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The persistence of phase-separation in $LiFePO_4$ with two-dimensional Li^+ transport: The Cahn–Hilliard-reaction equation and the role of defects

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ABSTRACT

We examine the solution of the two-dimensional Cahn–Hilliard-reaction (CHR) equation in the *xy* plane as a model of Li^+ intercalation into $LiFePO_4$ material. We validate our numerical solution against the solution of the depth-averaged equation, which has been used to model intercalation in the limit of highly orthotropic diffusivity and gradient penalty tensors. We then examine the phase-change behaviour in the full CHR system as these parameters become more isotropic, and find that as the Li^+ diffusivity is increased in the *x* direction, phase separation persists at high currents, even in small crystals with isotropic coherency strain included. The resulting voltage curves decrease monotonically, which has previously been considered a hallmark of crystals that fill homogeneously.

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1. Introduction

In recent years, phase-field models have been used to simulate various properties of $LiFePO_4$ material [1–6]. These phase-field models typically result in the concentration distribution of Li^+ being represented by the solution of the fourth-order Cahn–Hilliard (CH) equation. The CH equation is a thermodynamically consistent approach to modelling phase-separating materials, where the phase interface is "diffuse". This is in contrast to the sharply defined interface assumed in Stefan equation models that have traditionally been used to represent phase-separation in $LiFePO_4$ [7–9]. The CH equation is normally closed with no-flux boundary conditions, however Singh et al. [3] coupled a reaction condition to the boundary of a crystal, which drives Li^+ intercalation in the material, to arrive at the so called Cahn–Hilliard-reaction (CHR) system. Singh et al. [3] then examined the properties of a simplified second-order, depth-averaged equation derived from the CHR system. In particular, Bai et al. [5] showed that applying a large fixed current to the depth-averaged equation results in $LiFePO_4$ material that fills homogeneously, which helps explain the high-rate behaviour of nanoscale $LiFePO_4$. Cogswell and Bazant [6] also included coherency strain to this model system, and found that this further suppresses phase-separation.

Up to this point, analysis of the phase-separating behaviour of $LiFePO_4$ under a fixed current has been performed on the simplified depth-averaged equation. For example, Tang et al. [2] investigated the use of the full CHR system in $LiFePO_4$, though not under a fixed current and hence no connection was made to the suppression of phase-separation. The depth-averaged equation is derived by assuming Li^+ transport in the crystal is one-dimensional, in the *y* direction. For small, defect-free nanocrystals, this is likely to be an excellent approximation. In this work, we examine the behaviour of the full CHR system under parameter regimes where the depth-averaged equation is no longer valid. The numerical solution of the fourth-order, nonlinear CHR system is however, very difficult to compute. Previously, we presented a general numerical method for solving the CHR system on an unstructured grid [10]. We use this numerical approach to solve the CHR IBVP, and validate our numerical solution against the depth-averaged equation by assuming one-dimensional Li^+ transport. We then alter both the gradient penalty and diffusivity tensors ($\tilde{\mathbf{K}}$ and $\mathbf{D}$, respectively).

In a one-dimensional regime, the gradient penalty in the *y* direction, $\tilde{\mathbf{K}}_{yy}$, is assumed to be large, given that phase-boundaries in the *y* direction have not been observed experimentally. We examine the behaviour of the CHR system as this parameter is decreased. We then modify $\mathbf{D}$, altering the Li^+ transport in the crystal from a one-dimensional process to a two-dimensional process. This is motivated by recent experimental and theoretical [11,12] work that shows Li^+ transport in $LiFePO_4$ material that contains anti-site defects is at least a two-dimensional process. Examining the

