

A new approach to the estimation of electrocrystallization parameters

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Abstract

To overcome the drawbacks in estimating electrocrystallization parameters using traditional methods, we propose a genetic algorithm using a novel crossover operator based on the non-convex linear combination of multiple parents to estimate the electrocrystallization parameters A (the nucleation rate constant), N_0 (the nucleation density) and D (the diffusion coefficient of Zn^{2+} ions) simultaneously in the general current-time expression of Scharifker and Mostany for nucleation and growth by fitting the whole current transients for zinc electrodeposition onto glassy carbon electrode immersed in the acetate solutions. By running the algorithm, we obtained for different step potentials, D values close to $2.10 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$, which are comparable to reported values. The values of A obtained for all step potentials are identical, $1.41 \times 10^9 \text{s}^{-1}$, which indicates that zinc deposition onto glassy carbon electrode follows three-dimensional instantaneous nucleation and growth. In addition, from the values of N_0 obtained, one can observe that an increase in step potential leads to a higher N_0 . These results show that our algorithm works stably and effectively in solving the problem of estimating the electrocrystallization parameters, and more importantly, it can be extended easily to a general algorithm to estimate multiple parameters in an arbitrary chemical model. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Electrocrystallization parameters; Zinc; Parameters estimation; Genetic algorithm

1. Introduction

In considering of the overlap of the diffusion fields of randomly growing nuclei, Scharifker and coworkers [1] proposed the following potentiostatic current–time expressions for instantaneous and progressive nucleation with diffusion controlled growth respectively

$$I = \frac{zFD^{1/2}c}{\pi^{1/2}t^{1/2}} [1 - \exp(-N_0\pi kDt)]$$

(instantaneous nucleation) (1)

$$k \equiv (8\pi cM/\rho)^{1/2}$$

$$I = \frac{zFD^{1/2}c}{\pi^{1/2}t^{1/2}} [1 - \exp(-A\pi k'Dt^2/2)]$$

(progressive nucleation) (2)

$$k' \equiv \frac{4}{3}(8\pi cM/\rho)^{1/2}$$

where z is the charge number of the reaction, D the diffusion coefficient, c the concentration of active cation, M the molar mass, ρ the density of deposit, and N_0 is the nucleation density (cm^{-2}) while A is the nucleation rate constant ($\text{cm}^{-2} \text{s}^{-1}$). The two expressions have been used widely for a great variety of systems [2–7], including our previous publication describing the effects of organic additives on zinc deposition [5]. But they can deal only with two extreme cases in quantitative analysis, and the electrocrystallization of metals from many systems cannot be described by them (e.g. as Ag^+ deposition onto a glassy carbon electrode from $[\text{Ag}(\text{NH}_3)_2]^+$ solutions [8]). Moreover each equation can determine only one kinetic parameter, A or N_0 . In view of these limitations, Scharifker and Mostany [9] deduced the following general current–time expression

$$I = \frac{zFD^{1/2}c}{\pi^{1/2}t^{1/2}} \left[1 - \exp\left(-N_0\pi kD\left(t - \frac{(1 - \exp(-At))}{A}\right)\right)\right]$$

(3)

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in which one can estimate simultaneously the kinetic parameters A and N_0 with no necessity to classify the nucleation mechanisms. The most utilized approach [8–11] for estimating these parameters in the general expression is to construct the following system of transcendental equations

$$\begin{cases} \ln\left(1 - \frac{I_m t_m^{1/2}}{a}\right) + x - \alpha \left[1 - \exp\left(\frac{-x}{\alpha}\right)\right] = 0 \\ \ln\left\{1 + 2x \left[1 - \exp\left(\frac{-x}{\alpha}\right)\right]\right\} - x + \alpha \left[1 - \exp\left(\frac{-x}{\alpha}\right)\right] = 0 \end{cases} \quad (4)$$

