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Nonlinear phase-field model for electrode-electrolyte interface evolution

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A nonlinear phase-field model is proposed for modeling microstructure evolution during highly nonequilibrium processes. We consider electrochemical reactions at electrode-electrolyte interfaces leading to electroplating and electrode-electrolyte interface evolution. In contrast to all existing phase-field models, the rate of temporal phase-field evolution and thus the interface motion in the current model is considered nonlinear with respect to the thermodynamic driving force. It produces Butler-Volmer-type electrochemical kinetics for the dependence of interfacial velocity on the overpotential at the sharp-interface limit. At the low overpotential it recovers the conventional Allen-Cahn phase-field equation. This model is generally applicable to many other highly nonequilibrium processes where linear kinetics breaks down.

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I. INTRODUCTION

The phase-field method is a versatile mesoscale computational approach that has been successfully applied to modeling temporal and spatial microstructure evolution of materials undergoing a wide variety of processes such as phase transformations, deformation, and particle coarsening [1–5]. However, all existing phase-field models are based on linear kinetics, i.e., the rate of change of a phase field is assumed to be linearly proportional to the thermodynamic driving force, which is, in principle, only valid for systems close to equilibrium. For example, the diffusion flux of an atomic species is assumed to be linearly proportional to the local chemical potential gradient of the species, and the rate of changes of a nonconserved phase order parameter field is assumed to be linearly proportional to the variational derivative of the total free energy with respect to the phase order parameter. In reality, however, many material microstructure evolution processes take place in systems highly out of equilibrium. Examples include an undercooled liquid well below the melting temperature, phase transformations under a strong external force, electrochemical reactions under a large overpotential, and many others. In this letter, we present a nonlinear phase-field formulation that is applicable not only to systems near equilibrium but also to systems that are highly out of equilibrium or the thermodynamic driving force is large, using electrode-electrolyte interface evolution arising from an electrode reaction, e.g., electrode plating, as an example.

Electrochemical reactions are ubiquitous, taking place in batteries and fuel cells or during corrosion, etc. [6–13]. Many electrochemical processes such as electrodeposition and dissolution lead to electrode-electrolyte interface evolution including interface shape and topology changes under the chemical and electrical driving forces.

Existing mathematical modeling of electrochemical processes [14] involves the solutions to coupled ionic-electronic diffusion equations within the electrolyte or electrode with the electrochemical reactions at the electrode-electrolyte interface specified as boundary conditions. The positions of electrode-electrolyte interfaces are assumed to be fixed, and thus the conventional mathematical models [15–17] are not suitable for modeling phase evolutions and morphological changes during electrochemical reactions leading to the electrode-electrolyte interface motion such as Li plating and dendrite formation in Li-ion batteries.

Existing phase-field models of Li intercalation into and out of an intercalation compound such as $LiFePO_4$ describe diffusion and the phase separation process using the Cahn-Hilliard equation in which the flux is assumed to be linearly proportional to the chemical potential gradient, i.e., based on linear kinetics. The electrode reaction rate, which is assumed to be exponentially dependent on the variation of free energy with respect to lithium concentration, i.e., the nonlinear electrode reaction kinetics, is specified as the boundary condition at the fixed electrode-electrolyte interface [18–23].

The present paper is focused on the nonlinear electrode-electrolyte interface evolution kinetics driven by the overpotential for the electrode reaction. The first attempt to model electrodeposition processes using the phase-field method was made by Guyer *et al.* [8,9]. It involves the solutions to a set of coupled diffusion equations for ion and electron transport, the Poisson equation for electrostatics, and an Allen-Cahn kinetics equation for the electrode-electrolyte interface evolution, i.e., assuming linear kinetics. Despite employing a linear phase-field equation, Guyer *et al.* obtained the nonlinear Butler-Volmer type of kinetics. In this case, the nonlinear kinetics arises from the space charge double layer near the electrode-electrolyte interface and its response to overpotential rather than the nonlinear electrode reaction itself. In an attempt to mimic Butler-Volmer electrode reaction kinetics, Okajima *et al.* [24] assumed an exponential dependence of diffusional mobility on the overpotential for electrode reactions while the rate of electroplating is still linearly proportional to the thermodynamic driving force.