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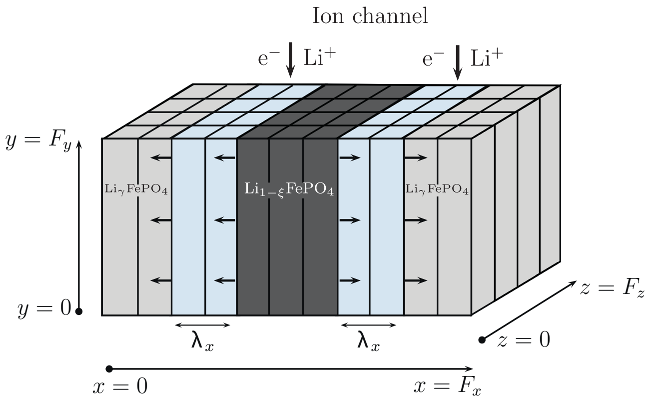

Fig. 1. Schematic of a $LiFePO_4$ crystal undergoing intercalation at a low current without anisotropic strain. The *x*, *y* and *z* axes correspond to the *a*, *b* and *c* crystallographic planes.

phase-change behaviour at high currents with two-dimensional Li^+ transport reveals complex dynamics that cannot be captured by a depth-averaged equation.

2. Model equations

We begin with a brief overview of the phase-field equations [3–5] used to model the intercalation of Li^+ into a crystal of $LiFePO_4$. Fig. 1 shows a schematic of a single crystal of $LiFePO_4$ of length F_x, F_y and F_z in each of the spatial dimensions, which has undergone phase-separation. The phase-boundary in Fig. 1 is aligned parallel to the *z*-axis, which is indicative of phase separation without the inclusion of anisotropic strain [6]. A region of highly lithiated material ($Li_{1-\xi}FePO_4$, where $\xi \ll 1$) is moving throughout the crystal in the *x* direction. A "mushy" region of length λ_x separates the $Li_{1-\xi}FePO_4$ phase from the lowly lithiated phase ($Li_\gamma FePO_4$, where $\gamma \ll 1$) and it is in this region where charge is inserted into the crystal according to the reaction,

$$FePO_4 + Li^+ + e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} LiFePO_4. \tag{1}$$

We will also refer to λ_y and λ_z as the length of the phase-separated region in the *y* and *z* direction, respectively, though Fig. 1 does not show phase-separation in either of these directions.

At early and late times with a low applied current, the crystal fills homogeneously. This process is not shown in Fig. 1 and involves Li^+ intercalating into the empty crystal to form $Li_\gamma FePO_4$ before phase-separating. The phase boundary then moves throughout the crystal as shown in Fig. 1, until the entire crystal is composed of $Li_{1-\xi}FePO_4$. Homogeneous filling then continues until the crystal reaches the fully lithiated state $LiFePO_4$. The dynamics of a phase-field model capture all of this behaviour without assuming that a phase-boundary exists (which is unlike a shrinking-core model [7,9]).

We assume that the crystal shown in Fig. 1 is comprised of an ordered series of unit lattice cells of volume V_{cell} (m^3) with N_{sv} individual Li^+ intercalation sites per unit cell. We can write the exposed area of a unit cell on the *xz* plane at $y = F_y$ as A_{cell} (m^2), with N_{ss} of the N_{sv} sites in the unit cell directly exposed to the reaction on the surface. The average area of a single intercalation site can then be written as $A_s = A_{\text{cell}}/N_{\text{ss}}$ (m^2). The constant site density is given by $\rho = N_{\text{sv}}/V_{\text{cell}}$ (m^{-3}), and the surface site density by $\rho_s = N_{\text{ss}}/A_{\text{cell}}$ (m^{-2}). Each surface site is associated with an ion channel along which Li^+ is transported from the surface of the crystal to the interior. As shown in Fig. 1 the ion channels extend in the *y* direction and are associated with a single reaction site, with $N_H = \rho A_s F_y$ lithium sites in each channel. Over both of the *xz* facets at $y = 0$ and $y = F_y$, we have $N_{As} = 2F_xF_z/A_s$ active surface sites (or twice the number of ion channels).

