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Monte Carlo simulation of the spontaneous oscillation in electrochemical deposition

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Abstract. We report a new Monte Carlo model to simulate the spontaneous oscillating growth in Cu(II)-acid electrochemical deposition system, and present the one-to-one correspondence between the oscillation of pH and the layered structure. Two mechanisms essential for the oscillation behavior, i.e. the adsorption and buffering, are incorporated into the deposition sequences. The simulation results are qualitatively in agreement with the experimental observations. Some system parameters essential for the oscillation generation are discussed. And through adjusting the adsorption ratio, the spatially columnar deposited structure is generated and the columnar alternative growth of copper and cuprous oxide phases is achieved.

PACS. 82.40.Bj Oscillations, chaos, and bifurcations – 74.78.Fk Multilayers, superlattices, heterostructures – 21.60.Ka Monte Carlo models

1 Introduction

Oscillating growth was often observed in electro- chemical deposition systems and attracted much attention in recent years. Among these, the spontaneous oscillation interests many researchers. Switzer et al. [1–3] reported a self-oscillating Cu(II)-lactate system, and observed a Cu/Cu_2O nanoscale layered structure.

In acidic systems, Wang et al. [4–6] developed the deposition in an ultrathin layer of supercooled Cu_2SO_4 electrolyte solution, and their observations included the periodical nanostructures on the filament, the spontaneous oscillations of applied current density (voltage), given a fixed voltage (current). They proposed an analytic model to describe the oscillating growth and dynamic behaviors.

The oscillating growth is always accompanied with an oscillation of pH at the interface between the electrolyte and metal-covered cathode [7]. Typically, it is established that copper deposits at the positive potential shifts and cuprous oxide deposits at the negative potential shifts. However, the spontaneous oscillation in Cu(II)-acid deposition is not understood in details yet. For example, how does the coupling of these two reactions and the reductions (copper and cuprous oxide) induce an oscillation rather than a near-equilibrium state with a composition-homogeneous deposit? What kinds of reactions take place at the positive and negative potential shift, and how these reactions affect the pH and each other?

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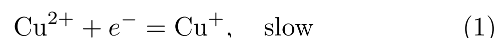
In this paper, we report a Monte Carlo model to simulate the oscillating growth in Cu(II)-acid system. The model reproduces the observed layered structure, spontaneous oscillation of interface pH, and the correspondence between the phase composition and pH at interface. Furthermore, a transformation of the deposit morphology from spatially planar one to columnar one occurred as the parameter of adsorption ratio changes.

2 Model and algorithm of simulation

2.1 Chemical reaction scheme

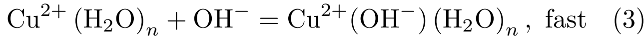
In Cu(II)-acid system, Cu(II)-ions and Cu(I)-ions can form complexes with acid radical, water molecules, or hydroxyl anions. These complexes have different stability constants for the equilibrium, as well as different kinetics to take part in their reactions. Reactions of the complexes are intricate, involving formation, decomposition, electron- acceptance and losing, etc. It is impossible to consider all the complexes and reactions in simulation. To overcome these difficulties, we separate acid radical and Cu(II), Cu(I) cations as independent of one and another. First, consider the reactions involving Cu(II) and Cu(I). At the beginning of the electrodeposition, cations of Cu(II) are mostly reduced through the following reactions when the pH of the interface is low enough [8]:



$$Cu^{2+} + e^- = Cu^+, \quad \text{slow} \tag{1}$$

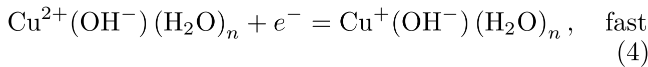
$$Cu^+ + e^- = Cu, \quad \text{fast.} \tag{2}$$

Because of the fast reaction (2), most cations of Cu(II) are transferred into copper. On the contrary, when the pH of the interface increases, hydroxyl anions stabilize the hydroxides of Cu(II) and Cu(I) complexes, and the Cu(II)-hydroxide complexes most likely result in the production of cuprous oxide with the possibility to react with the hydroxide ions:

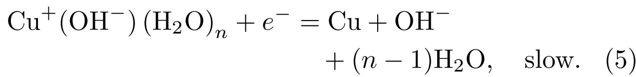


$$Cu^{2+}\left(H_2O\right)_n + OH^- = Cu^{2+}\left(OH^-\right)\left(H_2O\right)_n, \text{ fast} \quad (3)$$

And these complexes are different in chemical activity from the Cu(II) cations:

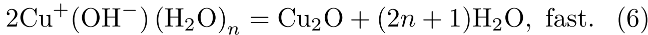


$$Cu^{2+}\left(OH^-\right)\left(H_2O\right)_n + e^- = Cu^{+}\left(OH^-\right)\left(H_2O\right)_n, \quad \text{fast} \quad (4)$$



