

Phase-field study of electrochemical reactions at exterior and interior interfaces in Li-Ion battery electrode particles

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Abstract

To study the electrochemical reaction on surfaces, phase interfaces, and crack surfaces in lithium ion battery electrode particles, a phase-field model is developed which describes fracture in large strains and anisotropic Cahn-Hilliard-Reaction. Thereby the concentration-dependency of the elastic properties and the anisotropy of diffusivity are also considered. The implementation in 3D is carried out by the isogeometric finite element method in order to treat the higher order terms in a straightforward manner. The electrochemical reaction is modeled through a modified Butler-Volmer equation to account for the influence of the phase change on the reaction on exterior surfaces. The reaction on the crack surfaces is considered through a volume source term weighted by a term related to the fracture order parameter. Based on the model, three characteristic examples are considered to reveal the electrochemical reactions on particle surfaces, phase interfaces, and crack surfaces, as well as their influence on the particle material behavior. The results show that both the anisotropy and the ratio between the timescales of reaction and diffusion can have a significant influence

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on the phase segregation behavior. In turn, the distribution of the lithium concentration strongly influences the reaction on the surface, especially when the phase interfaces appear on exterior surfaces or crack surfaces. The reaction rate increases considerably at phase interfaces due to the large lithium concentration gradient. Moreover, the simulations demonstrate that the segregation of a Li-rich and a Li-poor phase during delithiation can drive the cracks to propagate. The results indicate that the model can capture the electrochemical reaction on the freshly cracked surfaces.

Keywords: Electrochemical reaction, Phase-field modeling of fracture, Cahn-Hilliard-type diffusion, Isogeometric analysis, Lithium-ion battery electrode particles, Anisotropic diffusion

1. Introduction

Lithium ion batteries, with their high energy densities and light-weight designs, have found wide applications in portable electronics and electric vehicles. A typical lithium ion battery cell is illustrated in Figure 1. The current collectors and the binders between the electrodes (not depicted here) conduct the electrons, while the separator only permits the diffusion of lithium ions. The anode and cathode particles are surrounded by the electrolyte. Lithium ions intercalate into the electrodes through electrochemical reactions on the surface of the particles. Due to this process, certain electrode active materials experience large deformations during charge-discharge circles. For instance, a volumetric expansion of as much as 400 % of silicon anode has been observed during lithiation [1]. In the electrochemical system of a battery, the reaction rate is a key issue since it is directly related to the charge/discharge performance of a battery. The phenomenological Butler-Volmer (BV) equation, which is based on a dilute solution model, may not be able to account for a separation of phases with different Li concentrations in materials, such as silicon and LiFePO_4 . In the work of Singh et al. [2], a generalized BV kinetics model was proposed, which includes the influence of the phase transition on the surface reaction in a 1D case. Based

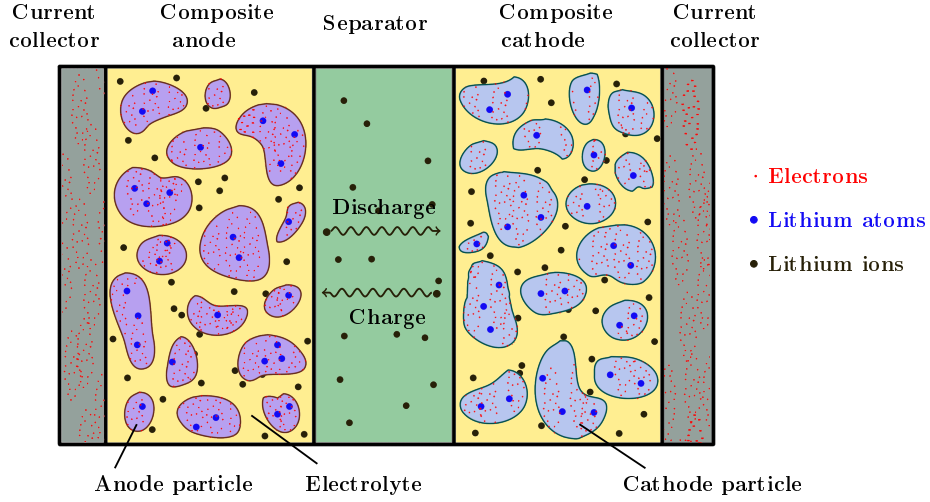


Figure 1: Schematic of a lithium-ion battery cell.

on this model, Bai et al. [3] discussed the suppression of the phase segregation
 20 under large reaction rate. The two dimensional case, which also coupled the
 Cahn-Hilliard bulk diffusion was studied by Dargaville and Farrell [4]. Using
 different limits of the 1D case, they discussed when the orthotropic diffusivity
 becomes more isotropic. In mechanically coupled modeling, there has also been
 a tendency recently to treat the electrochemical reaction on the surface directly
 25 through the BV equation rather than simply to replace the reaction by a source
 of constant or time dependent flux [5, 6].

The mechanical degradation of the electrode particle is widely believed to
 be closely related to the failure of the batteries. This issue has been inten-
 sively studied in various chemo-mechanical coupled models [7–10]. However,
 30 those models mainly treat the diffusion process as in a dilute solution, where
 the concentration smoothly changes with the incoming/outgoing flux, accompa-
 nied by a homogeneous “breathing-like” expansion and shrinkage of the particle,
 which will hardly lead to the failure of the electrode particles. In the work of
 Huttin et al. [11] and Walk et al. [12], the Cahn-Hilliard equation was em-
 35 ployed to investigate the stress state and to compare the results with those in
 the case of a dilute solution. The diffusion process was treated as isotropic in

both works. However, as Rohrer et al. [13, 14] pointed out from first principle calculations, the anisotropic volumetric expansion in Silicon will indeed initiate cracking, especially in large particles, where the segregation between amorphous and crystalline silicon phases can not be suppressed. Moreover, in positive electrode materials such as LiFePO_4 , striped phase boundaries have been observed by Chen et al. [15, 16] because of strong anisotropy and phase segregation. It demonstrated the necessity to employ a Cahn-Hilliard model and to consider the anisotropic diffusion property coupled with large deformations for describing the bulk behavior of the particle.

