A Reaction-Diffusion Model of Spatial Pattern Formation in Electrodeposition

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Abstract. In this paper we deal with a reaction-diffusion system to model the coupling between surface morphology and surface composition, as a means of understanding the formation of morphological patterns found in electrodeposition (ECD). The discussion is restricted to the case of one chemical species adsorbed at the surface of the growing cathode and source terms for both the chemical and the morphological equations of a simple form. We investigate the nonlinear dynamics of the system from the analytical and numerical points of view. The stability analysis shows the initiation of spatial patterns induced by diffusion, i.e. the diffusion-driven or Turing instability phenomenon. The obtained simulations are in good agreement with experiments for the electrodeposition of Au-Cu alloys.

1. Introduction
Electrodeposition of Au-Cu alloys from cyanocomplex baths has been shown to exhibit electrokinetic instabilities that can lead to compositional heterogeneity in the electrodeposit bulk [1]. Such instabilities derive from a hysteretic current-voltage characteristic related to the buildup of CN⁻ concentration in the catholyte and attending variations the Cu(I)-cyanocomplex nobility [2]. In this paper we develop a model coupling the surface morphology and CN⁻ concentration, in order to rationalise the formation of the morphological patterns sometimes developing in electrodeposition (ECD). This phenomenon is a special case, original within the realm of metal electrochemistry, of a more general, well-known type of chemical and electrochemical dynamics (electrocatalysis [3], corrosion of Cu [4], Fe-group metals [3] and Ag [5]). To qualitatively describe such dynamics, in Section 2 we introduce a simple model based on a reaction-diffusion approach, which is shown to be able to capture the essential features of pattern development observed in experiments. A detailed presentation of a class of models including this one as a particular case, with full discussion of the underlying physics, is reported in [6].

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In Section 3, we present a stability analysis to investigate the nonlinear dynamics of the reaction-diffusion system. In particular, we obtain a set of conditions in terms of the model parameters that guarantee the initiation of spatial patterns induced by diffusion, i.e. the \textit{diffusion-driven} or \textit{Turing} instability phenomenon \cite{7}. Hence, in Section 4, we deal with the numerical approximation of the equations to present some simulations related to the Turing instability that are in good agreement with electrodeposition experiments.

2. The model
In this paper we consider a 1D model in space, based on the assumption that the electrodeposit surface can be regarded as isotropic in the substrate plane (see Figure 2).

The equation for the morphological dynamics is

\[
\frac{\partial \eta}{\partial \tau} = D^*_\eta \frac{\partial^2 \eta}{\partial \xi^2} + S^*, \quad \text{with} \quad S^* = \alpha \frac{\eta^2}{1 + \eta} - \beta \eta \theta,
\]

where $\eta(\xi, \tau)$ is the dimensionless electrode shape (i.e. the intersection of the electrodeposit surface with a plane normal to the substrate), $\xi$ is the dimensionless space coordinate (i.e. the real coordinate along the intersection of the substrate plane with the plane perpendicular to it), $\tau$ is the dimensionless time and $D^*_\eta$ is the dimensionless form of the surface diffusion coefficient of adatoms. In the source term $S^*$, the parameters $\alpha$ and $\beta$ are strictly positive and $\theta(\xi, \tau)$ is the surface coverage with the adsorbed chemical species. The source term $S^*$ accounts for: (i) localisation of the ECD process $\frac{\eta^2}{1 + \eta}$ and (ii) effects on the ECD rate of surface chemistry, i.e. the presence of adsorbates at the growing cathode, $-\eta(\xi, \tau)\theta(\xi, \tau)$.

