparison between the predicted and experimental values.

The values of β and k_2 were calculated from their relation with the constants A_1 and A_3 according to the system of equations:

$$\begin{aligned} A_1 &= \beta k_2 \\ A_3 &= \frac{\beta k_2^2}{2} \end{aligned} \quad (26)$$

Figure 6: Fractal dimension over time for R as the independent variable in a hypothetical system with $k_2 = 1$, and $\beta = 2$.

Table 1: Statistical adjustments of the model for the experimental results

	$I = 10.3 \text{ mA}$	$I = 3 \text{ mA}$
Adjusted model	$D = 1.06 + 0.65 \frac{t}{R} - 0.025 \left(\frac{t}{R}\right)^2 - 0.00065 \frac{t^2}{R}$	$D = 1.7 + 0.09 \frac{t}{R} - 0.007 \left(\frac{t}{R}\right)^2 - 0.0005 \frac{t^2}{R}$
R^2	61.4343%	29,4001%
β	323.48	67,310
k_2	0.0020	0,0010

Figure 7: Comparison between the observed (O) and the predicted (P) fractal dimension results according to the adjusted models for each experimental test a) 10.3 mA and b) 3 mA

CONCLUSIONS

For the morphological analysis, it was found that the growth achieves a stabilization limit, which follows the mathematical analysis where $\lim_{t \rightarrow \infty} dD/dt = 0$ it is applicable for both: rings analysis and mass-radius fractal dimension for the total image. Fractal dimension is 1.71 for the final image, and for the first ring, it decreases to an average value of 1.4, which is expected for a zinc distribution as it zooms out through the branches. The stabilization of the fractal dimension is achieved for $100 \leq R \leq 375$ pixels. The stochastic model showed a better correlation (61.43%) for the highest current value, which indicates that the faster deposition velocity produces a more stable fill-up effect of the spaces in the surface.

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NOMENCLATURE

$A_{1,2,3}$ Constants of the adjusted model for experimental data

C Proportional constant

D Fractal Dimension

I Current (A)

k Adjustment constant

$k_{1,2}$ Velocity constants for the system expansion process

l Length of the fractal perimeter (m)

t Time (s)

m Mass of a compound deposit (g)

n Number of entities in the electrodeposition process

N_0 Total ions (Zn^{+2}) in the solution

R Radius (pixel)

W Transition probabilities over time

Greek Symbols

α Condition of the steady-state

β Subparameter of α

ε Total quantity of substance deposited

μ Potential function of Φ

ρ Density

σ Variance

ϕ Surface occupied by the entities n

Φ Temporal behavior of the expected value of ϕ

Ω Ratio R/l

Subscripts

qs Quasi-stationary