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Modeling of metal electrodeposits: Analytical solutions

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From a model of metal electrodeposition, expressions of the concentration and current for diffusion, convection, and voltage in one dimension are derived. Our models are exact solutions of differential equations. The effect of dissolution of the anode, direction and speed of convection, and voltage on the concentration, current, and growth speed are determined. The origin of currents that are independent of the applied potential is explained.

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I. INTRODUCTION

Mathematical modeling of electrochemical deposition has attracted attention because it helps our understanding of the growth mechanism and may explain experiments from theory. Chazalviel [1] has proposed a set of differential equations as a mathematical model, which takes into account the displacement of the cations and anions in the solution due to both diffusion and electrical migration. His model gives a deep insight into the growth mechanism as analytical solutions for concentration, current, and potential in the steady state are derived. Consider a linear cell containing a metal salt with cation charge z_c and anion charge z_a at bulk concentration C^0 with the cathode at $x=0$ and the anode at $x=L$. By dividing the concentration map from an arbitrary boundary x_l into two regions, the space-charge region $(0<x<x_l)$ and the quasineutral region $(x_l<x<L)$, and considering both diffusion and electrical migration, he obtained expressions for the concentration in the quasineutral region, $2C^0(x-x_l)/L$, and for the current density $-2eDC^0(1+z_c/z_a)/L$, where e is the electric charge and D is the diffusion constant. However, this model did not consider convection. Fleury, Chazalviel, and Rosso [2,3] have shown experimentally that there is convective motion in the vicinity of the cathode, near the growing tips. This convection leads to an additional transport mechanism: the advection of cations and anions in the fluid flow. By introducing convection into Chazalviel's model, Fleury, Kaufman, and Hibbert [4] derived the concentration and current expressions from a model of diffusion, convection, and electrical migration, and presented the concentration profiles as a function of convection speed. Current that is independent of the applied potential is a problem in Chazalviel's model. The same problem is still in Fleury *et al.*'s current expressions for both the general case and the case of very small fluid speeds, although both models involve electrical migration and potential.

A feature of the work presented in this paper is the effect of different boundary conditions resulting from different models of the dissolution of the anode. Experimental arrangements may involve a metallic anode which dissolves (e.g., Cu, Zn) or one at which oxygen is evolved (e.g., Pt). We propose models of electrochemical deposition with diffusion, convection, and electric fields for different dissolutions of the anode in one dimension. From differential equations we derive expressions of the concentration and current. Our models are exact solutions of differential equations though our mathematical treatment is simpler than that found in the literature. Then we discuss the effect of dissolution of the anode, the direction and speed of convection, and voltage on the concentration, current, and growth speed. By comparison with the results in the literature, we demonstrate that Chazalviel's concentration and current density expressions are in fact valid only for pure diffusion, instead of for both diffusion and electromigration. We can explain the origin of Chazalviel's and Fleury *et al.*'s currents that are independent of the applied potential.

II. MODEL

We consider the electrochemical deposition in a two-dimensional rectangular thin cell of width W and length L with two linear electrodes (cathode at $x=0$ and anode at $x=L$). Assume that the deposit grows very slowly and is governed by diffusion, convection, and electric fields. For a practical value of the concentration, the charged layer is very narrow and the cell will be quasineutral, so the electric field gradient can be ignored (i.e., $\partial E/\partial x=0$). If the deposit is flat, we assume that a smooth and uniform deposit grows (i.e., the deposit looks like a flat uniform sheet with a straight edge). In this case the two-dimensional differential equation can be approximately reduced to the one-dimensional steady-state differential equation. The concentration C satisfies the differential equation

$$D\frac{\partial^2 C}{\partial x^2}-v\frac{\partial C}{\partial x}-\mu E\frac{\partial C}{\partial x}=0\ , \tag{1}$$

where v is the convection velocity ($v<0$ for convection toward the cathode, and $v>0$ for convection toward the

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anode), μ is the mobility of the ions, the electric field $E=-U/L$, and U is the voltage applied between two electrodes. The first term is the diffusion term, the second term is the convection term, and the last term is the electric field term. The cation is totally reduced at the cathode, so the concentration on the surface of the deposit is zero. Equation (1) may be solved for two cases of dissolution at the anode.