The description of the dynamics of crack propagation in lithium ion battery electrode particles has long been a challenge. Recently, as the concept of phase-field modeling found more applications in different disciplines, phase-field methods have also been introduced to predict the crack propagation coupled with diffusion. In phase-field fracture models, the damaged and undamaged parts of the material are considered as two different phases, indicated by the distinct values of the order parameter. Schneider et al. [17] proposed a model coupling the mechanics with a general multiphase and multicomponent phase-field approach to describe the diffusion and crack propagation in brittle materials. Liang et al. [18] developed a phase-field model to predict the crack evolution in LiFePO_4 cathode nanoparticles in of Li-ion batteries. Concurrently, the phase-field fracture simulation in silicon anodes was also carried out by Zuo et al. [19]. Recently, Miehe et al. [20] conducted a comprehensive study on chemo-mechanical induced fracture in the framework of phase-field fracture modeling, and took into account the chemical reactions not only on fracture surfaces but also on exterior surfaces.

In this paper, the authors propose a phase-field model which accounts for electrochemical reactions on different interior and exterior surfaces of phases and crack surfaces based on the fully coupled Cahn-Hilliard-Reaction (CHR) model proposed in the work of Bazant [21]. To meet the demand of higher-order continuity arising from the Cahn-Hilliard equation, isogeometric analysis is employed.

The paper is organized as follows. In section 2, the phase-field fracture model coupled with the anisotropic Cahn-Hilliard-Reaction problem model is formulated in large strains. The modeling of electrochemical reactions on the surface, phase interface, and on the crack surface is shown in section 3. Numerical details are given in section 4. Finally, three examples are presented in section 5 to discuss the reaction rate, the anisotropic diffusion, and the reaction on the crack surface.

2. Phase-field model of fracture and phase separation

2.1. Kinematics

According to continuum theory, the material coordinates $\mathbf{X}$ label each material point, while the spatial coordinates $\mathbf{x}$ denote points in the space. The motion of the body can be described by tracking the spatial coordinates of the material points at time t , i.e. $\mathbf{x} = \phi(\mathbf{X}, t)$. The deformation gradient at a given time is then defined as

$$\mathbf{F} = \nabla_{\mathbf{R}} \phi \quad (1)$$

in which $\nabla_{\mathbf{R}}$ denotes the gradient with respect to the material point $\mathbf{X}$ in the reference (material) configuration. The deformation gradient is multiplicatively decomposed into two parts:

$$\mathbf{F} = \mathbf{F}^e \mathbf{F}^c, \quad (2)$$

where $\mathbf{F}^e$ denotes the elastic distortion and $\mathbf{F}^c$ the (de-)intercalation-induced deformation. The (de-)intercalation-induced deformation is usually assumed to be volumetric, and it can be further defined as

$$\mathbf{F}^c = (J^c)^{\frac{1}{3}} \mathbf{1} \quad \text{with} \quad J^c = 1 + \Omega c_{\mathbf{R}} \quad (3)$$

in which $c_{\mathbf{R}}(\mathbf{X}, t)$ is the molar concentration per unit volume in the reference configuration and Ω is the constant partial molar volume. Applying the normalization with respect to the maximum concentration $c_{\max}$,

$$c = c_{\mathbf{R}}/c_{\max}, \quad \Omega^* = \Omega c_{\max}. \quad (4)$$

one has

$$J^c = 1 + \Omega^* c. \quad (5)$$

On the other hand, one can also define the volumetric part of the elastic contribution $\mathbf{F}^e$,

$$J^e = \det \mathbf{F}^e = J/J^c \quad \text{with} \quad J = \det \mathbf{F}. \quad (6)$$

The right Cauchy-Green deformation tensors are

$$\mathbf{C} = \mathbf{F}^T \mathbf{F}, \quad \mathbf{C}^e = (\mathbf{F}^e)^T \mathbf{F}^e = (J^c)^{-\frac{2}{3}} \mathbf{C}. \quad (7)$$

Due to the volumetric feature of $\mathbf{F}^c$, the deviatoric part of the total deformation equals that of the elastic deformation, i.e.,

$$\bar{\mathbf{C}} = \bar{\mathbf{C}}^e \quad \text{with} \quad \bar{\mathbf{C}} = J^{-\frac{2}{3}} \mathbf{C}, \quad \bar{\mathbf{C}}^e = (J^e)^{-\frac{2}{3}} \mathbf{C}^e. \quad (8)$$

It follows that

$$\bar{I}_1 = \bar{I}_1^e \quad \text{with} \quad \bar{I}_1 = \text{tr}(\bar{\mathbf{C}}), \quad \bar{I}_1^e = \text{tr}(\bar{\mathbf{C}}^e). \quad (9)$$

From the deformation gradient, the Green-Lagrange strain tensor is then defined as

$$\mathbf{E} = \frac{1}{2} (\mathbf{F}^T \mathbf{F} - \mathbf{1}) = \frac{1}{2} (\mathbf{C} - \mathbf{1}). \quad (10)$$

2.2. Free energy density

We assume a free energy, coupling the chemical and the mechanical field with a damage variable ξ as

$$\psi_{\text{R}}(c_{\text{R}}, \nabla_{\text{R}} c_{\text{R}}, \mathbf{C}, \xi, \nabla \xi) = \psi_{\text{R}}^c(c_{\text{R}}) + \psi_{\text{R}}^i(\nabla_{\text{R}} c_{\text{R}}) + \psi_{\text{R}}^f(\xi, \nabla_{\text{R}} \xi) + \psi_{\text{R}}^e(c_{\text{R}}, \mathbf{C}, \xi), \quad (11)$$

where ψ_{R}^c , ψ_{R}^i , ψ_{R}^f and ψ_{R}^e are the bulk chemical free energy, the phase interface free energy, the fracture free energy, and the elastic free energy, respectively. In 80 this paper, entities with subscript R indicate those defined per volume in the reference configuration, unless otherwise indicated.

The first two terms allow for the coexistence of two phases with different Lithium concentration, which are separated by a diffuse interface. The bulk free energy ψ_{R}^c is only dependent on the concentration c and is given as

$$\psi_{\text{R}}^c(c) = \text{RT}c_{\text{max}} [c \ln c + (1 - c) \ln(1 - c)] + \text{RT}c_{\text{max}} \chi c(1 - c), \quad (12)$$

in which R and T are the gas constant and the reference temperature, respectively. To achieve a double-well function of ψ^c , so that this energy density allows for the coexistence of two phases, one needs to choose $\chi > 2$. In the simulation,
85 $\chi = 2.5$ is adopted.