The distribution of Li^+ in the crystal can be described by the Cahn–Hilliard-reaction equation and a depth-averaged version of the CHR equation [3,4,13,5]. The following sections briefly describe the CHR and depth-averaged equations, and comment on the assumptions necessary (as outlined in detail by Burch [14]) to derive the depth-averaged equation.

2.1. Cahn–Hilliard-reaction equation

We adopt the notation of Burch [14] and assume that the free energy in our system is given by the CH functional [15] $G[c(\mathbf{x}, t)]$ (J), where $c(\mathbf{x}, t) \in [0, 1]$ is the concentration of Li^+ in a $LiFePO_4$ crystal (nondimensionalised by ρ), with spatial coordinates $\mathbf{x}$ (m), through time *t* (s). For a more detailed derivation of the following model equations, we refer the reader to Refs. [14,15]. On an N_D-dimensioned domain Ω with boundary Γ the free energy in a CH model can be written as

$$G(t) \equiv G[c(\mathbf{x}, t)] = \int_\Omega \left[g_{\text{hom}}(c) + \frac{1}{2}(\nabla c)^T \mathbf{K}(\nabla c) + \frac{B(\hat{\mathbf{n}}_0)}{2\rho}(c - c_{\text{avg}})^2 \right] \rho \, d\Omega, \tag{2}$$

where g_{hom} (J) is the free energy per molecule of a homogeneous system at a uniform concentration and $\mathbf{K}$ (J m^2) is a gradient penalty tensor, which we have assumed is symmetric positive definite, orthotropic and constant (where the diagonal elements of this tensor follow from the width of the phase-boundaries in each direction). The final term in the free energy functional isotropically approximates the effect of coherency strain in the crystal [16,17,6], where $B(\hat{\mathbf{n}}_0)$ (Pa) is the elastic energy in the minimising direction $\hat{\mathbf{n}}_0$ and c_{avg} is the average concentration of Li^+ over Ω. In Section 4, we examine the phase-separation dynamics in both the simple strain-free case and with isotropic coherency strain included.

We assume g_{hom} obeys a regular solution model [14,5,15,18] and is written as

$$g_{\text{hom}}(c) = \Omega_m c(1 - c) + 2k_B T(c\ln(c) + (1 - c)\ln(1 - c)), \tag{3}$$

where k_B (J K^{-1}) is Boltzmann's constant, *T* (K) is the temperature and Ω_m (J) is the enthalpy of mixing per site. Writing (1) as

$$LiFePO_4 - FePO_4 \rightleftharpoons Li^+ + e^-, \tag{4}$$

the chemical potential of the LHS of (4) is called the diffusional chemical potential μ (J). This is the potential of Li^+ in the lattice, per molecule. Noting (3), the variational derivative of (2) [19] gives us the diffusional chemical potential,

$$\mu(\mathbf{x}, t) = \Omega_m(1 - 2c) + 2k_B T \ln\left(\frac{c}{1 - c}\right) - \nabla \cdot (\mathbf{K}\nabla c) + \frac{B(\hat{\mathbf{n}}_0)}{\rho}(c - c_{\text{avg}}) = k_B T \ln a(\mathbf{x}, t), \tag{5}$$

where *a* is the activity of the Li^+ in the lattice.

The mass flux $\mathbf{j}$ ($m^{-2}\,s^{-1}$) per molecule is proportional to a gradient in chemical potential, namely

$$\mathbf{j}(\mathbf{x}, t) = \rho c \mathbf{M} \nabla \mu, \tag{6}$$

where $\mathbf{M}$ ($m^2\,J^{-1}\,s^{-1}$) is a mobility tensor. As mass is conserved in this system, the Cahn–Hilliard equation is given by

$$\frac{\partial c}{\partial t} + \frac{1}{\rho}\nabla \cdot \mathbf{j} = 0, \quad \mathbf{x} \in \Omega. \tag{7}$$

The CH equation (7) can also be rewritten directly in terms of the concentration $c(\mathbf{x}, t)$ and using the Einstein relation to write the

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