Case 1. Dissolution of the anode keeps the total number of cations unchanged. The boundary conditions are

$$C=0 \quad \text{at } x=0 \quad \text{and} \quad \int_0^L C\,dx = C^0 L \ . \tag{2}$$

Case 2. Dissolution keeps $C=C^0$ (the bulk concentration) at the anode or at an arbitrary boundary L, but the total number of cations may be changed. We presume this arises from oxygen evolution at the anode or hydrogen evolution at the cathode. This case may simulate a diffusion layer which is maintained at a particular distance from the cathode. The boundary conditions are

$$C=0 \quad \text{at } x=0 \quad \text{and} \quad C=C^0 \quad \text{at } x=L \ . \tag{3}$$

In order to write the differential equation in a dimensionless form, we set $c=C/C^0$ for the dimensionless concentration, $V=vL/D$ for the dimensionless convection velocity, $X=x/L$ for the dimensionless distance, and $M=\mu L/D$ for the dimensionless mobility. By multiplying $L^2/(DC^0)$ on both sides of Eq. (1), it is rewritten in a dimensionless form as

$$\frac{\partial^2 c}{\partial X^2} - V\frac{\partial c}{\partial X} - ME\frac{\partial c}{\partial X} = 0 \ . \tag{4}$$

The boundary conditions (2) and (3) respectively for cases 1 and 2 become

$$c=0 \quad \text{at } X=0 \quad \text{and} \quad \int_0^1 c\,dX = 1 \ , \tag{5}$$

$$c=0 \quad \text{at } X=0 \quad \text{and} \quad c=1 \quad \text{at } X=1 \ . \tag{6}$$

A. Model for diffusion

First consider the simplest case of pure diffusion, where $V=0$ and $E=0$. So Eq. (4) is reduced to a single diffusion term in the equation as a function of the distance X from the cathode:

$$\partial^2 c/\partial X^2 = 0 \ . \tag{7}$$

By integrating this equation twice, we get the solution for the concentration

$$c = k_1 X + k_2 \ , \tag{8}$$

where k_1 and k_2 are constants and their values depend on the boundary conditions.

For case 1 (dissolution of the anode keeps the total number of cations unchanged) by applying the boundary conditions (5) to Eq. (8), we obtain $k_1=2$ and $k_2=0$. By replacing k_1 and k_2 with their values, Eq. (8) is written as

$$c=2X$$

or

$$C=2C^0 x/L \ . \tag{9}$$

This expression shows that the concentration is linear across the cell.

The diffusion current density J_{d1} is

$$J_{d1} = -zeD\frac{\partial C}{\partial x} = -2zeD\frac{C^0}{L} \ , \tag{10}$$

where z is the number charge of the ions and e is the electronic charge.

For case 2 [dissolution of the anode keeps $C=C^0$ (the bulk concentration) at the anode], by applying the boundary conditions (6) to Eq. (8), we obtain $k_1=1$ and $k_2=0$. By replacing k_1 and k_2 with their values, Eq. (8) is written as

$$c=X$$

or

$$C=C^0 x/L \ . \tag{11}$$

This expression shows that the normalized concentration is exactly equal to the normalized distance X.