In this work, we propose a nonlinear phase-field model to describe the electrode-electrolyte interface evolution driven by the overpotentials that exist in electrochemical reactions. The model reproduces the Butler-Volmer type of electrochemical kinetics at the sharp-interface limit of the diffuse-interface phase-field model. The results are compared to the linear

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Allen-Cahn equation and classical sharp-interface Butler-Volmer equation results.

II. MODEL FORMULATION

To discuss our nonlinear phase-field model which is applicable to electrode-electrolyte interface motion under highly nonequilibrium electrode reactions, we consider a simple, general electrode reaction,

$$M^{z+} + ze^- \leftrightarrow M, \tag{1}$$

where the ions M^{z+} in the electrolyte solution react with electrons e^- in the electrode to produce the electrode M atoms. The thermodynamic driving force is given by

$$\Delta G = \mu_M - \mu_{M^{z+}} - z\mu_{e^-}, \tag{2}$$

where μ represents the electrochemical potential of a species. To simplify the discussion, we assume that the electrode is a pure metal under a voltage ϕ, while the voltage in the electrolyte is assumed to be zero, and hence

$$\Delta G = \Delta G^{\mathrm{o}} + zF\phi - RT\ln a_{M^{z+}}, \tag{3}$$

where ΔG^{o} is the standard free energy change for the electrode reaction, F is the Faraday constant, and $a_{M^{z+}}$ is the activity of M^{z+} in the electrolyte, which, in general, depends on temperature and on the concentrations of other ions. Since we are focused on the electrode kinetics, we assume that $a_{M^{z+}}$ is a constant and does not evolve with time. In this case, there will be no overpotential drop for the charge transport in the electrolyte and electrode, and there is no space charge double layer, i.e., the entire overpotential drop is associated with the electrode reaction. At equilibrium,

$$\Delta G^{\mathrm{o}} + zF\phi^{\mathrm{o}} - RT\ln a_{M^{z+}} = 0, \tag{4}$$

where ϕ^{o} is the equilibrium potential for the reaction at a given temperature and a given ion concentration in the electrolyte. Therefore, by subtracting Eq. (4) from Eq. (3) the thermodynamic driving force can also be expressed as

$$\Delta G = zF(\phi - \phi^{\mathrm{o}}) = zF\eta, \tag{5}$$

where η is the overpotential. If $\eta < 0$, the electrolyte is reduced; whereas if $\eta > 0$, the electrode is being oxidized. The change of energy landscape along the reaction coordinate with the overpotential is schematically shown in Fig. 1. The energy landscape for $\eta = 0$ is represented by curve I (dashed line above) while for $\eta < 0$ it is changed to curve II (solid line). The energy barrier is shifted by $\alpha zF\eta$ for the forward reaction and $\beta zF\eta$ for the backward reaction.

To model the interface migration, we introduce a phase-field variable $\xi(r,t)$ to distinguish the electrolyte and the electrode. The value of $\xi(r,t)$ varies continuously from 1 to 0 in the interfacial region, i.e., a diffuse-interface description with a finite thickness [1].

We employ a simple double-well free energy function $g(\xi)$ to describe the two equilibrium states for the electrode ($\xi = 1$) and electrolyte ($\xi = 0$) under zero overpotential,

$$g(\xi) = W\xi^2(\xi - 1)^2, \tag{6}$$

where $W/16$ represents the potential height of the double-well potential at $\xi = 0.5$. Under a driving force, ΔG, we use $f(\xi)$ to represent the local free energy density of the electrode and electrolyte two-phase mixture,