The interfacial free energy ψ_R^i gives an energetic penalty for the interface which is expressed as

$$\psi_R^i(\nabla c_R) = \frac{1}{2} c_{\max} \nabla_R c \cdot \mathbf{K} \nabla_R c. \quad (13)$$

Here, $\mathbf{K}$ is an interfacial parameter which is defined as

$$\mathbf{K} = \begin{bmatrix} \kappa_x & & \\ & \kappa_y & \\ & & \kappa_z \end{bmatrix} \quad (14)$$

to exhibit an orthotropy of the interface. The parameters κ_x , κ_y and κ_z are related to the interfacial thickness in the corresponding directions. For a 1D case, if the elastic influence is absent, we can obtain the interfacial thickness and the integrated interfacial energy as [22]

$$s = \Delta c / \tan \theta = (c_\beta - c_\alpha) \sqrt{\kappa^* / (2 \Delta \psi_{\max}^c)}, \quad (15)$$

$$\Psi^i = \int_{-\infty}^{\infty} \frac{\psi_R^i}{RT c_{\max}} dx = \int_{-\infty}^{\infty} \frac{1}{2} \kappa^* (c_{,x})^2 dx = \int_{c_\alpha}^{c_\beta} \sqrt{\kappa^* \Delta \psi^c / 2} dc, \quad (16)$$

where s is the interface thickness defined as depicted in Figure 2(a), c_α , c_β and $\Delta \psi^c$ are shown in Figure 2(b), and $\kappa^* = \kappa / (RTL_0^2)$ with L_0 being a characteristic length scale. One can see from (15) and (16) that, for a given bulk free energy, the interface thickness and the total energy are proportional to the square root
90 of κ , that is, $s, \Psi_i \propto \sqrt{\kappa}$. It can be further concluded that, in the 3D case, if the interfacial parameter κ in one direction is much smaller than those in the other two directions, the interfacial thickness and the energy expended across the interface will be much smaller in this direction. For instance, $\kappa_x \ll \kappa_y = \kappa_z$ gives $s_1 \ll s_2 = s_3$ and $\Psi_1^i \ll \Psi_2^i = \Psi_3^i$.

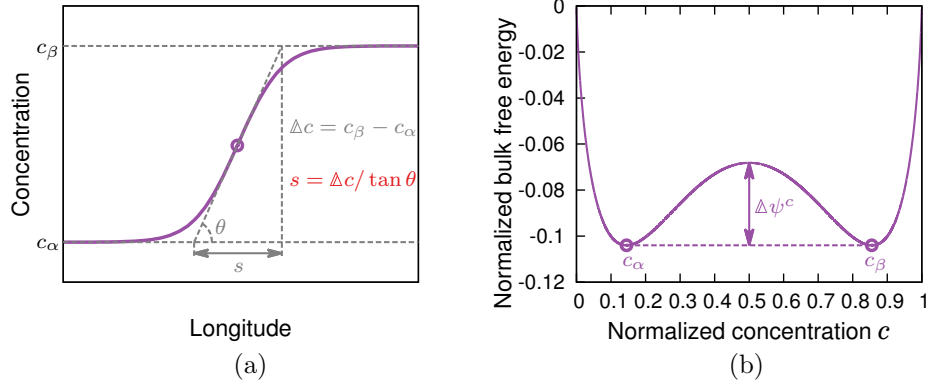


Figure 2: Definition of the interface thickness for a 1D problem.

The damage-like order parameter ξ is introduced to describe the damage state of the material, with a value of 1 when the material is unbroken and being 0 when it is fully broken. According to Bourdin et al. [23], the fracture free energy density is given by,

$$\psi_{\text{R}}^f(\xi, \nabla_{\text{R}}\xi) = \mathcal{G}_c \left[\epsilon |\nabla_{\text{R}}\xi|^2 + \frac{1}{4\epsilon} (1 - \xi)^2 \right]. \quad (17)$$

95 Here, $\mathcal{G}_c$ is the critical energy release rate and ϵ is a length scale which determines the width of the transition zone between the unbroken and the broken region.

The elastic energy ψ_{R}^e represents the stored energy of the elastic deformation. Although a crystal with anisotropic chemical properties will also show an anisotropy in mechanical properties, the quantitative relation is still unknown. For simplicity, for the undamaged region an isotropic neo-Hookean model is assumed

$$\psi_{\text{R}}^{e0}(c_{\text{R}}, \mathbf{C}) = J^c \left[\frac{K_c}{2} (J^e - 1)^2 + \frac{G_c}{2} (\bar{I}_1 - 3) \right] \quad (18)$$

in which K_c and G_c are phase-dependent elastic moduli which are expressed as

$$K_c = K_0 (c - c_{\text{in}}), \quad G_c = G_0 (c - c_{\text{in}}). \quad (19)$$

Here, K_0 , G_0 and c_{in} are constants which can be determined by a linear fitting of the measurements of the elastic moduli at different concentrations. For more

100 details of an isotropic model without damage we refer the reader to our previous work [24].

Following Schneider et al. [17] and Zuo et al. [19], we ignore the direct influence of diffusion on the crack propagation. That is, the chemical field will not directly lead to fracture, but indirectly through the induced stress field. Moreover, to account for the fact that cracks will not propagate under hydrostatic compression, the elastic free energy can be split into a positive part ψ_{R}^{e+} and a negative part ψ_{R}^{e-} . The latter will not be involved in the coupling with the fracture. More specifically, the two parts take the form

$$\psi_{\text{R}}^{e+}(c_{\text{R}}, \mathbf{C}) = J^c \left[\frac{K_c}{2} (J^{e+} - 1)^2 + \frac{G_c}{2} (\bar{I}_1 - 3) \right], \quad (20a)$$

$$\psi_{\text{R}}^{e-}(c_{\text{R}}, J) = J^c \frac{K_c}{2} (J^{e-} - 1)^2 \quad (20b)$$

in which

$$\begin{cases} J^{e+} = J^e, & J^{e-} = 1, & \text{if } J^e \geq 1; \\ J^{e+} = 1, & J^{e-} = J^e, & \text{if } J^e < 1. \end{cases} \quad (21)$$

The elastic energy is defined as

$$\psi_{\text{R}}^e(c_{\text{R}}, \mathbf{C}, \xi) = (\xi^2 + \eta) \psi_{\text{R}}^{e+} + \psi_{\text{R}}^{e-}, \quad (22)$$

in which $0 < \eta \ll 1$ is a constant introduced to prevent a singularity inside the broken phase when $\xi = 0$. This method has been successfully implemented in the works of Kuhn et al. [25, 26] and Schlüter et al. [27] with a careful choice of η .