Similarly to case 1, the diffusion current density is

$$J_{d2} = -zeDC^0/L \ . \tag{12}$$

Comparison of J_{d1} to J_{d2} leads to

$$J_{d1}/J_{d2} = 2 \ . \tag{13}$$

B. Model for diffusion, convection, and electric field

Adding the convection and electric field terms to Eq. (7), we have Eq. (4). A general solution of this differential equation is

$$c = k_1 + k_2 e^{V_s X} \ , \tag{14}$$

where V_s is the sum of velocities of convection and electric migration,

$$V_s = V + ME = (v+\mu E)L/D \ .$$

1. *Case 1: Dissolution of the anode keeps the total number of cations unchanged*

By applying the boundary conditions (5) to Eq. (14), the concentration is

$$c = \frac{V_s(e^{V_s X}-1)}{e^{V_s} - V_s - 1} \ . \tag{15}$$

In the case of pure diffusion $v_s=0$, then $\lim_{V_s \to 0} c = 2X$, so Eq. (15) is reduced to Eq. (9). For practical units,

$$C = C^0 \frac{V_s(e^{V_s x/L}-1)}{e^{V_s} - V_s - 1} \ . \tag{16}$$

This is the concentration expression that takes account of diffusion, convection, and electric field when dissolution of the anode keeps the total number of cations unchanged.

The current density in this case is

$$J_1 = ze\left[-D\frac{\partial C}{\partial x}+(v+\mu E)C\right] = -\frac{zeC^0DV_s^2}{L(e^{V_s}-V_s-1)} . \tag{17}$$

The ratio of the current of diffusion, convection, and electric fields to the diffusion current J_1/J_{d1} leads to

$$J_1/J_{d1}=\frac{V_s^2}{2(e^{V_s}-V_s-1)} . \tag{18}$$

For $|V_s| \ll 1$ by the Taylor series expansion of $\exp(V_s)$ to the third order, Eq. (18) approximately leads to

$$J_1/J_{d1} \approx \frac{3}{V_s+3} . \tag{19}$$

In the case of pure diffusion, then $\lim_{V_s \to 0} J_1 = J_{d1}$, so Eqs. (18) and (19) are simplified to Eq. (10).

For large negative values of V_s (e.g., $V_s \to -\infty$ or very large voltage), the current ratio is reduced to

$$J_1/J_{d1} \approx \frac{V_s}{2} . \tag{20}$$

2. *Case 2: Dissolution of the anode keeps concentration constant (the bulk concentration) at the anode*

By applying the boundary conditions (6) to Eq. (14), the concentration becomes

$$c=\frac{(e^{V_sX}-1)}{e^{V_s}-1} . \tag{21}$$

In the case of pure diffusion, then $\lim_{V_s \to 0} c = X$, so Eq. (21) is reduced to Eq. (11). For practical units,

$$C=C^0\frac{(e^{V_sx/L}-1)}{e^{V_s}-1} . \tag{22}$$

This is also the concentration expression that applies for a cell in which any transport mechanism (for example, stirring) keeps the concentration of the cations unchanged at an arbitrary distance L.

Similarly to case 1, the current density is

$$J_2=J_{d2}\frac{V_s}{e^{V_s}-1} . \tag{23}$$

For $|V_s| \ll 1$ by the Taylor series expansion of $\exp(V_s)$ to the second order, the above equation approximately leads to

$$J_2/J_{d2} \approx \frac{2}{V_s+2} . \tag{24}$$

In the case of pure diffusion, then $\lim_{V_s \to 0} J_2 = J_{d2}$, so Eqs. (23) and (24) are reduced to Eq. (12).

For large negative values of V_s (e.g., $V_s \to -\infty$ or very large voltage), the current ratio is simplified to

$$J_2/J_{d2} \approx V_s . \tag{25}$$

III. RESULTS AND DISCUSSION

A. Concentration

1. *Effect of convection*

Equations (9) and (11) show that the concentrations of cations for both cases 1 and 2 are linear across the cell for pure diffusion. This conclusion matches the one first treated by Chazalviel [Eq. (33) of Ref. [1]] if the charged layer is negligible (this is true for a practical value of the concentration). However, the mathematical treatments are different. Equation (9) is an exact solution of the pure diffusion equation, in contrast to Chazalviel's approximate solution.