The presence of adsorbable species in the ECD bath gives rise to the fact that $\theta(\xi, \tau)$ develops at a growing electrochemical interface, as a function of space and time. $\theta(\xi, \tau)$ is controlled by the nature of the adsorbable species and of the surface active sites. The surface coverage dynamics can be described, as customary in chemical kinetics, in terms of a material balance with a source term containing positive and negative contribution related to adsorption and desorption. More precisely, the dimensionless form for the surface chemical dynamics can be expressed as

\[
\frac{\partial \theta}{\partial \tau} = D^*_\theta \frac{\partial^2 \theta}{\partial \xi^2} + S^* \theta^*, \quad \text{with} \quad S^* \theta^* = K^*_{\text{ads}}(\eta, \theta)(1 - \theta) - K^*_{\text{des}}(\eta, \theta) \theta,
\]

where $D^*_\theta$ is the surface diffusion coefficient of CN$^-$, $S^* \theta^*$ is the chemical source term defined in terms of $K^*_{\text{ads}}$ and $K^*_{\text{des}}$ which represent the adsorption and desorption rate constants, respectively.

By coupling equations (1) and (2), one obtains the following general model in dimensionless form

\[
\begin{align*}
\frac{\partial \eta}{\partial \tau} &= D^*_\eta \frac{\partial^2 \eta}{\partial \xi^2} + \alpha \frac{\eta^2}{1 + \eta} - \beta \eta \theta, \\
\frac{\partial \theta}{\partial \tau} &= D^*_\theta \frac{\partial^2 \theta}{\partial \xi^2} + K^*_{\text{ads}}(\eta, \theta)(1 - \theta) - K^*_{\text{des}}(\eta, \theta) \theta.
\end{align*}
\]

We define

\[
K_\epsilon(\eta, \theta) = K^*_{\text{ads}}(\eta, \theta), \quad K_\tau(\eta, \theta) = K^*_{\text{ads}}(\eta, \theta) + K^*_{\text{des}}(\eta, \theta),
\]

and, for purposes of theoretical analysis, let us consider the reaction-diffusion system in the following form
which is defined for \((\xi, \tau^*) \in [0, L] \times [0, T]\), with \(L\) a characteristic length of the electrode, \(T\) a characteristic time of the electrodeposition process, and where
\[
\tau^* = D_v \tau, \quad d = \frac{D_v}{D_v}, \quad \varepsilon = \frac{\alpha}{\beta}, \quad \sigma = \frac{1}{D_v}, \quad \rho = \frac{\beta}{D_v}.
\]
The system (5) is equipped with: (i) zero-flux boundary conditions, that is: in \(\xi = 0\) and \(\xi = L\) the normal derivatives are \(\frac{\partial \eta}{\partial n} = 0, \frac{\partial \theta}{\partial n} = 0\), and (ii) with initial conditions for \(\tau^* = 0\) given by
\[
\eta(\xi, 0) = \eta_0(\xi), \quad \theta(\xi, 0) = \theta_0(\xi), \quad \xi \in [0, L].
\]

3. Stability analysis

In this section we analyze the stability properties of the non-trivial homogeneous equilibrium of model (5) both in the space-independent case and in the presence of diffusion (\(d \neq 0\)).

The homogeneous steady-states are the solutions of the following set of equations
\[
\begin{aligned}
\eta \left( \frac{\varepsilon \eta}{1 + \eta} - \theta \right) &= 0, \\
K_1(\eta, \theta) - K_2(\eta, \theta) \theta &= 0.
\end{aligned}
\]

The positive homogeneous steady-state \((\eta_e, \theta_e)\) is given by
\[
\begin{aligned}
\theta_e &= \frac{\varepsilon \eta_e}{1 + \eta_e}, \\
K_1(\eta_e, \theta_e) &= K_2(\eta_e, \theta_e) \theta_e,
\end{aligned}
\]
with both \(\eta_e\) and \(\theta_e\) strictly positive.

We want to investigate the stability properties of this homogeneous steady state by requiring that, in the spatially independent case, \((\eta_e, \theta_e)\) is a stable equilibrium. To this aim, we consider the Jacobian matrix of the system (5)
\[
J(\eta_e, \theta_e) = \begin{pmatrix}
\rho \theta_e & -\rho \eta_e \\
\sigma(\Phi - \theta_e \gamma) & \sigma(\Psi - \theta_e \zeta - K_2(\eta_e, \theta_e))
\end{pmatrix}
\]
where
\[
\Phi = \frac{\partial K_1}{\partial \eta}(\eta_e, \theta_e), \quad \Psi = \frac{\partial K_1}{\partial \theta}(\eta_e, \theta_e), \quad \gamma = \frac{\partial K_2}{\partial \eta}(\eta_e, \theta_e) \quad \text{and} \quad \zeta = \frac{\partial K_2}{\partial \theta}(\eta_e, \theta_e)
\]
and moreover the second equation in (9) holds.

