Modulation of dendritic patterns during electrodeposition: A nonlinear phase-field model

Lei Chen [a, b, *], Hao Wei Zhang [a], Lin Yun Liang [a], Zhe Liu [a], Yue Qi [c], Peng Lu [d], James Chen [e], Long-Qing Chen [a]

[a] Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA
[b] Department of Mechanical Engineering, Mississippi State University, MS 39762, USA
[c] Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824, USA
[d] General Motors Research and Development Center, Warren, MI 48090, USA
[e] Division of Engineering, Pennsylvania State University, The Altoona College, Altoona, PA 16601, USA

HIGHLIGHTS

- A nonlinear phase-field model was developed for the dendritic growth.
- The model accounts for the Butler–Volmer electrochemical reaction kinetics.
- The model was verified by the Nernst equation.
- Three different dendritic patterns were discovered.
- A design map was proposed to avoid undesired dendritic patterns.

ARTICLE INFO

ABSTRACT

A nonlinear phase-field model, accounting for the Butler–Volmer electrochemical reaction kinetics, is developed to investigate the dendritic patterns during an electrodeposition process. Using lithium electrodeposition as an example, the proposed model is first verified by comparison with the Nernst equation in a 1D equilibrium system. The nonlinear electrochemical kinetics is also confirmed at non-equilibrium condition. The dendritic patterns are examined as a function of applied voltage and initial electrode surface morphology. A design map is proposed to tailor the electrode surface morphology and the applied voltage to avoid undesired dendritic patterns.

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1. Introduction

Electrodeposition has been widely observed in numbers of applications such as electroplating, electroforming, electrocorrosion and battery charging. However, dendrites characterized as multi-level branching usually occur at the electrode-electrolyte interface during electrodeposition processes if they are not carefully controlled [1–4]. Such dendrites generated far from equilibrium have also fascinated scientists for decades due to their important effects on physical and chemical properties of the electrodeposition systems and the performance of electrochemical devices. For example, Lithium (Li) electrodeposition on a Li-metal electrode often takes place in high capacity Li–O$_2$ (lithium-oxygen) and Li–S (lithium-sulfur) batteries [5–7]. These newly developed high capacity lithium batteries, however, still suffer from unexpectedly failure by short-circuiting via the dendrites that grow even across electrodes upon recharging [8].

The important role of dendrites in electrodeposition systems has stimulated numerous efforts on modulating the dendritic patterns. These works were mostly based on the modification of electrode materials [9], electrode surface morphology [10,11], solvent and electrolyte composition [12,13] and operational current density or voltage [14,15]. The basic idea behind these treatments is

* Corresponding author. Department of Mechanical Engineering, Mississippi State University, MS 39762, USA.
E-mail addresses: luc28@psu.edu, chen@me.msstate.edu (L. Chen).

to control the kinetics and the instability of interface that are intricately combined.

The present paper aims to formulate a thermodynamically consistent model to predict the dendritic patterns during an electrochemical process using Li-electrodepostion as an example. The first attempt to model the electrochemical dendrite growth was made by Monroe and Newman [16]. They presented a comprehensive mathematical model for temporal evolution of dendrite tip height and growth velocity in Li-polymer cells. Recently, Akolkar [17,18] extended this model by incorporating a concentration-dependent diffusion coefficient, with application to liquid electrolytes. More recently, Aryanfar et al. [19] proposed a coarse-grained Monte Carlo calculation to uncover the Li-dendrite mechanism, by dealing explicitly with Li$^+$ migration in time-dependent non-uniform electric fields. However, they did not explicitly simulate the temporal evolution of electrode-electrolyte interface.

Phase-field method has been applied to a vast range of phenomena in materials processes, e.g., solidification, solid-state phase transformation, recrystallization, and grain growth [20,21]. Phase-field method is formulated based on the theory of irreversible thermodynamics, and is advantageous in addressing the time-dependent evolving morphologies process, which is hard to implement in traditional sharp-interface model [16]. The early attempt along this line was made by Guyer et al. [22,23] who developed a 1-D phase-field model to investigate the equilibrium state and kinetic behavior of electrochemistry. Later, Okajima et al. [24] simulated the 2-D electrodeposition process by linking a Cahn—Hilliard equation with a Butler—Volmer type equation. Recently, Liang et al. [25] proposed a 1-D formulation that captures the Butler—Volmer kinetics of electrodeposition. More recently Ely et al. [26] conducted a phase-field study on the kinetics of Li electrodeposits by extending the asymptotic analysis of the phase field theory. However, all these models either are assuming a linear electrochemical reaction kinetics that breaks down when the system is highly out of equilibrium [25,27], e.g., under high charging voltage, or do not capture an apparent dendritic growth of electrodeposits, or are not derived within a thermodynamic framework based on the electrochemical potential, thus leading to the loss of thermodynamic consistency.