The concentration profiles as a function of the fluid speed may be visualized when we plot Eq. (15) in Fig. 1, and Eq. (21) in Fig. 2, respectively for case 1 and case 2. When the flow is turned on, the concentration changes and the concentration profile is no longer linear. If the convection flows toward the cathode (i.e., $v<0$), the concentration near the cathode becomes larger than the one without convection. Furthermore, as the fluid speed v becomes more negative, the concentration near the cathode increases. By contrast, when the convection flows toward the anode (i.e., $v>0$), the concentration near the cathode is less than the one without convection. Furthermore, it decreases as the convection increases.

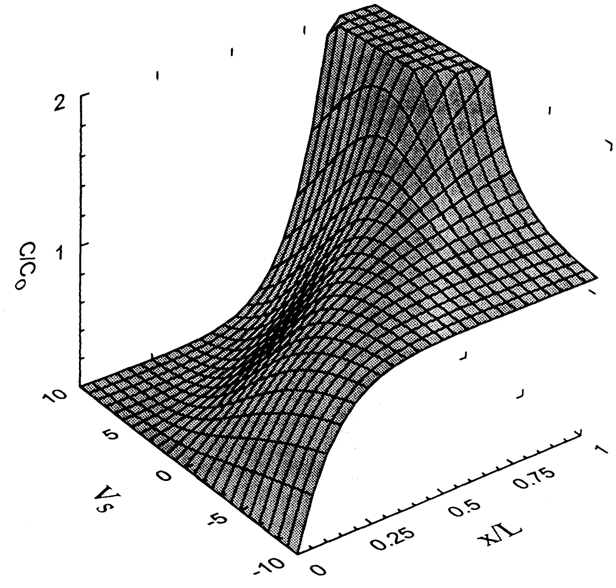

FIG. 1. The concentration profile in the cell for case 1, in which dissolution of the anode keeps the total number of cations unchanged, as a function of convection velocity V_s.

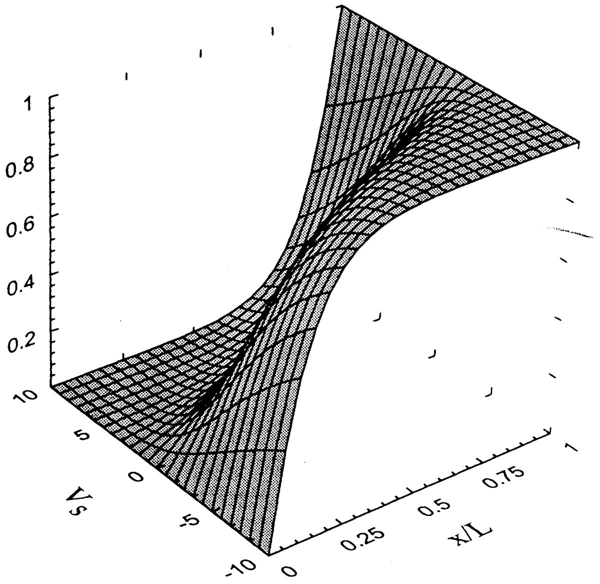

FIG. 2. The concentration profile in the cell for case 2, in which dissolution of the anode keeps the concentration constant at the bulk concentration at $x = L$, as a function of convection velocity V_s.

2. *Effect of dissolution of anode*

In the case of pure diffusion, the concentration at the anode is $2C^0$ for the requirement of constant total cation concentration (case 1). When convection is turned on, the concentration near the anode increases (approaching infinity for large flows) for flow towards the anode, while it levels out for flow away from the anode (Fig. 1). The concentration at the anode is always larger than the bulk concentration regardless of both speed and direction of convection.

Figure 2 shows that for case 2 dissolution of the anode keeps the concentration constant (the bulk concentration) at the anode, but the concentration near the anode reaches the limit of the bulk concentration more quickly as convection increases toward the cathode or dramatically decreases as convection increases toward the anode. In the limiting case $V_s \rightarrow -\infty$, then $c \rightarrow 1$. The concentration is uniform across the cell if the flow speed becomes very large. This demonstrates that the convection forces cations moving toward the cathode to increase the concentration near the cathode when convection flows toward the cathode. However, when the convection flows toward the anode, the concentration becomes less than that without convection. Furthermore, as the fluid velocity increases, the concentration decreases, except at both electrodes. Convection drives ions going away from the cathode to decrease the concentration when convection flows toward the anode.