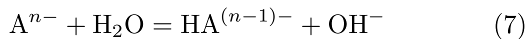
$$Cu^{+}\left(OH^-\right)\left(H_2O\right)_n + e^- = Cu + OH^- + (n-1)H_2O, \quad \text{slow.} \quad (5)$$

The cuprous oxide is converted from $Cu^+(OH^-)(H_2O)_{n-1}$:



$$2Cu^{+}\left(OH^-\right)\left(H_2O\right)_n = Cu_2O + (2n+1)H_2O, \text{ fast.} \quad (6)$$

Meanwhile, the acid radical, which forms complexes with Cu(II) or Cu(I) originally, is released after the reduction of the cations. The hydrolyzation of acid radicals consumes H^+ and leads to the increase of pH at the interface, as shown in equation (7) below. Besides, the H^+ near the electrode would compete with Cu(II) and Cu(I) for reduction, described by equation (8) below, also result in the increasing pH:



$$A^{n-} + H_2O = HA^{(n-1)-} + OH^- \quad (7)$$

$$2H_2O + 2e^- = H_2 + 2OH^-. \quad (8)$$

Therefore, each of all the processes leading to increasing of the pH could be considered as an independent increment of hydroxyl at the interface. Note here that all the reactions above represent, respectively, a group of similar reactions which are possible to occur in the electrolyte.

In spontaneous oscillation systems, there are some buffering species such as lactate or sodium sulfate or their complexes. As soon as hydroxyls are generated, the buffering reactions take place between hydroxyls and buffering species, and the pH at the interface would not change too much until the buffering species are exhausted [7]. Due to the similar reasons, the buffering reactions take place too when the hydroxyls are exhausted.

2.2 Model

Based on the reaction kinetics scheme discussed above, we propose a Monte Carlo simulation to approach the oscillation processes. The whole simulation is built on a 100×120 square lattice with the horizontal orientation L and growth orientation H. Along the L orientation the periodic boundary condition is applied. Each growth unit occupies a site on the lattice. A source line is set above a certain distance from the growth front. All the particles are released from the source in sequence, and randomly walk to the growth front. This configuration for simulation is similar as the counterpart of the well-known diffusion-limited aggregation (DLA) model [9].

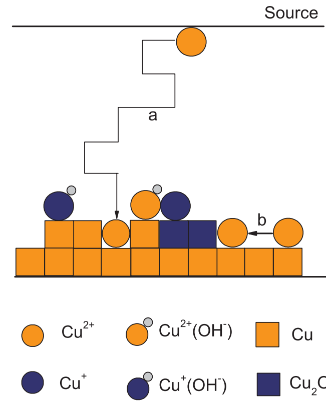


Fig. 1. Schematics of the simulation process. Particles are released from the source, and the source is moved upward to keep a constant distant from the growth front. An ion walks randomly until it lands on the growth front. Process a represents the walking ion reaches to the interface and become an adsorbing ion. Process b represents the diffusion of an adsorbing ion.

The simulation algorithm is described below.

(1) Calculate the probability to release a new particle from the source. We assume the probability as a function of the adsorption ratio (to be defined below). It is settled as 0.5 when the adsorption ratio equals to the equilibrium adsorption ratio. That means there are equal amounts of particles respectively arriving at the interface and incorporating into the crystal from the interface.

The adsorption ratio is defined as the ratio of the number of waiting ions at the interface to the area of interface. When the rates of adsorption and desorption equal to each other, the adsorption reaction reaches an equilibrium, the ratio is the equilibrium adsorption ratio, Q.

(2) A Cu(II) cation is determined by the above probability to release from the source, and walks randomly until it arrives at the interface (Fig. 1). After arriving in the interface, the cation becomes an adsorbing ion (as shown in Fig. 1, event a). Otherwise, an adsorbing ion is chosen in the program. And it will either take part in electrochemical reactions, or diffuse (Fig. 1, event b) on the interface [11].

The reason we introduce the adsorbing ion is that the adsorbing ions have to wait on the interface, until an electron could climb over the potential barrier to tunnel to it [10]. Different reactions have different potential barriers, thus different probabilities to take place.

