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Travelling waves in a reaction-diffusion model for electrodeposition

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Abstract

In this paper we consider an analytical and numerical study of a reaction-diffusion system for describing the formation of transition front waves in some electrodeposition (ECD) experiments. Towards this aim, a model accounting for the coupling between morphology and composition of one chemical species adsorbed at the surface of the growing cathode is addressed. Through a phase-space analysis we prove the existence of travelling waves, moving with specific wave speed. The numerical approximation of the PDE system is performed by the Method of Lines (MOL) based on high order space semi-discretization by means of the Extended Central Difference Formulae (D2ECDF) introduced in [1]. First of all, to show the advantage of the proposed schemes, we solve the well-known Fisher scalar equation, focusing on the accurate approximation of the wave profile and of its speed. Hence, we provide numerical simulations for the electrochemical reaction-diffusion system and we show that the results obtained are qualitatively in good agreement with experiments for the electrodeposition of Au–Cu alloys.

Keywords: High order finite difference schemes; Method of Lines; Travelling waves; Fisher equation; Electrochemical modeling

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1. Introduction and the model

Electrodeposition of Au–Cu alloys from cyanocomplex baths containing free cyanide has been shown to exhibit electrokinetic instabilities that can lead to compositional heterogeneity in the electrodeposit bulk [4]. 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 [6]. The technological drawbacks deriving from such instabilities can be efficiently removed by changing the solution chemistry: (i) removing the free-CN^- and (ii) changing the Cu(I)-cyanocomplex for a Cu(II)-EDTA compound [5]. Notwithstanding the technological improvement, a rich dynamic scenario is still attached to the presence of adsorbed CN^- at the growing metal interface [9].

In this paper we consider a general model coupling the surface morphology and CN^- concentration, in order to rationalise the formation of the morphological patterns sometimes developing in electrodeposition (ECD). Some dynamic details will be discussed with model parameter values typically corresponding to the more industrially widespread free-CN^- solutions. 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 [18], corrosion of Cu [15], Fe-group metals [18] and Ag [8]).

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The proposed model reveals a surprisingly rich phenomenology: in [9] theoretical and numerical investigations were performed, showing the initiation of spatial patterns induced by diffusion, i.e. related to the mechanism introduced by Turing in [23]. In this paper, we show the existence of travelling wave solutions, corresponding to transition front waves, sometimes occurring in the experiments.

We present an analytical study of the model, its numerical approximation by accurate space discretization and comparisons between simulations and electrochemical experiments. To the aim of completeness, we now briefly recall the model derivation proposed in [7,9]. First, we stress the following basic assumptions: (i) the electrodeposit surface can be regarded as isotropic in the substrate plane, so that we will consider a 1D model in space (ii) one chemical species adsorbed at the surface of the growing cathode is addressed, so that we deal with a system of two reaction-diffusion equations, one for *the morphology* and one for *the chemistry*.

The equation for the morphological dynamics is:

$$\frac{d\eta}{d\tau} = D_s^* \frac{d^2\eta}{d\xi^2} + S^*, \tag{1}$$

with

$$S^* = \alpha_1 \frac{\eta^2}{1+\eta} - \beta_1 \eta\theta.$$

Here $\eta(\xi, \tau)$ is the dimensionless electrode shape (i.e. the intersection of the electrodeposit surface with a plane normal to the substrate), ξ is the dimensionless space coordinate, τ is the dimensionless time and D_s^* is the dimensionless surface diffusion coefficient of adatoms. In the source term S^*, $\theta(\xi, \tau)$ is the surface coverage with the adsorbed chemical species, the parameters α_1 and β_1 are strictly positive and weight the two terms in S^* accounting for: (i) localization of the ECD process and (ii) effects on the ECD rate of surface chemistry, i.e. the presence of adsorbates at the growing cathode, respectively. 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:

$$\frac{d\theta}{d\tau} = D_{sc}^* \frac{d^2\theta}{d\xi^2} + S_c^*, \tag{2}$$

where D_{sc}^* is the surface diffusion coefficient of $CN^-$and S_c^* is the chemical source term, given by

$$S_c^* = K_{ADS}^*(\eta, \theta)(1-\theta) - K_{DES}^*(\eta, \theta)\theta$$

and defined in terms of K_{ADS}^* and K_{DES}^* which represent the adsorption and desorption rate constants, respectively.

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

$$\begin{cases} \dfrac{\partial\eta}{\partial\tau^*} = \dfrac{\partial^2\eta}{\partial\xi^2} + \rho f(\eta, \theta), \\ \dfrac{\partial\theta}{\partial\tau^*} = d\dfrac{\partial^2\theta}{\partial\xi^2} + \sigma g(\eta, \theta), \end{cases} \tag{3}$$

with

$$f(\eta, \theta) = \frac{\epsilon\eta^2}{1+\eta} - \eta\theta, \quad g(\eta, \theta) = K_{ADS}^*(\eta, \theta) - [K_{ADS}^*(\eta, \theta) + K_{DES}^*(\eta, \theta)]\theta, \tag{4}$$

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

$$\tau^* = D_s^*\tau \quad d = \frac{D_{sc}^*}{D_s^*}, \quad \epsilon = \frac{\alpha_1}{\beta_1}, \quad \sigma = \frac{1}{D_s^*}, \quad \rho = \frac{\beta_1}{D_s^*}.$$