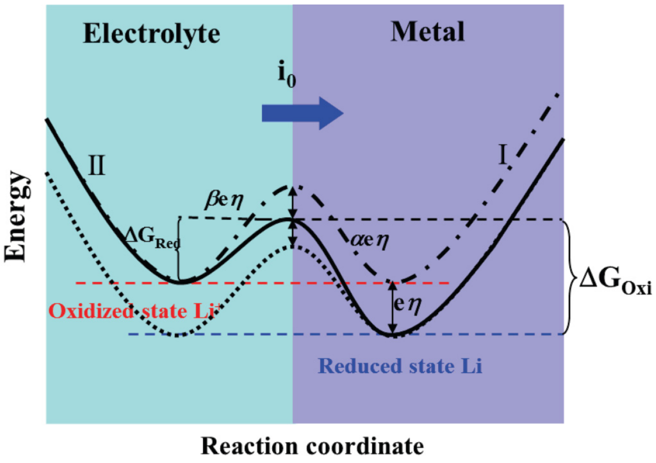

FIG. 1. (Color online) Energy landscape vs reaction coordinate at equilibrium (curve I for $\eta = 0$) and during reduction reactions (curve II for $\eta < 0$).

$$f(\xi,\eta) = h(\xi)\Delta G + g(\xi) = h(\xi)zF\eta + g(\xi), \tag{7}$$

where $h(\xi) = \xi^3(6\xi^2 - 15\xi + 10)$ is an interpolating function.

The total free energy of an inhomogeneous system is then given by

$$F = \frac{1}{v_m}\int_V \left[f(\xi,\eta) + \frac{1}{2}\kappa(\nabla\xi)^2 \right] dV, \tag{8}$$

where κ is the gradient energy coefficient.

Rather than assuming a linear kinetics in which the rate of a phase transformation or an interface motion is linearly proportional to the thermodynamic driving force, one natural nonlinear model to describe the temporal and spatial evolution of the phase-field variable, motivated by classical rate theory of chemical reaction kinetics, is

$$\frac{\partial\xi}{\partial t} = -RTk_n\left[\exp\left(\frac{\alpha\,\delta F/\delta\xi}{RT}\right) - \exp\left(-\frac{\beta\delta F/\delta\xi}{RT}\right)\right], \tag{9}$$

where t is time, R is the gas constant, T is temperature, k_n is a reaction rate constant, and α and β are constants satisfying the relation that $\alpha + \beta = 1.0$. Under a small driving force, the equation is reduced to the conventional Allen-Cahn equation. Based on the sharp-interface limit of Eq. (9) using the asymptotic analysis method and actual numerical simulations, it is shown that the kinetics described by Eq. (9) is sensitive to the choice of the interpolating function, $h(\xi)$. Furthermore, its sharp-interface limit lacks a simple analytical form, and hence it is difficult to map the parameters to the conventional models for electrode kinetics. Therefore, we seek a simplified form of nonlinear equation. We consider the fact that the driving force for interface migration consists of two contributions: interfacial free energy reduction and the electrode reaction affinity. While the driving force for the electrode reactions can be much larger than the thermal energy depending on the overpotential, the driving force from interfacial energy or curvature reduction relative to thermal energy (k_bT or RT) is usually small. Therefore, we assume that the interface migration velocity is linearly proportional to the interfacial free energy reduction but nonlinear with respect to the overpotential. We assume that the nonlinearity of electrode reaction rate dependence on the driving force follows the usual kinetic rate theory for chemical reactions, i.e., the reaction rate is exponentially dependent on the activation energy for both forward and backward reactions. A simplified nonlinear model to describe the temporal and spatial evolution of the phase-field variable can be written as

$$\frac{\partial \xi(r,t)}{\partial t} = -L_\sigma \frac{\delta \sum}{\delta \xi(r,t)} - L_\eta RT h'(\xi)\left[\exp\left(\frac{\alpha \Delta G}{RT}\right) - \exp\left(-\frac{\beta \Delta G}{RT}\right)\right], \tag{10}$$

where L_σ is the interface mobility, L_η is a reaction rate constant, and $\sum$ is the total interfacial free energy of an inhomogeneous system consisting of a mixture of electrode and electrolyte given by

$$\sum = \int_V \left[g(\xi) + \frac{1}{2}\kappa(\nabla\xi)^2\right] dV. \tag{11}$$