105 2.3. Governing equations

In this model, there are three sets of field variables: a molar concentration c_{R} , the displacements $\mathbf{u}$ and a damage variable ξ . The variation of the total free energy can be expressed in terms of variations of those variables as

$$\delta \Psi = \int_{\text{B}_{\text{R}}} \mathbf{S}_{\text{R}} : \delta \mathbf{E} \, \text{dB} + \int_{\text{B}_{\text{R}}} \mu_{\text{R}} \delta c_{\text{R}} \, \text{dB} + \int_{\text{B}_{\text{R}}} \zeta \delta \xi \, \text{dB}, \quad (23)$$

in which $\mathbf{S}_{\text{R}}$ is the second Piola-Kirchhoff stress tensor, μ_{R} is the chemical potential and ζ is the driving force for the fracture. Ψ is defined as the free

energy over the whole body as

$$\Psi = \int_{B_R} \psi_R(c_R, \nabla_R c_R, \mathbf{C}, \xi, \nabla \xi) \, dB. \quad (24)$$

With ψ_R defined in (11), the variation of Ψ is given by

$$\begin{aligned} \delta \Psi &= \int_{B_R} \left[\frac{d\psi_R^c}{dc_R} \delta c_R + \frac{d\psi_R^i}{d\nabla_R c_R} \cdot \delta \nabla_R c_R + \frac{\partial \psi_R^e}{\partial c_R} \delta c_R + \frac{\partial \psi_R^e}{\partial \mathbf{C}} : \delta \mathbf{C} \right. \\ &\quad \left. + \frac{\partial \psi_R^e}{\partial \xi} \delta \xi + \frac{\partial \psi_R^f}{\partial \xi} \delta \xi + \frac{\partial \psi_R^f}{\partial \nabla \xi} \cdot \delta \nabla \xi \right] dB \\ &= \int_{B_R} \left\{ \left(\frac{d\psi_R^c}{dc_R} - \nabla_R \cdot \mathbf{K} \nabla_R c_R + \frac{\partial \psi_R^e}{\partial c_R} \right) \delta c_R + \nabla_R \cdot (\mathbf{K} \nabla_R c_R \delta c_R) + \frac{2\partial \psi_R^e}{\partial \mathbf{C}} : \delta \mathbf{E} \right. \\ &\quad \left. + \left[2\xi \psi_R^{e+} + \frac{\mathcal{G}_c}{2\epsilon} (\xi - 1) - 2\mathcal{G}_c \epsilon \Delta_R \xi \right] \delta \xi + \nabla_R \cdot (\nabla_R \xi \delta \xi) \right\} dB \\ &= \int_{B_R} \left(\frac{d\psi_R^c}{dc_R} - \nabla_R \cdot \mathbf{K} \nabla_R c_R + \frac{\partial \psi_R^e}{\partial c_R} \right) \delta c_R \, dB + \int_{B_R} \frac{2\partial \psi_R^e}{\partial \mathbf{C}} : \delta \mathbf{E} \, dB \\ &\quad + \int_{B_R} \left[2\xi \psi_R^{e+} + \frac{\mathcal{G}_c}{2\epsilon} (\xi - 1) - 2\mathcal{G}_c \epsilon \Delta_R \xi \right] \delta \xi \, dB \\ &\quad + \int_{\partial B_R} \mathbf{K} \nabla_R c_R \cdot \mathbf{n}_R \, \delta c_R \, dS + \int_{\partial B_R} \nabla_R \xi \cdot \mathbf{n}_R \, \delta \xi \, dS. \end{aligned} \quad (25)$$

Comparing (23) and (25), $\mathbf{S}_R$, μ_R and ζ can be written as

$$\mathbf{S}_R = \frac{2\partial \psi_R}{\partial \mathbf{C}} = (\xi^2 + \eta) \frac{2\partial \psi_R^{e+}}{\partial \mathbf{C}} + \frac{2\partial \psi_R^{e-}}{\partial \mathbf{C}}, \quad (26a)$$

$$\mu_R = \frac{d\psi_R^c}{dc_R} + \frac{\partial \psi_R^e}{\partial c_R} - \nabla_R \cdot \mathbf{K} \nabla_R c, \quad (26b)$$

$$\zeta = 2\xi \psi_R^{e+} - 2\mathcal{G}_c \epsilon \Delta_R \xi + \frac{\mathcal{G}_c}{2\epsilon} (\xi - 1), \quad (26c)$$

with two boundary conditions $\mathbf{K} \nabla_R c_R \cdot \mathbf{n}_R = 0$ and $\nabla_R \xi \cdot \mathbf{n}_R = 0$ to be fulfilled on the boundary surface in the reference configuration ∂B_R , in addition to the Dirichlet and Neumann boundary conditions from physical constraints and fluxes.

As for the governing equation of the mechanical part, we assume a quasi-static loading, thus ignoring the inertia terms. The governing equation for the local force balance in the body of the reference configuration B_R reads

$$\nabla_R \cdot \mathbf{P}_R = \mathbf{0}, \quad (27)$$

where $\mathbf{P}_R$ is the first Piola-Kirchhoff stress, defined as

$$\mathbf{P} = \mathbf{F} \mathbf{S}_R. \quad (28)$$

The molar concentration c_R is a conserved order parameter and subject to the Cahn-Hilliard-type kinetics. In the authors' previous paper [24], the species are assumed to be driven by a flux defined in the reference configuration which leads to a simplification in the finite element implementation. In the present paper, a more physically based kinetics is employed which defines the flux by the gradient of chemical potential at the current configuration. More specifically,

$$\frac{\partial c_C}{\partial t} = -\nabla_C \cdot \mathbf{j}_C \quad (29)$$

110 where the subscript C denotes quantities defined in the current configuration.