The concentration profile for convection toward the cathode in case 1 in Fig. 1 is similar to the concentration map of Fleury, Kaufman, and Hibbert (Fig. 2 of Ref. [4]), but the mathematical expression (15) differs from theirs [Eq. (28) of Ref. [4]].

3. *Effect of voltage*

It is seen from Eqs. (15), (16), (21), and (22) that the electric field or voltage has an effect on the concentration map. As voltage increases, the electric field ($E < 0$) becomes more negative. Then V_s is more negative, so the concentration near the cathode increases. This is because the stronger electric field drives more cations to the cathode.

B. Current

1. *Effect of voltage*

Chazalviel claimed that he derived the current expression for both diffusion and electromigration [Eq. (29) of Ref. [1]], but his current is independent of the applied potential. Why did he get this unpractical result? We note that his current expression is equivalent to Eq. (10), for pure diffusion in case 1.

Equations (20) and (25) show that the current driven by diffusion, convection, and electric field increases as the potential increases. When a greater voltage is applied to the cell, the electric field and V_s become more negative, so the current increases. This is also different from Fleury *et al.*'s current expressions [Eqs. (31) and (32) of Ref. [4]] which are also independent of the applied potential. The same problem as that of Chazalviel is still in Fleury *et al.*'s current expressions for both the general case and the case of very small fluid speed, although both of them have involved electric migration or potential in their models. It may be demonstrated that Fleury *et al.*'s current expressions also hold only for diffusion and convection, as they are independent of potential. Notice that Fleury *et al.*'s current for the case of very fast fluid flow, which is a function of voltage [Eq. (41) of Ref. [4]], conflicts with his current for the general case which is independent of voltage.

2. *Effect of direction of convection*

Equations (18), (19), (23), and (24) also show that different directions of convection have different effects on the current. The currents for diffusion, convection, and electric field are larger than the diffusion currents when convection flows toward the cathode ($v < 0$, $V_s < 0$), but are less than the diffusion current when convection flows toward the anode ($v > 0$, $V_s > 0$). When convection is toward the cathode, more cations are carried near the cathode to react and the current increases. On the contrary, when convection is toward the anode, convection drives cations away from the cathode, the concentration near the cathode decreases, and the current decreases.

3. *Effect of dissolution of anode*

By comparison of the potential-independent diffusion currents for different dissolutions of the anode (i.e., comparison of case 1 with case 2), the current J_{d1} is twice as much as the current J_{d2}. Comparison of J_1 with J_2 leads to

$$J_1/J_2 = V_s \frac{e^{V_s}-1}{e^{V_s}-V_s-1} . \tag{26}$$

For $|V_s| \ll 1$ by the Taylor series expansion of $\exp(V_s)$ the second order, the above equation approximately leads to

$$J_1/J_2 \approx V_s + 2 . \tag{27}$$

In the case of pure diffusion, then $\lim_{V_s \to 0} J_1/J_2 = 2$, so Eqs. (26) and (27) are simplified to Eq. (13).

For large negative values of V_s (e.g., $V_s \to -\infty$ or very large voltage), then J_1 approximately equals J_2.

4. Effect of bulk concentration

The current Eqs. (10), (12), and (17) indicate that all currents are proportional to the bulk concentration. Removal of cations at the cathode is faster when the bulk concentration increases.

C. Growth speed

As the growth speed is proportional to the current, the current expressions (20) and (25) predict that the metal tree grows faster when the applied potential or the concentration increases.

IV. CONCLUSION

From differential equations we set up models and derive expressions of the concentration and current for diffusion, convection, and electric fields in one dimension. Our models are exact solutions of the differential equations. The effects of different models of dissolution of the anode, directions, and speeds of the convection, and electric field lead to different current expressions. The assumptions made in previous work are shown to lead to expressions that are correct only for pure diffusion.

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