(3) As the chemical reactions, involved Cu(II) or Cu(I) ions, take place, the pH at the interface should be altered accordingly. However, there are some other reactions hard to be considered immediately, such as reactions (7) and (8), for we only trace metal ions in our model. Thus we consider the reactions involving no metal ions as a function of the concentration of OH^-, C_{OH^-}. When the growth front proceeds to a new height, update the pH at interface according to this function. Similarly, the diffusion of hydroxyl could also be considered as a function of C_{OH^-}. The increment of pH, $I_{[OH]^-}$, according to two factors, could be written as (details to be presented below):

$$I_{[OH^-]} = a \exp\left[b + \log C_{OH^-}\right] - D\frac{C_{OH^-}}{l} \quad (9)$$

where a and b are two adjustable parameters, C_{OH^-} is the concentration of hydroxyl at the interface, D is the diffusion coefficient, l is the thickness of diffusion layer.

The first term in equation (9) originates from the chemical reactions which generate hydroxyl. Take reactions (8) as an example, the rate of this reaction, v, is [10]

$$v \propto K \exp\left(-\beta F \frac{\Delta\phi}{RT}\right) \tag{10}$$

where K is the rate constant, β is the symmetry factor which is greater than zero but less than unity, $\Delta\phi$ is the equilibrium potential, F is Faraday constant, and R is mole gas constant, T is temperature. $\Delta\phi$ is a function of C_{OH^-}:

$$\Delta\phi = \Delta\phi_0 + \frac{RT}{F}\ln\frac{1}{C_{OH^-}} = \Delta\phi_0 - \frac{RT}{F\log e}\log C_{OH^-} \tag{11}$$

where $\Delta\phi_0$ is the standard potential which could be calculated from the rate constants of the reaction.

Besides reaction (8), there might be other reactions generating hydroxyl near the electrode. However, different reactions satisfy the similar equations as equations (10) and (11), only $\Delta\phi_0$, β and K might be different. To include the cooperative influences we introduce two new parameters a and b, and express it as the first term of equation (9).

The second term in equation (9) is due to the diffusion effect, which is in proportion to the concentration gradient, $\partial C_{OH^-}/\partial l$. Taking a linear approximation, it becomes C_{OH^-}/l, where l is the thickness of the diffusion layer. It is assumed that the pH far from the diffusion layer is the same as that in the electrolyte.

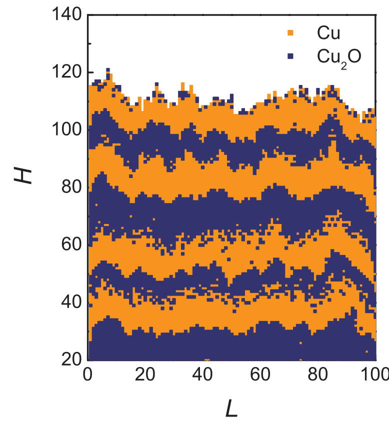


Fig. 2. Multilayered structure of the deposition, $Q = 0.9$.

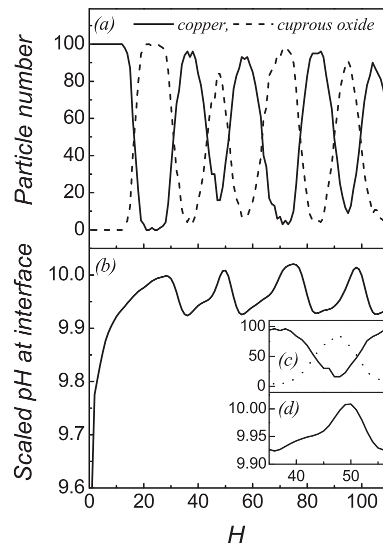


Fig. 3. Correspondence between phase composition and pH oscillation for the deposition shown in Figure 2. (a) The particle numbers of copper and cuprous oxide of each layer as a function of the number H of deposits. (b) The oscillation of pH at the interface. The inset is a close view of an oscillation period for both the particle number and pH.

3 Results and discussion

3.1 Layered structure and spontaneous oscillation

Figure 2 shows the simulated multilayered structure, with $Q = 0.9$. At the beginning of the deposition, when the pH at interface equals to that of electrolyte, copper is preferred. After several copper layers are deposited, the cuprous oxide follows. Subsequently, these two kinds of substances are deposited in turn, although the inter-layer interface fluctuates remarkably. In Figure 3 are presented the correspondences between phase composition (particle number) and oscillation of interface pH. As the two phases deposit alternatively, the pH oscillates in the synchronizing form, ranging from 9.9 to 10, noting here that the pH is a scaled quantity. From a close view of one oscillation period, one could see the details of the relationship: cuprous oxide increases as the pH increases and decreases when pH decreases, whiles the copper phase varies reversely. In both Figures 2 and 3 are shown the spontaneous oscillations of the deposition in terms of deposited phase and pH at the interface. These results are all qualitatively in agreement to experimental results [1–7].

In fact, the spontaneous oscillation is not necessary for the present model, unless some conditions are fulfilled. For example, an exclusion of the buffering species will destroy the oscillation. The deposition then turns to be a mixture of the two phases, and the pH remains steady. Neither layered structure nor phase separation can be observed.