The first term on the right-hand side of Eq. (10), $\delta \sum / \delta\xi = g'(\xi) - \kappa\nabla^2\xi$, is the contribution of interface energy to the phase-field parameter evolution. The second term on the right-hand side of Eq. (10) is the contribution due to the electrode reaction. The second term can also be viewed as an additional source term to the diffusion-reaction equation, $\partial\xi/\partial t = -L_\sigma[g'(\xi) - \kappa\nabla^2\xi]$. For a flat interface or a one-dimensional model, the electrode reaction source term is the only contribution which leads to the interface motion since there is no interfacial energy change. In the second term of Eq. (10), the function $h'(\xi) = 30\xi^2(1-\xi)^2$ limits the electrode reaction to take place at the electrode-electrolyte interface. Other forms of $h'(\xi)$ such as $h'(\xi) = 6\xi(1-\xi)$ can also be used, but our test results show that the reaction kinetics is little affected by the choice of the $h(\xi)$-function [2]. At low overpotential, linearization of Eq. (10) immediately recovers the well-known Allen-Cahn equation [1],

$$\frac{\partial\xi}{\partial t} = -M\frac{\delta F}{\delta \xi}, \tag{12}$$

where $F = \int_V [g(\xi) + h(\xi)\Delta G + 1/2\kappa(\nabla\xi)^2] dV$, and $M = L_\sigma = RTL_\eta$.

To obtain an analytical solution of the interfacial velocity, v, under the sharp-interface limit of the nonlinear phase-field model, we first multiplied Eq. (10) by $\partial\xi/\partial u$ and then integrated over $-\infty < u < \infty$, where u is a coordinate normal to the interface [25],

$$v = -\frac{\kappa L_\eta RT}{\sigma}\left[\exp\left(\frac{\alpha z F \eta}{RT}\right) - \exp\left(-\frac{\beta z F\eta}{RT}\right)\right], \tag{13}$$

in which σ is the interfacial energy per unit area between electrode and electrolyte. Equation (13) shows that the interface velocity varies nonlinearly with respect to the overpotential across the interface, which has a similar form as the well-known Butler-Volmer equation for the electrode reaction kinetics. Under low overpotential, linearization of Eq. (13) leads to

$$v = -\frac{\kappa L_\eta z F}{\sigma}\eta, \tag{14}$$

which is the sharp-interface limit of the Allen-Cahn equation. Under a high positive overpotential, the forward electrode reaction, the reduction reaction, dominates over the reverse reaction, and the sharp-interface limit of the nonlinear phase-field equation reduces to the Tafel equation [14],

$$v = -\frac{\kappa L_\eta RT}{\sigma}\exp\left(\frac{\alpha z F \eta}{RT}\right). \tag{15}$$

Similarly, under a high negative overpotential, the reverse reaction, the oxidation reaction, dominates.

III. NUMERICAL RESULTS AND DISCUSSION

To numerically demonstrate the electrode reaction and thus the interface migration velocity of the electrode-electrolyte interface, we employ a one-dimensional model. We start with a phase parameter profile ξ which is equal to 1 in the electrode and 0 in the electrolyte, and it changes abruptly at the phase boundary (Fig. 2). We employ the finite difference method to solve the phase-field equation [Eq. (10)]. The dimensionless parameters used for the calculations are as follows: grid size $\Delta x = 0.001$, number of grid points = 20 000, double-well potential height $W = 100.0$, gradient coefficient $\kappa = 0.0009$, mobility $L_\sigma = 0.1$, valence of $M^{z+}z = 1$, time step

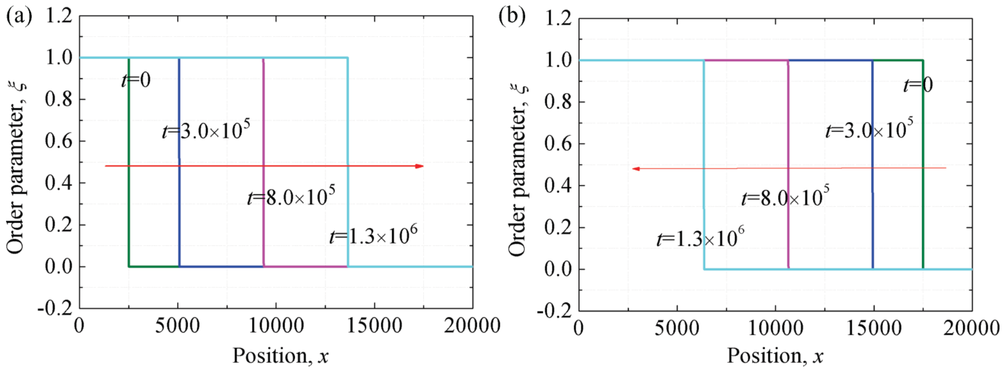

FIG. 2. (Color online) Phase order parameters evolve with time: (a) reduction reaction at overpotential $\eta = 0.1$ V; (b) oxidation reaction at overpotential $\eta = -0.1$ V.