In this article, we solve these discrepancies by formulating a *thermodynamically consistent phase-field model*. In the model, the phase-field evolves nonlinearly with the variational electrochemical overpotential that is a function of electrostatic potential and ion concentration. Such treatment allows us to capture the Butler—Volmer electrochemical reaction kinetics naturally. The mass and current conservation equations are further formulated to solve the ion transport and the local electrostatic potential variation, respectively. Anisotropic surface energy at the interface, evidenced by first principles calculations [28], is incorporated in the model. The present phase-field model is generally applicable to any non-equilibrium electrodeposition system exhibiting the dendritic growth.

2. Phase-field model

Consider a simple and general electrodeposition, M^{n+} cations in a binary dilute electrolyte M^{n+}A^{n-} react with electrons e$^-$ at the surface of the electrode, and are reduced to M-atom. This process can be illustrated by Ref. M^{n+} + ne$^-$ → M. For simplicity, we assume a dilute electrolyte solution. Further, the electrons are assumed to be always supplied on the surface of the electrode. The shape of protuberant at the electrode surface represents the initial morphology of electrode-electrolyte interface as shown in Fig. 1. As detailed in Appendix A, the Gibbs free energy of the system can be
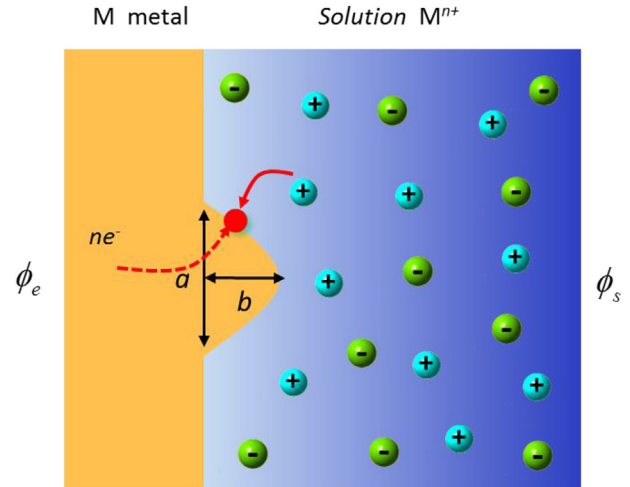

Fig. 1. Schematic-diagram showing a representative electrodeposition system. A protuberant of size $a \times b$ is present on the electrode surface.

expressed by

$$G = \int_V \left[f_{ch}(\overrightarrow{c}) + f_{grad}(\nabla \overrightarrow{c}) + f_{elec}(\overrightarrow{c}, \phi) \right] dV, \tag{1}$$

where $\overrightarrow{c} = \{c, c_+, c_-\}$ is the set of concentrations for M-atom, M^{n+} cation and A^{n-} anion respectively, $f_{ch}(\overrightarrow{c})$ is the Helmholtz free energy density and $f_{grad} = 1/2 \nabla \overrightarrow{c} \cdot \kappa \nabla \overrightarrow{c}$ is the gradient energy density associated with surface energy. The surface energy anisotropy, i.e., its dependence on the orientation of the electrode-electrolyte interface, is introduced in the system by expanding the gradient coefficient as $\kappa(\theta) = \kappa_0[1 + \delta cos(\omega\theta)]$, where δ and ω are the strength and mode of the anisotropy, κ_0 is related to the surface energy γ, θ is the angle between the normal vector of interface and the reference axis. $\overrightarrow{\tilde{c}}$ is the set of dimensionless concentrations as $\{\tilde{c} = c/c_s, \ \tilde{c}_+ = c_+/c_0, \ \tilde{c}_- = c_-/c_0\}$, where c_s is the site density of M-metal and c_0 the standard bulk concentration of electrolyte solution. $f_{elec} = \rho_e \phi$ is the electrostatic energy density where ϕ is the electrostatic potential, and ρ_e is the charge density that is expressed as $\rho_e = F \sum z_i c_i$ where z_i is the valence of species i and F is Faraday's constant. A continuous phase-field variable, ξ, with a physical correspondence to the dimensionless concentration of M-atom, as $\xi = \tilde{c}$, is introduced to separate the metal and the electrolyte solution during the interface migration. The value of ξ varies continuously from 1 to 0 in the interfacial region, i.e., corresponding to a diffuse-interface description with a finite thickness. The free energy density is then given by

$$f_{ch}(\overrightarrow{c}) = g(\tilde{c}) + f_{ion}(\tilde{c}_+, \tilde{c}_-) + \sum_i c_i \mu_i^{\Theta}, \tag{2}$$

where $g(\tilde{c}) = W\tilde{c}^2(1 - \tilde{c})^2 = W\xi^2(1 - \xi)^2$ is an arbitrary double well function to describe the two equilibrium states for the electrode ($\tilde{c} = 1$) and the electrolyte ($\tilde{c} = 0$) respectively. $W/16$ represents the barrier height. For a dilute electrolyte, $f_{ion} = c_0 RT(\tilde{c}_+ \ln\tilde{c}_+ + \tilde{c}_- \ln\tilde{c}_-)$, without phase separation. The last term in Eq. (2) stands for the free energy density at the standard (reference) state, with μ_i^{Θ} defined as the reference chemical potential of species i, which could be M^{n+} cations, or electrons e$^-$, or M-atom.

Having these definitions, the electrochemical reaction rate, R_e, takes the variational form of