In the body B_C , the Cahn-Hilliard-type diffusion applies in the virgin state, while in the damaged region no diffusion is considered. It leads to

$$\mathbf{j}_C = -\xi^2 \mathbf{M}_c \nabla_C \mu_R \quad \text{in } B_C, \quad (30)$$

where $\mathbf{M}_c$ is a mobility tensor defined as

$$\mathbf{M}_c = c(1-c) \begin{bmatrix} M_x & & \\ & M_y & \\ & & M_z \end{bmatrix} = c(1-c) \mathbf{M}, \quad (31)$$

with $c(1-c)$ representing a degenerated mobility towards $c = 0$ and $c = 1$. On the boundary surface ∂B_C and the surface of a newly created crack Γ_f , the flux depends on the electrochemical reaction, which follows a phenomenological Butler-Volmer equation. More details will follow in sections 3.1 and 3.2. Therefore, the flux is given as

$$\mathbf{j}_C \cdot \mathbf{n}_C = -\hat{j}_s \quad \text{on } \partial B_C \cup \Gamma_f. \quad (32)$$

Based on density functional theory calculations, Rohrer et al. [14] have found that the anisotropy of mobility is a consequence of orientation-dependent interface energies and that high-energy interfaces are more mobile than low-energy interfaces. By recalling (16), it can be concluded that a higher κ leads

to a larger M . For simplicity, a proportional relation is assumed, that is, $M_x/\kappa_x = M_y/\kappa_y = M_z/\kappa_z$. The chemical potential μ_R expresses the free energy change for adding/subtracting one mole lithium to/from the system, thus being the same for any configuration. The subscript R only indicates the fact that it is calculated by quantities in the reference configuration. Given the condition that the total mass should be conserved in different configurations,

$$\int_{B_C} \frac{\partial c_C}{\partial t} dB = \int_{B_R} \frac{\partial c_R}{\partial t} dB, \quad (33)$$

equation (29) can be pulled back straightforwardly to the reference configuration as

$$\frac{\partial c_R}{\partial t} = \nabla_R \cdot [\xi^2 c(1-c) J \mathbf{F}^{-1} \mathbf{M} \mathbf{F}^{-T} \nabla_R \mu_R] \quad \text{in } B_R. \quad (34)$$

For later discussion, a dimensionless activity a is introduced by

$$RT \ln a = \mu_R, \quad (35)$$

and an activity coefficient γ as the ratio $\gamma = a/c$. Note that, when $a = c$ and thus $\gamma = 1$, this model degenerates to an ideal dilute model.

As for a non-conserved order parameter ξ , the evolution equation follows an Allen-Cahn-type equation

$$\frac{\partial \xi}{\partial t} = -M_\xi \zeta = -M_\xi \left[2\xi \psi_R^{e+} - 2\mathcal{G}_c \epsilon \Delta_R \xi + \frac{\mathcal{G}_c}{2\epsilon} (\xi - 1) \right] \quad (36)$$

with M_ξ as the mobility for the evolution of ξ . Following Miehe et al. [28, 29] and Borden et al. [30], to mimic the irreversibility of the crack, a strain-history field $\mathcal{H}_R$ is introduced as a substitution of ψ_R^{e+} , which satisfies the Kuhn-Tucker conditions

$$\mathcal{H}_R \geq \psi_R^{e+}, \quad \dot{\mathcal{H}}_R \geq 0, \quad \dot{\mathcal{H}}_R (\psi_R^{e+} - \mathcal{H}_R) = 0. \quad (37)$$

The evolution for ξ then reads

$$\frac{\partial \xi}{\partial t} = -M_\xi \left[2\xi \mathcal{H}_R - 2\mathcal{G}_c \epsilon \Delta_R \xi + \frac{\mathcal{G}_c}{2\epsilon} (\xi - 1) \right]. \quad (38)$$

In summary, the governing equations for three field variables $\mathbf{u}$, c and ξ are given by (27), (34) and (38), respectively.

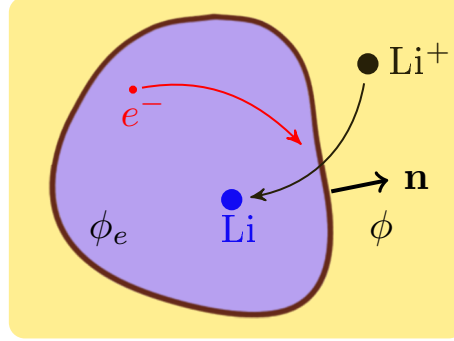


Figure 3: Illustration of the electrochemical reaction on the surface

115 3. Modeling of electrochemical reaction

3.1. Reaction on particle surfaces

On the particle surface, a Faradaic reaction



takes place, during which a Li-ion consumes an electron, as shown in Figure 3. The resultant neutral Lithium inserts into the host material.

The rate of the reaction is described by a phenomenological Butler-Volmer (BV) equation,

$$\hat{j}_s = c_s R_{BV} = c_s \frac{a_+^{1-\beta} a^\beta}{\tau_0 \gamma_A} \left[\exp \left(-\beta \frac{F \eta_R^s}{RT} \right) - \exp \left((1-\beta) \frac{F \eta_R^s}{RT} \right) \right], \quad (40)$$

in which c_s with the unit of mol m^{-2} is the molar concentration of intercalation sites on the surface and R_{BV} is the reaction rate in unit s^{-1} . Moreover, τ_0 is the mean time for a single reaction step which will be set differently to mimic a slow or fast reaction process in the simulation. The parameter γ_A denotes the chemical activity coefficient of the activated state which is taken as $(1-c)^{-1}$, while β is a symmetry factor for a forward and backward reaction indicated in (39) and which is set to be 0.5. The Faraday constant F describes the amount of electric charge of one mole electrons. For more details on the coefficients of this model one can refer to the work of Bai et al. [3] and Dargaville et al. [4].