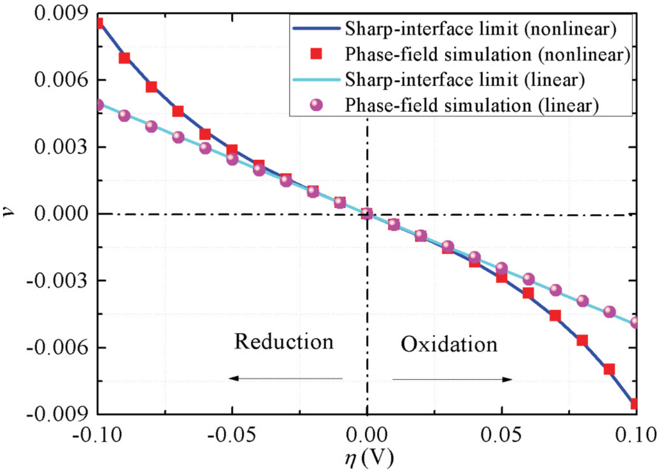

FIG. 3. (Color online) Comparison of interface kinetics from the nonlinear phase-field equation, Allen-Cahn equation, and the corresponding sharp-interface limits.

$\Delta t = 0.001$, symmetry factors $\alpha = \beta = 0.5$, and overpotential $-0.10V \leqslant \eta \leqslant 0.10V$ (positive sign for oxidation and negative sign for reduction).

The phase order parameter develops a diffuse-interface profile across the electrode-electrolyte phase boundary after only a few time steps. Figure 2 shows the phase order parameter evolution with time for both reduction (overpotential less than 0) and oxidation (overpotential larger than 0). The appearance of sharpness in the phase order parameter changes across the interface is due to the large scale for the simulation cell compared to the interfacial thickness. For the reduction case, the electrode grows while it shrinks under a positive overpotential. We determine the interface velocity for a given potential from the interface position as a function of time.

The interface velocities numerically computed from both the nonlinear phase-field equation [Eq. (10)] and the classical Allen-Cahn equation [Eq. (12)] are compared to the analytical solutions from the corresponding sharp-interface limits [Eq. (13)] and [Eq. (14)] at different overpotentials in Fig. 3. The phase-field simulation results agree well with the analytical sharp-interface limit results for both the linear and the nonlinear cases. For the Allen-Cahn equation, the interface migration velocity is linearly proportional to the driving force (overpotential). The nonlinear phase-field model is very close to the Allen-Cahn equation at lower overpotentials, but it exhibits strong nonlinearity at higher overpotentials. The discrepancy between the nonlinear phase-field model and the Allen-Cahn equation increases with overpotential as expected. The results indicate that the existing phase-field model based on the Allen-Cahn equation is valid only at small driving forces, and hence highly nonequilibrium processes such as electrochemical reactions at high overpotentials require nonlinear descriptions.

For an electrochemical reaction, Butler-Volmer equation [14] describing the current across the electrode-electrolyte interface is given by

$$i_n = i_0\left[\exp\left(\alpha\frac{F\eta}{RT}\right) - \exp\left(-\beta\frac{F\eta}{RT}\right)\right], \qquad (16)$$

