A 1-D Phase Field Crystal Model for Li-ion Battery Intercalation with Lattice Volume Changes

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A one-dimensional Cahn-Hilliard phase field crystal (CH-PFC) model is formulated based on lattice changes and volume changes based on the renormalization group. The model is tested for a lithium iron phosphate model to indicate that the periodicity and the volume changes are reproduced, and the effects of the lattice changes can also be seen in the concentration solution for the free energy. Future models will be used to model volume changes and lattice changes in nickel rich materials.

I. INTRODUCTION

Lithium ion batteries have been developed and commercialized heavily as energy storage devices because of their light weight and ease of transportation [1]. Despite their popularity, many unanswered questions remain from the complex scale of kinetics and transport in these systems, including degradation during user application and temperature effects [2]. Phase separation in lithium ion batteries has been observed experimentally as voltage plateaus during cycling, as well as directly in single particle experiments in lithium iron phosphate (LFP) and in voltage oscillations in lithium titanium oxide (LTO) [3–6]. Phase separating behavior in how electrodes fill has been found to have significant effects on the voltage curves, causing voltage plateaus and instability regions in batteries that are impossible to model with a simple solid solution model. It can affect lithium plating in graphite electrodes, which can lead to short circuiting and fire hazards. The inclusion of phase separation in battery models is important for battery stability and safety in porous electrode theory because it considers the heterogeneity of mass transport.

Lattice changes often happen when phase transitions happen in the system. Volume changes in these systems are inherently connected to changed in the host system lattice. These specifically have been observed in Li-ion intercalation, causing volume expansion, which begin by causing fracture for cathode materials, but can affect macroscopic properties such as porosity, active area, and particle shape for materials such as graphite, which experience up to 10% volume change during (de)intercalation [7, 8]. Materials such as silicon can even change up to 100% in volume during cycling, which is currently a barrier to the use of silicon electrodes in commercial scale batteries. Lattice collapse at deep depth of discharge for nickel rich cathode materials have also been observed [9, 10].

Phase separating behavior are in general modeled with a Cahn-Hilliard/Landau Ginzburg model, and has successfully been used to explain hysteresis, voltage oscillations, and other behavior in batteries [5, 11]. The fundamental connection between lattice changes and volume changes in these systems has been explored by combining a Cahn-Hilliard diffusion model with a phase field crystal model (CH-PFC) to model the peak density field changes of the system [12, 13], and been used to study grain boundary effects 2-D lattice changes in lithium iron phosphate (LFP) [14] and lithium manganese oxide (LMO) [15] by a CH-PFC method first originally used by Elder et al. [13]. The CH-PFC method in two dimensions, though successfully describing the equilibrium phases and dynamics of both materials well, is computationally expensive and cannot be incorporated into any larger scale battery models. One-dimensional battery models are usually used for larger scale porous electrode/particle scale simulations [16, 17]. Thus, we derive a one-dimensional CH-PFC model and use lithium iron phosphate as an example to be integrated into future porous electrode simulations to study the coupling of diffusion and lattice changes. A one-dimensional CH-PFC model provides a framework to study the fundamental coupling of volume changes, lattice changes, and free energy changes in the system.

II. THEORY

The free energy of an intercalation system can be formulated as follows, using the assumption that the total volume of the system is V at the current (deformed) state, where the original volume of the system is V_0. The volume elements of the equation are modeled using the "deformed" volumes to conserve the number of volume elements. Lattice deformations of the system cause a volume change to the scale of $\alpha\beta = V/V_0$, which can be quite large (up to 30%) for materials such as nickel manganese cobalt when experiencing lattice collapse and even higher for silicon (up to 400%) [9, 18, 19]. For most other materials, volume changes are usually within 10%. V_0 and N_0 both indicate the original volume/concentration of the intercalation material. α and β are defined as the length changes of the lattice parameters. The changes of "distance" at this scale require us to not only reformulate the free energy by a simple scaling of the free energy, but also

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requires a change of the parameters, which are necessary for even non phase-separating materials.

Starting for the Landau-Ginzburg free energy functional for a set of sets which can be empty or filled with probability c and $1-c$ [11], we obtain

$$F_{CH} = \int_V \left(\frac{t}{2}(c^2 + \Omega c(1-c) + uc^4 + \frac{K}{2}(\nabla c)^2 + ...) \right) dV. \tag{1}$$

A volume transformation of $\nu = V_0/V = c/c_0$ gives

$$\tilde{F}_{CH} = \int_{V_0} \left(\frac{\tilde{t}}{2} c^2 + \tilde{\Omega} c(1-c) + \tilde{u} c^4 + \frac{\tilde{K}}{2}(\nabla c)^2 + ... \right) dV_0, \tag{2}$$

with the rescaled variables $\tilde{t} = \nu t$, $\tilde{\Omega} = \nu \Omega$, $\tilde{u} = \nu^3 u$, and $\tilde{K} = \nu K$ different from the normal Landau-Ginzburg renormalization solution since the volume is also rescaled as well. It is seen that the higher order terms are more strongly affected by the volume changes. However, instead of changing the parameters in the following problem, we include the volume effects explicitly to simplify calculations.