where $a = zFD^{1/2}c/\pi^{1/2}$, $x = N_0\pi kDt_m$, $\alpha = N_0\pi kD/A$, using the single point, (I_m, t_m) , on the experimental current transient where I_m is the current maximum and t_m is the corresponding time, and then solve it using the graphical method or the iterative method. Obviously the diffusion coefficient, D , must be known in advance. As for this approach, we considered that some drawbacks exist when it is applied to solve practical problems. First, during the process of constructing and solving the system of equations, only the current maximum point on the whole experimental current transient is used, which limits the accuracy of the electrocrystallization parameters. Secondly, prior to estimating N_0 and A , the values of D must be determined by additional experiments. Thirdly, the graphical method is too crude and can give rise to large errors, and the iterative method requires restricted conditions to be placed on the model, such as being continuous and derivable. Essentially, the parameters A , N_0 and D can be estimated simultaneously by fitting the whole current transient to the general expression.

Recently, there has been great interest in developing adaptive methods, namely genetic algorithms (GAs), for solving computational problems in many fields. The approach mimics the process of biological evolution and the mechanisms of natural selection and genetic variation. Suitable codings are used to represent possible solutions to a problem, and the search is guided by using some genetic operators and the principle of 'survival of the fittest'. Due to the merits of self-adaptation, self-organization, self-learning, intrinsic parallelism and generality, GAs have been applied successfully in a wide range of economic, engineering and scientific computations [12]. The applications of GAs in chemistry are also very wide [13,14].

To overcome the drawbacks in estimating electrocrystallization parameters using traditional methods, we propose a genetic algorithm to approach the task of parameter estimation in our experiments. To be specific, we use the genetic algorithm to estimate the values of D , N_0 and A in Eq. (3) by fitting the experimental current transients.

GAs can have various forms due to different representations, fitness evaluations and genetic operators which may vary with specific problems. Among all these components, genetic operators, including crossover and mutation, are considered as the most important parts in a genetic algorithm which can directly affect the effectiveness and the efficiency of the algorithm for solving the specific problem. In contrast to the genetic operators used by other researchers [15–17], we used a novel crossover operator based on the non-convex linear combination of multiple parents during the recombination of the population, which proved to work stably and effectively in solving the problem of electrocrystallization parameters estimation.

2. Experimental

All the chronoamperometric experiments were carried out in a three-electrode system at $25 \pm 1^\circ\text{C}$. The end face of a Teflon-molded glassy carbon rod, 2 mm in diameter, was used as the working electrode, a 99.9% pure zinc sheet as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All potentials are reported with respect to the SCE. Prior to each experiment, the working electrode was polished to a mirror finish with successively finer grades of alumina powders, eventually to 0.05 μm , and cleaned ultrasonically in sequence in acetone, diluted HCl and distilled water. All solutions were prepared from analytical grade reagents and triply distilled water. The experimental electrolyte was 0.1 mol l^{-1} $\text{Zn}(\text{Ac})_2$ with 0.5 mol l^{-1} NaAc. The solutions was adjusted to pH 5.5 by adding acetic acid, and deaerated by bubbling with purified nitrogen. The step potentials were provided by a computer via a D/A card and the corresponding current transients were recorded via an A/D card. We set the initial potential for all chronoamperometric experiments equal to -1.00 V. A RDE4 potentiostat made by the Pine Instrument Company was used in all experiments. All the numerical calculations were performed on a Pentium 166/MMX computer with the Visual C++ 5.0 compiler.

3. Genetic algorithm

The detailed implementation of the genetic algorithm for estimating the electrocrystallization parameters can be described as follows:

3.1. Initialization of the population

The population is made up of individuals or chromosomes by analogy with genetics. In our case, each chromosome is encoded as an ordered set of the

parameters to estimate, a vector written in the form of (D, N_0, A) . During the initialization of the population, N such individuals are generated randomly by assigning each parameter to be a random floating number in its range of definition in sequence. In our experiments, these parameters, D , N_0 , A , are defined in the range of $[0, 1]$, $[0, 10^{10}]$ and $[0, 10^{12}]$, respectively. We set N , the size of the population, equal to 100.