Besides, the decrease of the pH at interface is not only due to the consumption of hydroxyl when cuprous oxide deposits, but also due to the diffusion in the concentration field. The latter factor is noteworthy when the hydroxyl concentration gradient near the interface is considerable. Without either of both, the oscillation disappears.

3.2 Effect of equilibrium adsorption ratio Q

It is interesting to investigate the role of Q. The deposition morphology becomes very different upon different values of Q. In Figure 4 are presented several patterns simulated given different Q. As Q varies from 0.9 to 0.1, the morphology transforms from planar form to the spatially columnar form, both with the alternative copper and cuprous oxide phases. It suggests a possible mechanism for the deposition of columns and filaments with multilayer structures in some experiments [4].

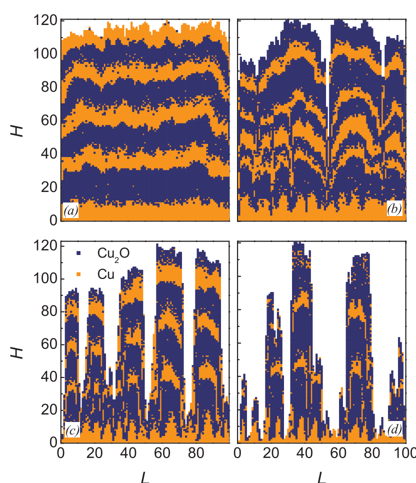


Fig. 4. Effect of Q on the deposition structure and pattern; $Q = 0.9$ (a), 0.45(b), 0.2(c), 0.1(d).

In Figure 4a where $Q = 0.9$, the deposition front keeps a planar morphology and the typical multilayered structure is observed. Copper layer and cuprous oxide layers grow alternately, while each layer is flat. Figure 4b shows the growth pattern with $Q = 0.45$. The growth front is spatially column-like and the layers become corrugated. However, the layered structure in each column remains there.

As shown in Figures 4c and 4d, where $Q = 0.2$ and 0.1, the growth front evolves into the columnar pattern. And the space-separation between columns in Figure 4c is obviously smaller than that shown in Figure 4d, demonstrating the significant influence of Q on the morphology. Note here that all the other parameters are identical in four cases.

The Cu/Cu_2O oscillation period also varies slightly upon different values of Q. In Figures 4c and 4d, the growth front turns to be columnar, indicating that the number of particles in each layer diminishes, thus the contribution of cuprous oxide to the consumption of hydroxyl is less than the cases shown in Figures 4a and 4b. However, the pH at interface is still updated according to equation (9). Therefore, a slower consumption leads to the increase of the oscillation period, and the augment of the proportion of cuprous oxide in the deposition. It also proves that in each oscillation period the dropping of pH depends on not only the diffusion in the concentration field, but also the chemical reaction itself, such as reaction (3).

3.3 Discussion

Using the developed model, we have studied the spontaneous oscillating growth in electrochemical deposition system. Figures 2 and 3 show the morphology of the deposition and oscillation in the pH. We have understood the reason for increasing of pH is that, when the pH at interface is low enough, little Cu_2O deposits are produced, thus less hydroxyls are consumed. Besides, the diffusion of hydroxyl is weak. The pH drops because, when the pH is high, more and more Cu_2O deposits and more hydroxyl is consumed, and the high concentration gradient helps the diffusion of hydroxyl from the interface to the electrolyte.

The simulation reveals that there are several important factors controlling the oscillation. First, the consumption of hydroxyl in chemical reactions (reaction (3)) is important to the drop of pH. These reactions often lead to the deposition of cuprous oxide (reaction (6)). Second, the diffusion (described by the second term in Eq. (9)) of hydroxyl and the buffering species are also indispensable to the oscillation of pH. However, the influence of Q on the deposition pattern becomes clear. In experiments, Q could be modulated by the electrode interface condition, current density, or adsorption of inactive species and bubbles of electrolyzed gas. It would be interesting to check these effects in future experiments.

It is necessary to note that some parameters in our simulation are quite hard to be measured experimentally, such as parameters a and b in equation (9). Although it is difficult to give the results quantitatively, we could study the general behaviors of the spontaneous oscillating system, such as the spontaneous oscillation of current density, and the related processes. These works are still going on.

4 Conclusion

In conclusion, we have proposed a new Monte Carlo model by introducing the adsorption and buffering mechanisms, to simulate the oscillating growth in electrochemical deposition of Cu(II)-acid system. The simulated layered structure of Cu/Cu_2O in deposition, as well as the correspondence between the oscillation of pH and phase composition are qualitatively supported by the experimental observations.

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