In this problem, accounting for the reference frame requires us to be very careful in deciding our frame of reference for the volume. To keep finite volume simulations simple, we use the modified reference frame V to define the system, and all subscripts $_0$ are the original reference frame.

Here, we start with the definition of the entropy

$$S = -k_B \left(Nc \ln Nc + N(1-c) \ln N(1-c) \right) \tag{3}$$

and recover the expression of the free energy as

$$F_{CH} = \int_V \left(\Omega Nc N(1-c) + \frac{\kappa}{2}(\nabla Nc)^2 \right) dV - TS, \tag{4}$$

where we realize that a volume change can also contribute to the homogeneous free energy terms. We rescale the concentrations relative to the original volume to be $\nu = V_0/V$, also changing the integration variable, with

$$\begin{aligned} F_{CH} = \int_{V_0} & \nu^2 \left(\Omega c(1-c) + \frac{\kappa}{2}(\nabla c)^2 \right) \\ & + \nu \left(c \ln c + (1-c) \ln (1-c) + \ln \nu \right) dV \end{aligned} \tag{5}$$

We realize that not only are there enthalpic contributions to the volume change, there are also entropic changes. As shown in Balakrishana et al. [12, 14], the Cahn-Hilliard phase field crystal method can account for lattice changes during intercalation, which has been parametrized for materials such as lithium iron phosphate and lithium manganese oxide [15].

The inclusion of lattice parameter changes in a phase field model [14] is written as a Swift-Hohenberg model, where the parameter descriptions are provided in [12], as [20] (normalized)

$$F_{el} = \int_V \gamma \left(\frac{\psi}{2} \left(r + \left(1 + \nabla_c^2\right)^2 \right) \psi + \frac{\psi^4}{4} \right) dV \tag{6}$$

to account for anisotropic stretch/strain of a lattice in the simplest way, where the lattice symmetry parameter is

$$\nabla_c^2 = \xi^2 \left(\left(A_{11}^2 + A_{22}^2 \right) \frac{\partial^2}{\partial x^2} + A_{22}^2 \frac{\partial^2}{\partial y^2} + 2A_{12}A_{22} \frac{\partial^2}{\partial x \partial y} \right) \tag{7}$$

with A_{ij} as the elements of the transformation matrix [13, 21]. In this system, the periodic orientation is defined through an order parameter ψ, as well as the deviations from the critical value r. The transformation matrix is affected by the concentration of the system,

$$\mathbf{A}(c) = \begin{bmatrix} \alpha(c) & \frac{-\alpha(c)}{\sqrt{3}} \\ 0 & \frac{2\beta(c)}{\sqrt{3}} \end{bmatrix}. \tag{8}$$

A simpler version of this equation, for which volume changes are isotropic is assumed so that a 1D structure can be assumed for simplicity in calculations, where $\alpha\beta = 1/\nu$ is the single volume change parameter. Here, we see that by the definition of the anisotropic Laplace operator, it is almost equivalent to the linear Laplace operator $\nabla_c^2 \approx \left(\frac{\xi}{\nu}\right)^2 \nabla^2$ in one dimension. Applying these simplifications, we can simplify this problem to a 1-dimensional problem where the volume fraction of the system is the mainly question of the system, as in [22]. Thus, the equation can be simplified to

$$F_{el} = \int_V \gamma \left(\left(r + \left(1 + \left(\frac{\xi}{\nu}\right)^2 \nabla^2 \right)^2 \right) \psi + \frac{\psi^4}{4} \right) dV \tag{9}$$

We claim that this simplification still retains the periodicity of the lattice, which is proven in Appendix A. This simplification proves to be incredibly useful in transforming the system to one dimension and relating the free energy with the Cahn-Hilliard portion. The total free energy is then the sum of the Cahn-Hilliard and the phase field crystal portions, which are related through the term γ through the normalizations,

$$F = F_{CH} + F_{el}. \tag{10}$$

The dynamical equations for the concentration field can be found as

$$\frac{\partial c}{\partial t} = \nabla^2 \frac{\delta F}{\delta c}. \tag{11}$$

The phase field crystal model can be assumed to be dissipative as and almost at equilibrium (≈ 0) with the lattice arrangement equation:

$$\frac{\partial \psi}{\partial n} = -\frac{\delta F}{\delta \psi} + \frac{1}{L} \int \frac{\delta F}{\delta \psi} dx. \tag{12}$$