3.2. Evaluation of the fitness

Suppose the experimental current transient contains m data points denoted as (I_i, t_i) ($i:1 \sim m$) where I_i is the experimental current value at time t_i . As for an arbitrary individual in the population, p_j ($j:1 \sim N$), represented as a vector (D, N_0, A) , we calculate the least-square error as its fitness value defined by the following equation

$$\text{fitness}(p_j) = \sum_{i=1}^m (\hat{I}_i - I_i)^2 = \sum_{i=1}^m \left(\frac{zFD^{1/2}c}{\pi^{1/2}t_i^{1/2}} \times \left[1 - \exp\left(-N_0\pi k D \left(t_i - \frac{(1 - \exp(-At_i))}{A} \right)\right) \right] - I_i \right)^2 \quad (5)$$

Obviously, the lower the fitness value, the better the individual. In our experiments, we chose 500 datum points on the experimental current transient for each step potential as fitting samples.

3.3. Recombination of the population

A new population with the same size is generated by recombining the old population using some genetic operators (At the beginning, the old population refers to the initial population). We use a novel crossover operator to create each individual in the new population. This is done by performing the following operations. Randomly select M different individuals from the old population ($M > 2$) denoted as X_1, X_2, \dots, X_M where $X_k = (D_k, N_{0k}, A_k)$ ($k:1 \sim M$), and accordingly produce M coefficients α_k where α_k ranges from a to b ($a < 0, b > 1$) and satisfies $\sum_{k=1}^M \alpha_k = 1$, then generate a new individual, X , by the non-convex linear combination of those M individuals as follows

$$X = \sum_{k=1}^M \alpha_k X_k \quad (6)$$

If any one of the three parameters D, N_0, A in X is out of its range of definition, then abandon this invalid individual and recreate a new one following the same procedure as above. There are three adjustable control parameters M, a, b in this procedure. The choice of optimal values depends upon the property of the specific problem. In our genetic algorithm program, we set $M = 8, a = -0.3$ and $b = 1.3$.

3.4. Replacement of the population

All the individuals in the old population and the new population are sorted according to their fitness values, and the better N individuals are selected as the members of the population in the next generation.

The whole algorithm is iterated between Section 3.2 and Section 3.4 until the termination criterion is satisfied whereby a maximum generation, MAX , is reached. In our experiments, we set $MAX = 400$.

It is worth noticing that in essence, the genetic algorithm described above can be extended easily to be a general algorithm for solving the problem of parameter estimation. One can conveniently adopt it to implement the optimization of multiple parameters in an arbitrary model with multiple independent variables by making some modifications to the model expression, the number and the range of the parameters accordingly. Our experiments demonstrate that this algorithm is stable and effective. The main advantage of the multi-parent crossover is that during the evolution, the search space of crossover is determined by multiple points rather than by only two points used in a pairwise crossover. By setting appropriate values of M, a, b , the algorithm can not only search the optimum of a problem in a much larger space but can also search it out of this space. This makes it more likely that the algorithm will find the stable global optimum more quickly. Also, the new idea of enlarging the search space by the crossover of multiple parents rather than by the use of a large population enables the algorithm to obtain satisfactory solutions with a small population size. This shortens the runtime significantly and a high efficiency is achieved.

4. Results and discussion

Fig. 1 shows a family of potentiostatic current transients at different step potentials for zinc electrodeposition onto a glassy carbon electrode. We can see that,

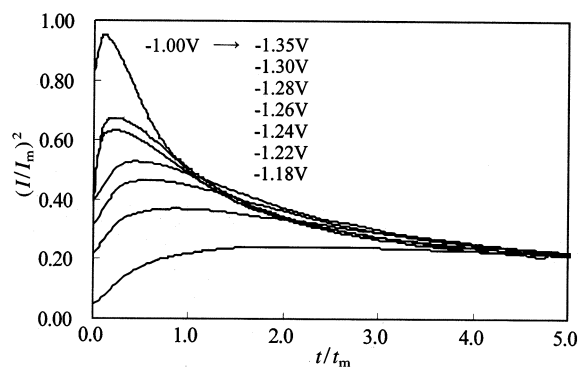


Fig. 1. A family of potentiostatic current transients at different step potentials for zinc deposition onto a glassy carbon electrode from $0.1 \text{ mol l}^{-1} \text{ Zn}(\text{Ac})_2$ and $0.5 \text{ mol l}^{-1} \text{ NaAc}$, pH 5.5.