The definition of a has been introduced in (35). The parameters a_+ and a are activities of Li^+ and Li , respectively. Since Li^+ diffuses in the electrolyte much faster than Li diffuses in the electrode [3], a_+ is set to be unity for simplicity. For a similar reason, the activity of electrons a_- is also set to be 1. The surface overpotential η_{R}^s is defined as the electrostatic potential of the working electrode relative to a reference electrode of the same kind placed in the solution adjacent to the surface of the working electrode. It can be expressed in terms of the electrochemical potentials as

$$F\eta_{\text{R}}^s = \mu_{\text{Li}} - \mu_{\text{Li}^+} - \mu_{e^-}, \quad (41)$$

where μ_{Li} , μ_{Li^+} , μ_{e^-} are the electrochemical potentials of Li , Li^+ and e^- , respectively, which are expressed as

$$\mu_{\text{Li}} = RT \ln a = \mu_{\text{R}}, \quad (42)$$

$$\mu_{\text{Li}^+} = RT \ln a_+ + F\phi_e = F\phi, \quad (43)$$

$$\mu_{e^-} = RT \ln a_- - F\phi = -F\phi_e. \quad (44)$$

Here, ϕ_e denotes the electrostatic potential of the electrode and ϕ represents that of the electrolyte. Insertion of the last three equations into the surface overpotential given in (41) leads to

$$F\eta_{\text{R}}^s = \mu_{\text{R}} + F(\phi_e - \phi) = \mu_{\text{R}} + F\Delta\phi, \quad (45)$$

where $\Delta\phi = \phi_e - \phi$ is the voltage drop across the electrode/electrolyte interface.

120 As mentioned, the subscript R in η is only to indicate that it is expressed by quantities in the reference configuration and it is independent from the chosen configuration. On the other hand, the flux $\hat{j}_s$ is flow rate per unit area and therefore it is dependent on the configuration. However, this dependence is fully described in the parameter c_s . Therefore Eq. (40), with the corresponding
125 c_s , is valid for both configurations. The same applies for the next section, where the reaction on the newly created crack surfaces is discussed.

By substituting (12), (26b) into (45), the normalized overpotential can be

expressed as

$$\eta^s = \frac{F\eta_R^s}{RT} = \ln \frac{c}{1-c} + \chi(1-2c) + \mu^e - \nabla \cdot \mathbf{K}^* \nabla c + \Delta\phi^*, \quad (46)$$

where $\mu^e = (1/RT)\partial\psi_R^e/\partial c_R$ is the normalized elastic chemical potential, $\Delta\phi^* = F\Delta\phi/(RT)$, $\mathbf{K}^* = \mathbf{K}/(RTL_0^2)$ and $\nabla = L_0 \nabla_R$. Here L_0 is a characteristic length which is introduced for normalization of the model discussed in Section 4.1

130 Note that, insertion of Li takes place on the surface for $\eta^s < 0$, while extrac-
tion of Li happens for $\eta^s > 0$. Thus, by choosing different voltage drop $\Delta\phi^*$,
the reaction can be controlled as forward and backward. In particular, when
the interfacial and elastic chemical potential is disregarded, $\eta^s = \mu^e + \Delta\phi^*$. As
shown in Figure 4(a), when $\Delta\phi^*$ is negative and large enough, the system will
135 absorb Li until $c = c_1$ is reached. On the other hand, as shown in Figure 4(c),
when $\Delta\phi^*$ is positive and large enough, Li will be deintercalated from the sys-
tem until $c = c_5$. However, when $-\Delta\phi^*$ stays between two spinodal points, as
shown in Figure 4(b), it is highly probable that both insertion and extraction
will take place at the same time towards $c = c_2$ and $c = c_3$, since the whole
140 system is unstable due to spinodal decomposition. Notice that c_2 and c_3 can be
different from the concentrations in two phases c_α and c_β , which are the results
of the spinodal decomposition. The values of c_2 and c_3 depend not only on the
chemical state of the material but also on the applied voltage potential drop
 $\Delta\phi^*$. The reaction on the surface will automatically constrain the concentration
145 in a way that the concentration will stay in the range from 0 to 1.

Substitution of (46) into (40) leads to

$$\hat{j}_s = \frac{c_s}{\tau_0} (1-c) \exp\left(-\frac{1}{2}\Delta\phi^*\right) - \frac{c_s}{\tau_0} c \exp\left[\chi(1-2c) + \mu^e - \nabla \cdot \mathbf{K}^* \nabla c + \frac{1}{2}\Delta\phi^*\right]. \quad (47)$$

3.2. Reaction on crack surfaces

In the framework of phase-field fracture models, the crack interface can be
tracked through $\xi(\xi-1) \neq 0$ or $\nabla\xi \neq 0$. Therefore, the boundary flux can be
weighted by functions containing either or both of these two terms, in order to
150 consider the reaction at the crack interface.

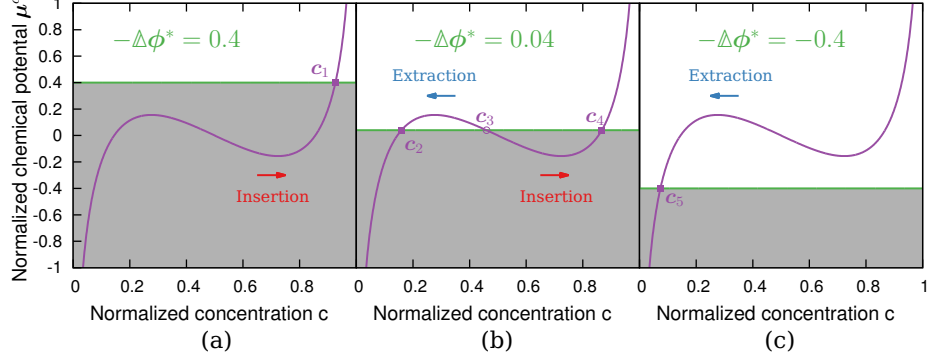


Figure 4: Insertion/extraction of Li under different normalized voltage drop $\Delta\phi^* = F\Delta\phi/(RT)$. The chemical potential $\mu^c = \ln c - \ln(1-c) + 2.5(1-2c)$.