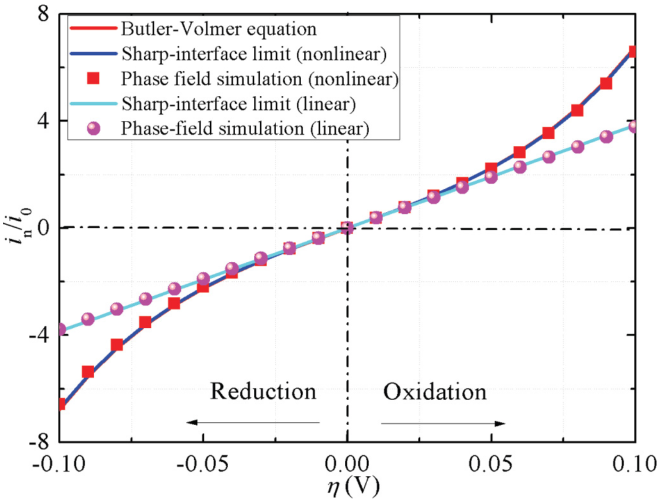

FIG. 4. (Color online) Comparison of the nonlinear phase-field model and Allen-Cahn equation with Butler-Volmer kinetics. The red line representing the Butler-Volmer equation overlaps with the blue line representing the sharp-interface limit of the nonlinear phase-field model.

where the exchange current density i_0 is the value of the current density at zero net current under an equilibrium condition. For migrating interfaces, the deposition or dissolution rate of the metal electrode M is directly related to the current flow across the electrolyte-electrode interface according to Faraday's law; *thus* the current density i_n during the electrochemical reaction can be related to the interface velocity. Simply multiplying the interface velocity [Eq. (13)] by the charge density Q gives the current flow associated with the interface migration. We converted the interface velocity in Fig. 3 to current flow (i_n/i_0) for both linear and nonlinear phase-field models, and compared the results with the current flow computed from the Butler-Volmer equation (red line) in Fig. 4. It is easy to see that the behavior of current flow obtained from interface velocity is essentially the same as the Butler-Volmer kinetics for current flow while the Allen-Cahn equation leads to linear kinetics.

Figure 5 shows the effect of symmetry factors on the reaction current. The dots represent the Butler-Volmer

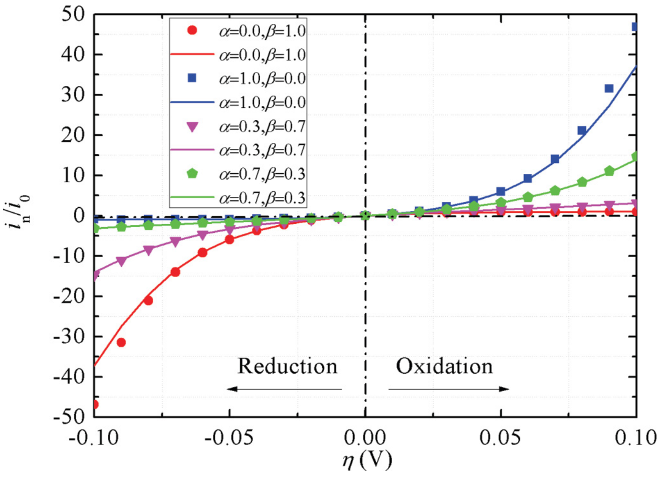

FIG. 5. (Color online) Comparison of the nonlinear phase-field model with Butler-Volmer kinetics under different symmetry factors.

equation and lines denote the results based on the interface migration velocity computed from phase-field simulations. The symmetry factors in Fig. 4, $\alpha = 0.3$ and $\beta = 0.7$, and $\alpha = 0$ and $\beta = 1.0$, lead to large oxidation current while the case of $\alpha = 0.7$ and $\beta = 0.3$ and the limiting case $\alpha = 1.0$ and $\beta = 0$ produce large reduction current. The phase-field simulation results reproduce the Butler-Volmer kinetics for different symmetry factors.

IV. CONCLUSIONS

We developed a nonlinear phase-field model for predicting interface motion and microstructure evolution involving highly nonequilibrium processes. Linearization of the nonlinear phase-field model recovers the conventional Allen-Cahn equation broadly used in essentially in all existing phase-field simulations. Its application to the electrode reactions leads to the Butler-Volmer kinetics of electrode-electrolyte interface migration during both oxidation and reduction. This work is an important step to demonstrate the validity through comparing with the classical sharp-interface Butler-Volmer kinetics.