Linear stability analysis assures that \((\eta_e, \theta_e)\) is linearly stable if and only if
\[
\det(J(\eta_e, \theta_e)) > 0 \quad \text{and} \quad \text{tr}(J(\eta_e, \theta_e)) < 0 \quad \Leftrightarrow \quad \rho \theta_e + \sigma(\eta_e + 1)[\Psi - \theta_e \zeta - K_2(\eta_e, \theta_e)] < 0.
\]
Now we search conditions assuring that the non trivial equilibrium \((\eta_e, \theta_e)\) can undergo Turing instability. We recall that a reaction-diffusion system exhibits Turing or diffusion-driven instability, if the homogeneous steady state is stable to small perturbations in the absence of diffusion, but it is unstable to small spatial perturbations when diffusion is present \([7]\). By using standard linear theory (see e.g. \([7]\)), it can be shown that \((\eta_e, \theta_e)\) can undergo Turing instability if the relationships in (12) and (13) are satisfied together with

\[
dJ_{11}^e + J_{22}^e > 0 \quad \text{and} \quad \frac{(dJ_{11}^e + J_{22}^e)^2}{4d} > \det(J(\eta_e, \theta_e)),
\]

where \(J_{ij}^e\) are the entries of the Jacobian matrix (10). In the next section, we will consider a special choice of the functions \(K_1\) and \(K_2\) which is meaningful from the physical point of view and for this case we investigate the spatial patterns arising in model (5).

As customary for electrochemical kinetics controlled by charge-transfer processes, \(K^*_{\text{ADS}}\) and \(K^*_{\text{DES}}\) in equation (2) can be chosen in the following form (see e.g. \([8]\))

\[
K^*_{\text{ADS}} = A \exp(\alpha a + b \theta), \quad K^*_{\text{DES}} = A_{1} \exp(a_{1} \eta + b_{1} \theta)
\]

where \(A, A_{1}, a, a_{1}, b, b_{1}\) are strictly positive parameters. In particular, we analyze the case \(A \neq A_{1}, a \neq a_{1}, b = b_{1}\). The physical-chemistry underlying these assumptions is that surface coverage is far from 50%, and that the cathodic and anodic Tafel slopes are not identical, while the lateral interaction parameter for adsorbates is well defined.

With the previous assumptions, the spatially independent equilibria are given by the trivial equilibrium \(E_1 = (0, \frac{A}{A + A_{1}})\) and the non trivial equilibrium \(E_2 = (\eta_e, \theta_e)\), where \(\eta_e\) and \(\theta_e\) satisfy equation (9). Stability analysis shows that, in the homogeneous case, the trivial equilibrium \(E_1\) is always stable, that is

\[
\det(J(0, \frac{A}{A + A_{1}})) > 0, \quad \text{and} \quad \text{tr}(J(0, \frac{A}{A + A_{1}})) < 0,
\]

and that, even when diffusion is present \((d \neq 0)\), the necessary condition for Turing instability is never satisfied, being \(d J_{11}(E_1) + J_{22}(E_1) < 0\).

On the other hand, by using standard linear theory we show that the non trivial equilibrium \(E_2\), which is more interesting from the physical point of view, can undergo diffusion driven instability.

We consider the special case obtained for \(a_{1} = a + \varepsilon \ln\frac{A}{A_{1}}\) and with \(A\) and \(A_{1}\) such that \(\frac{A}{A_{1}} = \frac{\varepsilon}{2}\). This further assumption boils down to the fact that the exchange current densities and Tafel slopes of metal discharge and electroosorption of ligands are coupled quantum charge-transfer effects \([9]\).