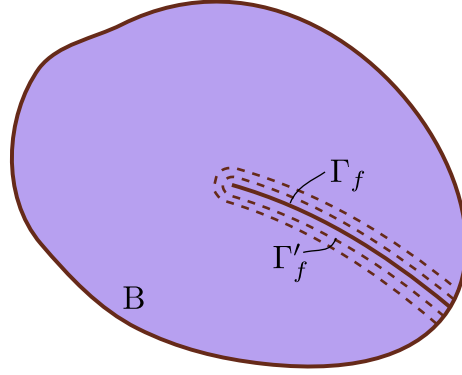


Figure 5: Schematics of the phase field crack

As shown in Figure 5, we denote the idealized crack surface by Γ_f (one crack will create two surfaces facing towards each other), and by Γ'_f the level surface in the phase-field model for a constant ξ . The damage variable gradient $\nabla\xi$ remains thus perpendicular to Γ'_f . Introduce a vector $\mathbf{s}$, which lies parallel to the damage variable gradient $\nabla\xi$. The flux on the crack surface can hence be approximated as the flux average across the interface

$$\int_{\Gamma_f} \hat{j}_s d\Gamma \approx \frac{1}{\epsilon} \int_s \int_{\Gamma'_f} g(\xi, \nabla\xi) \hat{j}_s d\Gamma' ds \approx \frac{1}{\epsilon} \int_B g(\xi, \nabla\xi) \hat{j}_s dB, \quad (48)$$

where ϵ is a length parameter which is related to the interface thickness. The weight function $g(\xi)$ contains either $\xi(\xi-1)$ or $\nabla\xi$ as a factor. If the flux is

kept constant across the interface or varies very little along the direction of $\nabla\xi$, we can observe the following relation

$$\frac{1}{\epsilon} \int_s \int_{\Gamma'_f} g(\xi, \nabla\xi) \hat{j}_s d\Gamma' ds \approx \frac{1}{\epsilon} \int_s g(\xi, \nabla\xi) ds \int_{\Gamma'} \hat{j}_s d\Gamma'. \quad (49)$$

It follows that the approximation of (48) is valid, if

$$\frac{1}{\epsilon} \int_s g(\xi, \nabla\xi) ds = 1. \quad (50)$$

It should be commented that there will be several factors that can influence the accuracy of the approximation.

- The phase-field approximation of the cracked phase interface will determine the choice of $g(\xi)$. Usually $g(\xi)$ is chosen based on an uncoupled model for simplicity. However, when the mechanical stresses come into play, the ξ profile can be different. The error can be even larger when $\xi(\xi - 1)$ is used as its weighting term, since ξ might not be 0 and 1 in two homogeneous phases, depending on the boundary condition given (the reader is referred to [30] for more details). Therefore $g(\xi)$ needs to be modified accordingly when the influence of stresses is not negligible;
- The flux can vary strongly across the phase interface, especially when the diffusion is so slow that the concentration varies strongly along the direction of $\nabla\xi$, making electrochemical reaction on/in the interface highly fluctuating in a small range. In these cases the equation (49) may not be accurate enough. One can, for instance, increase the polynomial order of $g(\xi)$, so that the fluctuation of the reaction will become negligible compared to $g(\xi)$.

As a simple case, we set $g(\xi) = A\xi^2(1 - \xi)^2$ with A being a coefficient to be determined. To this end, firstly, in the absence of stresses, the profile of $\tilde{\xi}(x)$ across the interface on one side can be obtained by solving the following

uncoupled 1D problem at equilibrium

$$\begin{cases} 0 = 2\mathcal{G}_c\epsilon\tilde{\xi}'' + \frac{1}{2}\frac{\mathcal{G}_c}{\epsilon}\left(1 - \tilde{\xi}\right), & (0 < x < L) \\ \tilde{\xi}|_{x=0} = 0, \\ \tilde{\xi}'|_{x=L} = 0. \end{cases} \quad (51)$$

The solution reads

$$\tilde{\xi}(x) = 1 - \cosh\left(\frac{x}{2\epsilon}\right) + \tanh\left(\frac{L}{2\epsilon}\right) \sinh\left(\frac{x}{2\epsilon}\right) = 1 - \cosh^{-1}\left(\frac{L}{2\epsilon}\right) \cosh\left(\frac{x-L}{2\epsilon}\right). \quad (52)$$

With the influence of the stress state, the equilibrium solution is assumed to be $\xi = \xi_0\tilde{\xi}$, where ξ_0 is the value of the damage variable in the homogeneous region after the relaxation but before the charging process. Inserting (52) into $g(\xi)$ and integrating over the whole length L , one obtains

$$\begin{aligned} 1 &= \frac{1}{\epsilon} A \int_0^L (\xi_0\tilde{\xi})^2 (\xi_0 - \xi_0\tilde{\xi})^2 dx \\ &= \frac{\xi_0^4}{\epsilon} A \int_0^L \left[1 - \cosh^{-1}\left(\frac{L}{2\epsilon}\right) \cosh\left(\frac{x-L}{2\epsilon}\right)\right]^2 \left[\cosh^{-1}\left(\frac{L}{2\epsilon}\right) \cosh\left(\frac{x-L}{2\epsilon}\right)\right]^2 dx \\ &\approx \frac{\xi_0^4}{\epsilon} A \cdot \frac{1}{6} \epsilon = \frac{A}{6} \xi_0^4, \end{aligned} \quad (53)$$

which gives $A = 6/\xi_0^4$ and $g(\xi) = 6\xi^2(\xi_0 - \xi)^2/\xi_0^4$. The evolution for the concentration can then be expanded from (34) as

$$\frac{\partial c_R}{\partial t} = \nabla_R \cdot [\xi^2 c(1-c) J \mathbf{F}^{-1} \mathbf{M} \mathbf{F}^{-T} \nabla_R \mu_R] + \frac{6}{\epsilon \xi_0^4} \xi^2 (\xi_0 - \xi)^2 \hat{j}_s, \quad (54)$$

in which $\hat{j}_s$ is given in (47) to account for the flux due to electrochemical reaction.