We realize that the chemical potential of the system changes to

$$\begin{aligned}\mu = \frac{\delta F}{\delta c} &= \nu^2 \left(\Omega(1-2c) - \frac{\kappa}{2}\nabla^2 c\right) + \nu \ln \frac{c}{1-c} \\ &+ 2\nu \frac{\partial \nu}{\partial c}\left(\Omega c(1-c) + \frac{\kappa}{2}\left(\nabla c\right)^2\right) \\ &+ \frac{\partial \nu}{\partial c}\left(\left(c \ln c + (1-c)\ln(1-c) + \ln \nu + 1\right)\right. \\ &- 4\gamma \left(\frac{\xi}{\nu}\right)^2 \frac{\partial \nu}{\partial c}\left(\nabla^2 \psi + \xi^2 \nu^{-2} \nabla^4 \psi\right),\end{aligned} \tag{13}$$

where the volume changes modify the enthalpic terms only. The term representing the volume change dependence on concentration can be neglected when those effects are minimal. The volume change effects in the second term are from the changes to be bulk concentration, while the last term is influenced by the peak distances. Higher order terms in Landau Ginzburg, which are neglected, would be influenced even more strongly by the volume changes.

The dependence of the free energy changes on the phase density is also found as

$$\frac{\delta F}{\delta \psi} = \gamma\left(\psi^3 + \left(r + \left(\frac{\xi}{\nu}\right)^2 \nabla^2\right)\psi\right), \tag{14}$$

which is used in the PFC equation.

III. DYNAMIC BEHAVIOR

To model the dynamic behavior, we use the finite difference method to study the behavior of this model in a simple 1D particle. A simple linear reaction boundary with a reaction coefficietn of $k_0 = 1$ is applied to the system, where 0 and 1 are the edges of the particle and 0.5 is the middle. A fixed chemical potential is applied at the boundaries of the particle to simulate voltage control. We assume that the peak density is always nearly at equilibrium with respect to the concentration changes of the particles. Without accounting for the effects of the peaks, the phase boundary is described as in Fig. 1. The result of a phase field simulation without a large effect of the peak field density on the free energy also results in a similar concentration field result as in Fig. 1. Similarly, the result of the peak density model for uncoupled behavior is shown in Fig. 3, where the periodicity of the model is obvious. Concentration changes do not affect the periodicity of the lattice when volume changes are not coupled through the variables.

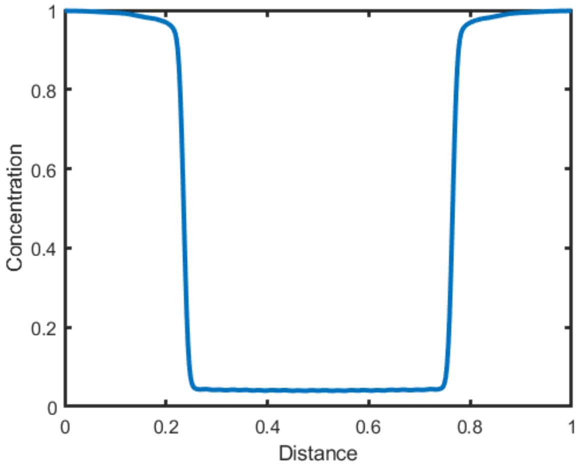

FIG. 1. Concentration Field (non-coupled) or $\gamma = 1$

To model the coupled behavior, for simplicity, we assume a 10% volume change between the charged and discharged state to model the coupled states. When a larger γ, or the effect of the peak density field on the free energy increases, the free energy also reflects the slightly periodic behavior of the concentration as in Fig. 2. The slightly oscillatory concentration fields in between the different lattice sites at high γ may increase the nonhomogeneity of the system, playing a role in triggering phase transformations more quickly. The peak concentration field in a coupled system is also affected by the concentration field through the volume changes of the system. As seen in this model, smaller peak density fluctuations are shown at more concentrated states because of the volume decrease of the system at higher concentrations in the PFC equation. This does not arise through any artificial creation, but rather through the volume changes affected be (de)intercalation.