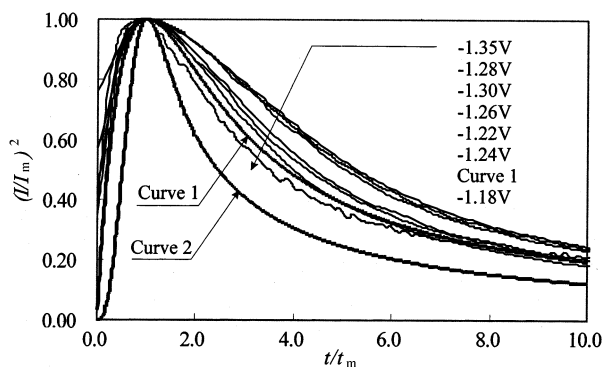


Fig. 2. Comparison of the theoretical non-dimensional plots for instantaneous nucleation (Curve 1) from Eq. (1) and progressive nucleation (Curve 2) from Eq. (2) with the normalized experimental current transients at different step potentials.

when a step potential, E , was employed, the current first increased with time sharply passing through a maximum, I_m , at t_m , and then decayed gradually with time which follows the Cottrell equation. Moreover I_m increases with E . To analyse further, we have normalized the current transients in Fig. 1 according to the $I^2/I_m^2 - t/t_m$ coordinate system and plotted them in Fig. 2. From this figure, we notice that the four non-dimensional $I^2/I_m^2 - t/t_m$ curves for $E = -1.18$, -1.22 , -1.24 and -1.26 V, respectively lie near the theoretical instantaneous curve, while the other three for $E = -1.28$, -1.30 and -1.35 V, respectively obviously deviate from it. This fact indicates that not all of the mechanisms of electrocrystallization of zinc onto glassy carbon electrode from acetate solutions at different step potentials follow instantaneous nucleation and growth strictly. In this case, if one asserts subjectively that the electrocrystallization mechanisms of zinc for $E = -1.28$, -1.30 and -1.35 V, respectively follow instantaneous nucleation, and use the following equations derived from Eq. (1) to determine N_0 and D , this will inevitably lead to inaccurate results.

$$D = \frac{I_m^2 t}{0.1629(zFc)^2} \quad (7)$$

$$N_0 = \frac{1.2564}{t_m \pi k D} \quad \text{and/or} \quad N_0 = \frac{I_m^2}{(0.6382zFDC)^2 k} \quad (8)$$

Table 1

The values of D , A and N_0 obtained, the fitting error, the r^2 and the mean runtime for different step potentials

E/V	$10^6 D/\text{cm}^2 \text{ s}^{-1}$	$10^{-6} N_0/\text{cm}^{-2}$	$10^{-9} A/\text{s}^{-1}$	$10^4 \times$ Fitting error	r^2	Mean runtime/s
-1.18	2.332	0.478	1.41	0.0492	0.99	192
-1.22	2.089	1.483	1.41	0.807	0.97	195
-1.24	2.109	2.330	1.41	1.42	0.97	169
-1.26	2.230	2.720	1.41	3.10	0.95	178
-1.28	1.924	5.435	1.41	5.48	0.92	260
-1.30	2.010	5.499	1.41	3.59	0.96	212
-1.35	2.040	10.93	1.41	9.82	0.95	280

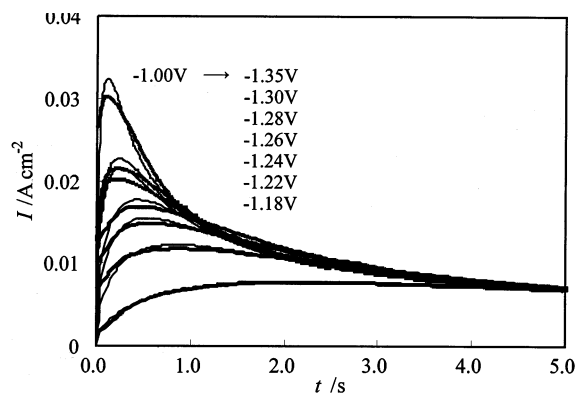


Fig. 3. The experimental current transients and fitting curves for zinc deposition onto glassy carbon electrode at different step potentials (—). The experimental current transient (—). The corresponding fitting curve.