With this parameter choice, the significant equilibrium is given by \(E_2 = (\eta_e, \theta_e) = (\frac{1}{\varepsilon} \frac{\varepsilon}{1 + \varepsilon})\) and

\[
K_1 = A \exp(\alpha a + b \theta), \quad K_2 = A \exp(a_{1} \eta + b_{1} \theta)[1 + \frac{2}{\varepsilon} \exp(\varepsilon \alpha \eta)]
\]

where \(\alpha = \ln(1/2) < 0\). If we set

\[
r_e = \frac{\theta_e}{\eta_e + 1}, \quad p_1 = \frac{\varepsilon}{\varepsilon + 1} A \exp(\alpha a + b \theta), \quad \text{and} \quad p_2 = -\alpha p_1,
\]

we observe that, since \(\alpha < 0\), then \(p_1 > 0\) and \(p_2 > 0\). The set of general conditions (12), (13) and (14) for diffusion-driven instability of \((\eta_e, \theta_e)\) obtained in the previous section, can thus be specialized as
Since these inequalities involve the model parameters, they allow us to locate a region in the parameter space such that $E_2$ is stable to small perturbations in the absence of diffusion, but it can be unstable to small spatial perturbations when the diffusion parameter $d$ is non-zero and greater than a critical value $d_T$. When the other parameters are fixed, $d_T$ can be determined by the third condition in the set of inequalities (19).

In the next section, by numerically solving system (5), we show that interesting spatial patterns arise, that qualitatively match those found in some electrodeposition experiments.

4. Numerical simulations and comparison with experiments
The coupled reaction-diffusion equations (5) have been solved numerically by Matlab [10] using the function pdepe based on the finite-element method. Several simulations have been performed by fixing the starting approximations $\eta_0(\xi)=2\eta_0+c_\eta \cos(\xi)$ and $\theta_0(\xi)=2\theta_0+c_\theta \cos(\xi)$ representing a spatial perturbation of the homogeneous non-trivial equilibrium $E_2$. To outline the destabilizing role of diffusion, $d$ has been considered as a bifurcation parameter whereas all the other parameters have been fixed such that the equilibrium $E_2$ is stable when $d=0$.

The numerical results reported here have been obtained by fixing the parameter values $\rho=40$, $\sigma=2$, $\varepsilon=0.5$, and $a=1$, $b=1$, $A=1$ for the rates defined in equation (15). With this choice, we have $E_2=(2,1/3)$ and the critical value $d_T \approx 74.07$. The initial profile solutions are those defined above with amplitudes: $c_\eta=0.05$, $c_\theta=0.001$. The spatial and temporal intervals considered are $\xi \in [0, 12\pi]$ and $\tau^* \in [0, 20]$, respectively. Figure 1a, shows the long-term behavior of the numerical approximation for the morphology $\eta(\xi, \tau)$ when $d=10$, i.e. $d < d_T$. For this value of the diffusion parameter, the homogeneous equilibrium $E_2$ is still attractive and no spatial pattern is found. By considering the same initial conditions, but a diffusion parameter $d=100$, that is $d > d_T$, the numerical solution in figure 1b shows that the homogeneous equilibrium $E_2$ loses its stability and a spatial pattern appears in the morphology long-term behavior. In particular, we note that the spatial structure presents a periodic behavior alternating zones of electrodeposits with zones of zero growth. In figure 1c, we present a further solution obtained for $d=4000$ and for longer times up to $T=40$. In this case the spatial pattern loses stability and different kinds of inhomogeneous spatial structures appear. Several simulations for very high values of the bifurcation parameter $d$ show a similar behavior. These aspects are subject of ongoing research.

Figure 1. (a) Case $d < d_T$, $d=10$: stable homogeneous long-term behavior of morphology; (b): Case $d > d_T$, $d=100$: diffusion driven (Turing) instability of $E_2$ and the arising of a spatial pattern; (c): Case $d > d_T$, $d=4000$ $T = 40$, the Turing spatial pattern loses stability and new spatial patterns arise.
In our opinion, the above results are interesting because they are able to qualitatively describe some essential features related to electrodeposition experiments for Au-Cu alloys. The Au-Cu alloys considered for our purpose were grown galvanostatically at 2 mA cm\(^{-2}\) onto X-ray amorphous Ni-P (P 9\%\), thickness 25\(\mu\)m) from the following baths: (A) K\text{Au(CN)}\(_2\) 5 gL\(^{-1}\) (as Au), K\text{2Cu(CN)}\(_3\) 25 gL\(^{-1}\) (as Cu), KCN 15 gL\(^{-1}\), pH 12, T 80\(^\circ\)C and (B) the same with added KCN 30 gL\(^{-1}\). The alloys were characterised by SEM (Cambridge Stereoscan 360 SEM, LaB\(_6\) electron source). Pattern formation can be detected for electrodeposits from the baths without added KCN (figure 2a and figure 2b), while a homogeneous alloy film is obtained from the free-CN\(^-\) system (figure 2c).