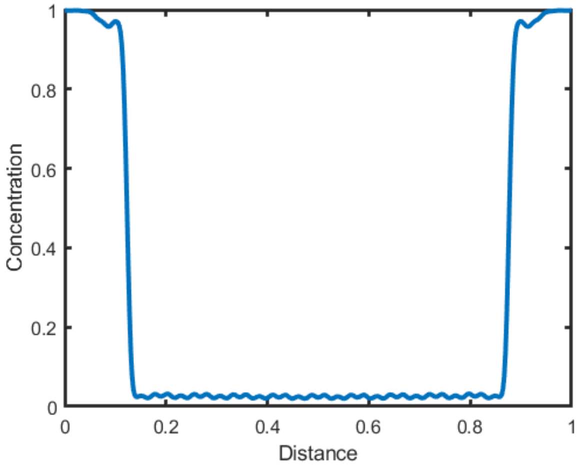

FIG. 2. Concentration Field Coupled ($\gamma = 10$)

IV. CONCLUSION

The 1-D CH-PFC is a simplification that has been shown to replicate the periodic behavior of the lattice, as well as the coupled effects of the concentration field and the peak density on each other through a simple,

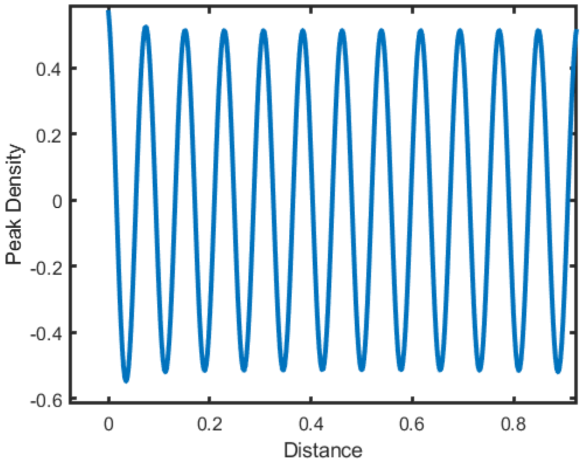

FIG. 3. Peak Concentration Field (non-coupled)

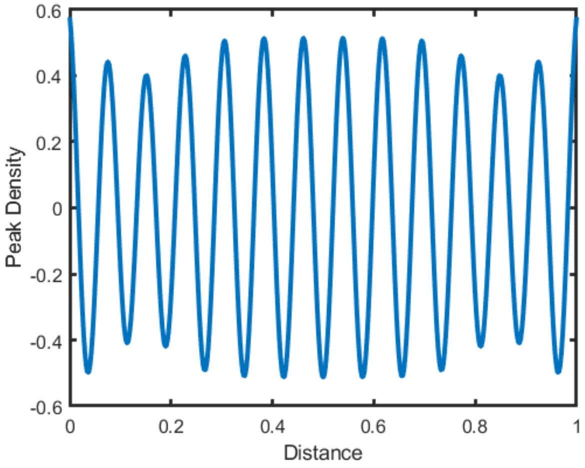

FIG. 4. Peak Concentration Field (coupled)

non-empirical way. We hope to implement these models into phase-separating battery electrodes in the future to further study the coupling of lattice and volume changes to each other, especially in relation to plastic deformations and stronger volume changes battery particles.

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Appendix A: Proof of Periodicity

Here, considering the density field as $\psi = P\cos(qx) + \bar{\psi}$, we integrate over a unit lattice of size $a_0 = \frac{2\pi}{q}$ to obtain

$$F = \int_0^{\frac{2\pi}{q}} \frac{dx}{2\pi/q}\left(\frac{\psi}{2}\left[r+\left(1+\left(\frac{\xi}{\nu}\right)^2\nabla^2\right)^2\right]\psi+\frac{\psi^4}{4}\right)$$
$$= \ldots + \frac{\psi}{2}\left(2\left(\frac{\xi}{\nu}\right)^2 q^2 + \left(\frac{\xi}{\nu}\right)^4 q^4\right) \tag{A1}$$

We minimize the equation to find $1/q^2 = \left(\frac{\nu}{\xi}\right)^2$, which proves the periodicity of the solution is minimized at the ”stretched” lattice size.

Appendix B: Modified Reaction Models

On a side note, as useful material for future work, we claim that the volume changes will also affect the reaction rate through changing the available sites in the system. For a reaction of A−A−, thermodynamically consistent reaction rates on surfaces are normally formulated as

$$R = f(c,\eta)g(\eta), \tag{B1}$$

where $f(c,\eta)$ is the transition state prefactor for the reaction rate and $g(\eta)$ is a Butler-Volmer type equation describing reversible reaction kinetics as $g(\eta) = \exp -\frac{\alpha\eta}{k_BT} - \exp\frac{(1-\alpha)\eta}{k_BT}$. The transition state should be modified to account for the site changes with $\tilde{c}$ replacing c, while the overpotential itself should also be modified to account for the volume changes as described in the calculation of the chemical potential.

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