In view of this, we used the genetic algorithm described in the previous section to fit the experimental current transients at different step potentials and to estimate A , N_0 and D simultaneously by taking 500 data points on the corresponding current transients as fitting samples. As the algorithm is a stochastic algorithm, 10 runs were conducted independently for each experimental current transient at different step potentials. Our numerical results show that, despite the fact that in initialization of the population, the ranges of definition of A , N_0 and D differ significantly ($[0, 1]$, $[0, 10^{10}]$ and $[0, 10^{12}]$, respectively), the values of these parameters obtained by this algorithm are very consistent and stable; any disparity in different runs appears only in the fourth digit after the decimal point. Table 1 lists the values of D , A and N_0 we obtained as well as the fitting error (i.e. fitness value) and the mean runtime for different step potentials. We also calculate the square of the correlation coefficient, r^2 , by the following formula

$$r^2 = 1 - \frac{\sum_{i=1}^m (I_i - \hat{I}_i)^2}{\sum_{i=1}^m (I_i - \bar{I})^2} \quad (9)$$

where $\bar{I} = \frac{1}{m} \sum_{i=1}^m I_i$ to assess the quality of the fit.

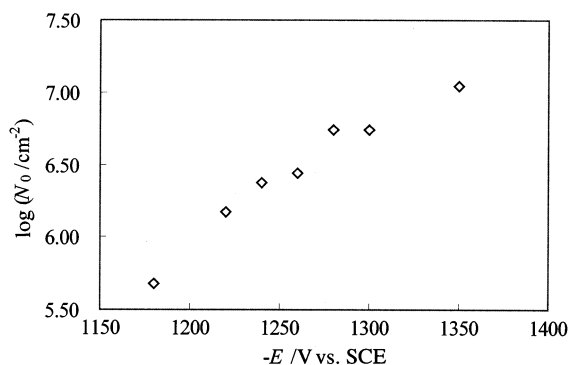


Fig. 4. Plot of $\log N_0$ versus E for zinc electrodeposition onto glassy carbon electrode.

Fig. 3 depicts a comparison of the experimental current transients and the corresponding fitting curves for zinc deposition onto glassy carbon electrode at different step potentials.

As shown in Table 1, the fitting errors for all the experimental current transients are very small and their r^2 values are all greater than 0.92. This indicates that the fitting curves coincide with the experimental current transients very well. Fig. 3 demonstrates this result more clearly. Meanwhile we can see that the diffusion coefficients obtained for different step potentials are very consistent, ($2.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) and comparable to values reported in Ref. [18].

By using the values of N_0 listed in Table 1, we plotted the dependence of $\log N_0$ versus E in Fig. 4. From this figure, we can see that an increase in E leads to a higher N_0 , but with a diminishing gradient. When E is high enough, N_0 will eventually saturate.

According to the following first order nucleation rate equation for three-dimensional nucleation

$$N(t) = N_s(1 - \exp(-At)) \quad (10)$$

where N_s is the number of active sites on the substrate, there are two extreme cases for this equation. One is $N(t) = N_s$ for large values of A which corresponds to instantaneous nucleation and the other is $N(t) = AN_s t$ for small values of A which corresponds to progressive nucleation. From Table 1, the values of A at different step potentials are identical, $1.41 \times 10^9 \text{ s}^{-1}$. This indicates that the mechanism of zinc electrocrystallization onto glassy carbon electrode at all step potentials follows three-dimensional instantaneous nucleation and growth. In addition, from the fact that the mean runtime listed in Table 1 is less than 5 min, our algorithm proved to be a fast and efficient method for estimation of the electrocrystallization parameters.

5. Conclusions

To estimate the electrocrystallization parameters A , N_0 and D simultaneously in the general current–time expression for nucleation and growth deduced by Scharifker and Mostany, we proposed a genetic algorithm using a novel crossover operator based on the non-convex linear combination of multiple parents by fitting the whole current transient for zinc electrodeposition onto glassy carbon electrode immersed in the acetate solutions.

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