The diffusion parameter \(D^*_\text{sc}\) in equation (3) can be regarded to scale with the surface fraction free from adsorbed CN\(^-\) and thus, according to the isotherms reported e.g. in [11], \(D^*_\text{sc} \approx \frac{1}{\ln(CN^-)}\). Since \(\theta \ll 1\), one can assume that \(\frac{\partial D^*_\text{sc}}{\partial(CN^-)} \approx 0\); thus, for the two above baths:

\[
\frac{d}{d_y} \approx \frac{\ln(CN^-)}{\ln(CN^-)} > 1.
\]

Therefore, spatial sections of the experiments shown in figure 2a and figure 2b can be described by the driven diffusion instability in figure 1b or figure 1c, while figure 2c can be related to the homogeneous simulated behavior shown in figure 1a.

![Figure 2](image)

Figure 2. (a): SEM micrograph of the electrodeposited alloy exhibiting unstable growth - magnification 50 x; (b) SEM micrograph of the electrodeposited alloy exhibiting unstable growth - magnification 5000 x; (c) SEM micrograph of the electrodeposited alloy exhibiting stable growth - magnification 5000 x.

5. **Concluding remarks**

This paper reports on a mathematical model for morphological pattern formation developing during galvanostatic electrodeposition of Au-Cu alloys from cyanocomplex solutions. As observed by SEM, such patterns tend to develop in baths containing comparatively low free-CN\(^-\) concentrations. This phenomenon has been rationalized in terms of a reaction-diffusion model coupling the dynamics of growing film morphology and adsorbed ligand surface coverage.

We have studied the nonlinear dynamics of the model through Turing instability both from an analytical and numerical points of view. Our results have shown that the variation of the parameter \(d\) related to diffusion can describe qualitatively real experimental situations. Future research on this topic will deal with a version of the model which is two-dimensional in space, in order to describe in a more realistic way more complicated patterns developing during electrodeposition processes (electrodeposit surfaces not isotropic along the substrate plane, e.g. owing to peculiar current density distributions prevailing in the electrodeposition reactor).
References

[1] Bozzini B, Giovannelli and G, Cavallotti P L 1999 *J. Appl. Electrochem.* **29** 685
[2] Bozzini B, Cavallotti and P L, Giovannelli G 2002 *Met. Fin.* **100** 50.
[3] Krischer K 1999 *Modern Aspects of Electrochemistry* **32** 1
[4] Hudson J L and Tsotis T T 1994 *Chem. Eng. Sci.* **49** 1493
[5] Bozzini B, Giovannelli G and Mele C 2007 *Surf. & Coat. Technol.* **201** 4619.
[6] Bozzini B, Sgura I and D'Urzo L 2007 Modelling of morphological control of electrodeposited Cu by adsorption of aminoacids and oligopeptides, in: New Developments in Electrodeposition and Pitting Research, edited by A. El Nemr, Research Signpost Pub., Fort P.O., Trivandrum-695 023, Kerala, India, 2007, in press
[7] Murray J D Mathematical Biology II; Spatial models and biomedical applications, Springer, 3rd Ed, 2002.
[8] Bozzini B and Sgura I 2006 *Jour. Appl. Electrochemistry* **36** 983
[9] Kahn S U M 1988 *J. Phys. Chem* **92** 2541
[10] Matlab 7, Release 14, Reference user's guide.
[11] Rogozhnikov N A and Beck R Y 1997 *J. Electroanal. Chem,* **434** 19.