The nonlinear phase-field model can be extended to many other complex electrochemical processes. For example, it can be coupled with electronic-ionic diffusion equations to predict the coupled electron-diffusion transport processes associated with electrode reactions under applied voltages such as the electrodeposition of metal from metal melt solution, uranium shape changes on the solid cathode in electrorefining processes, and lithium plating at the anode in lithium ion batteries. By coupling of the electrode reaction model with a heat conduction equation or an elasticity equation, it can be used to simulate the thermal or stress effects on the electrochemical reaction processes and electrode-electrolyte interface evolution.

Although the numerical simulations in this work were performed in one dimension, the model is equally applicable to two or three dimensions allowing complex morphologies of the electrode-electrolyte interface structures and their evolutions. In fact, we already coupled this nonlinear phase-field equation with the ion diffusion equation and Poisson's equation and demonstrated the possibility of lithium metal deposit growth and dendrite formation in lithium ion batteries. This nonlinear phase-field model is also applicable to many other general diffusion-reaction processes such as phase transformations under highly nonequilibrium conditions.

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[1] L.-Q. Chen, Annu. Rev. Mater. Res. **32**, 113 (2002).

[2] W. J. Boettinger, J. A. Warren, C. Beckermann, and A. Karma, Annu. Rev. Mater. Res. **32**, 163 (2002).

[3] N. Moelans, B. Blanpain, and P. Wollants, Comput. Coupling Phase Diagrams Thermochem. **32**, 268 (2008).

[4] I. Singer-Loginova and H. M. Singer, Rep. Prog. Phys. **71**, 106501 (2008).

[5] I. Steinbach, Modell. Simul. Mater. Sci. Eng. **17**, 073001 (2009).

[6] P. Córdoba-Torres, Phys. Rev. B **75**, 115405 (2007).

[7] D. Josell, D. Wheeler, W. H. Huber, and T. P. Moffat, Phys. Rev. Lett. **87**, 016102 (2001).

[8] J. E. Guyer, W. J. Boettinger, J. A. Warren, and G. B. McFadden, Phys. Rev. E **69**, 021603 (2004).

[9] J. E. Guyer, W. J. Boettinger, J. A. Warren, and G. B. McFadden, Phys. Rev. E **69**, 021604 (2004).

[10] M.-O. Bernard, M. Plapp, and J.-F. Gouyet, Phys. Rev. E **68**, 011604 (2003).

[11] D. Barkey, F. Oberholtzer, and Q. Wu, Phys. Rev. Lett. **75**, 2980 (1995).

[12] V. P. Zhdanov, Phys. Rev. E **67**, 042601 (2003).

[13] J. R. Melrose, D. B. Hibbert, and R. C. Ball, Phys. Rev. Lett. **65**, 3009 (1990).

[14] J. Newman and K. E. Thomas-Alyea, *Electrochemistry System* (John Wiley & Sons, Inc., Hoboken, NJ, 2004).

[15] C. Monroe and J. Newman, J. Electrochem. Soc. **150**, A1377 (2003).

[16] M. Tang, P. Albertus, and J. Newman, J. Electrochem. Soc. **156**, A390 (2009).

[17] A. M. Colclasure and R. J. Kee, Electrochim. Acta **55**, 8960 (2010).

[18] B. C. Han, A. Van der Ven, D. Morgan, and G. Ceder, Electrochim. Acta **49**, 4691 (2004).

[19] G. K. Singh, G. Ceder, and M. Z. Bazant, Electrochim. Acta **53**, 7599 (2008).

[20] D. Burch and M. Z. Bazant, Nano Lett. **9**, 3795 (2009).

[21] P. Bai, D. A. Cogswell, and M. Z. Bazant, Nano Lett. **11**, 4890 (2011).

[22] M. Tang, J. F. Belak, and M. R. Dorr, J. Phys. Chem. C **115**, 4922 (2011).

[23] D. A. Cogswell and M. Z. Bazant, ACS Nano **6**, 2215 (2012).

[24] Y. Okajima, Y. Shibuta, and T. Suzuki, Comput. Mater. Sci. **50**, 118 (2010).

[25] K. R. Elder, M. Grant, N. Provatas, and J. M. Kosterlitz, Phys. Rev. E **64**, 021604 (2001).