170 4. Numerical treatment

4.1. Normalization

For the convenience of finite element implementation, the model presented above is normalized first. Introduce a dimensionless form of space and time as

$$\bar{\mathbf{X}} = \frac{\mathbf{X}}{L_0}, \quad \bar{t} = \frac{D}{L_0^2} t \quad (55)$$

where L_0 is a characteristic length scale which is identical in the three directions, and D is a diffusion coefficient of one direction. The energy density is scaled by $RTc_{\max}$ and the other quantities can be normalized accordingly as

$$\psi = \frac{\psi_R}{RTc_{\max}}, \quad \mu = \frac{\mu_R}{RT}, \quad \mathbf{j} = \frac{L_0}{Dc_{\max}} \mathbf{j}_R, \quad \mathbf{S} = \frac{\mathbf{S}_R}{RTc_{\max}}, \quad \mathcal{H} = \frac{\mathcal{H}_R}{RTc_{\max}}. \quad (56)$$

For the fracture model, the normalized fracture length scale, energy release rate and the mobility are

$$\epsilon^* = \frac{\epsilon}{L_0}, \quad \mathcal{G}_c^* = \frac{\mathcal{G}_c}{L_0 RTc_{\max}}, \quad M_\xi^* = \frac{M_\xi L_0^2 RTc_{\max}}{D}. \quad (57)$$

For the reaction, the normalized surface site concentration c_s^* and the single reaction time step τ_0^* are

$$c_s^* = \frac{c_s}{c_{\max} L_0}, \quad \tau_0^* = \frac{D}{L_0^2} \tau_0. \quad (58)$$

Thus, the normalized governing equations can be summarized as:

$$\left\{ \begin{array}{ll} \nabla \cdot \mathbf{P} = \mathbf{0} & \text{in } B \times [0, \bar{\mathcal{T}}], \\ \dot{c} = \nabla \cdot [\xi^2 c(1-c) J \mathbf{F}^{-1} \mathbf{M}^* \mathbf{F}^{-T} \nabla \mu] + \frac{6}{\epsilon^* \xi_0^4} \xi^2 (\xi_0 - \xi)^2 \bar{j}_s, & \text{in } B \times [0, \bar{\mathcal{T}}], \\ \dot{\xi} = -M_\xi^* \left[2\xi \mathcal{H} - 2\mathcal{G}_c^* \epsilon^* \Delta \xi + \frac{\mathcal{G}_c^*}{2\epsilon^*} (\xi - 1) \right], & \text{in } B \times [0, \bar{\mathcal{T}}], \\ \bar{\mathbf{u}} = \hat{\mathbf{u}} & \text{on } S_{\bar{\mathbf{u}}} \times [0, \bar{\mathcal{T}}], \\ \mathbf{P} \cdot \mathbf{n} = \hat{\mathbf{t}} & \text{on } S_{\hat{\mathbf{t}}} \times [0, \bar{\mathcal{T}}], \\ \mathbf{j} \cdot \mathbf{n} = -\bar{j}_s & \text{on } \partial B \times [0, \bar{\mathcal{T}}], \\ \mathbf{K} \nabla c \cdot \mathbf{n} = 0 & \text{on } \partial B \times [0, \bar{\mathcal{T}}], \\ \nabla \xi \cdot \mathbf{n} = 0 & \text{on } \partial B \times [0, \bar{\mathcal{T}}], \\ c(\bar{\mathbf{X}}, 0) = c_0(\bar{\mathbf{X}}) & \text{in } B, \\ \xi(\bar{\mathbf{X}}, 0) = 0 & \text{on } \Gamma_f, \\ \xi(\bar{\mathbf{X}}, 0) = 1 & \text{in } B \setminus \Gamma_f, \end{array} \right. \quad (59)$$

with $\bar{j}_s$ defined as

$$\bar{j}_s = \frac{c_s^*}{\tau_0^*} (1-c) \exp\left(-\frac{1}{2} \Delta \phi^*\right) - \frac{c_s^*}{\tau_0^*} c \exp\left[\chi(1-2c) + \mu^e - \nabla \cdot \mathbf{K}^* \nabla c + \frac{1}{2} \Delta \phi^*\right]. \quad (60)$$

4.2. Implementation details

The model is implemented by using the finite element program FEAP [31] with Non-Uniform Rational B-Splines (NURBS) as shape functions for the spatial discretization, which allow for a straightforward treatment of the fourth-order Cahn-Hilliard equation. The displacements $\mathbf{u}$, the concentration c and the order parameter ξ are nodal degrees of freedom. In addition, to deal with the additional boundary condition $\mathbf{K}\nabla c \cdot \mathbf{n} = 0$ arising along with the Cahn-Hilliard equation, a Lagrange multiplier λ is introduced as an additional degree of freedom for each node. For more details about λ the reader is referred to our previous work [24]. A backward Euler method is employed for the time integration and the Newton-Raphson iteration scheme is used for the nonlinear system of equations at each time step.

The above mentioned 6 field variables are interpolated under an isoparametric/isogeometric concept as

$$\mathbf{u} = N^I \mathbf{u}^I, \quad c = N^I c^I, \quad \xi = N^I \xi^I, \quad \lambda = N^I \lambda^I \quad (61)$$

where $(\cdot)^I$ is the value at the I -th control point, and N^I is the NURBS shape function associated with the I -th control point. The repeated I invokes the Einstein summation. The gradient terms are thus given by

$$\delta \underline{\mathbf{E}} = \mathbf{B}_u^I \delta \mathbf{u}^I, \quad \nabla c = \mathbf{B}_c^I c^I, \quad \nabla \xi = \mathbf{B}_\xi^I \xi^I, \quad \nabla \lambda = \mathbf{B}_\lambda^I \lambda^I \quad (62)$$

where $\underline{\mathbf{E}}$ is the Green-Lagrangian strain tensor in Voigt notation,

$$\mathbf{B}_c^I = \mathbf{B}_\xi^I = \mathbf{B}_\lambda^I = \nabla N^I = \begin{bmatrix} N_{,1}^I & N_{,2}^I & N_{,3}^I \end{bmatrix}^T, \quad (63)$$

and

$$\mathbf{B}_u^I = \begin{bmatrix} F_{11}N_{,1}^I & F_{21}N_{,1}^I & F_{31}N_{,1}^I \\ F_{12}N_{,2}^I & F_{22}N_{,2}^I & F_{32}N_{,2}^I \\ F_{13}N_{,3}^I & F_{23}N_{,3}^I & F_{33}N_{,3}^I \\ F_{11}N_{,2}^I + F_{12}N_{,1}^I & F_{21}N_{,2}^I + F_{22}N_{,1}^I & F_{31}N_{,2}^I + F_{32}N_{,1}^I \\ F_{12}N_{,3}^I + F_{13}N_{,2}^I & F_{22}N_{,3}^I + F_{23}N_{,2}^I & F_{32}N_{,3}^I + F_{33}N_{,2}^I \\ F_{13}N_{,1}^I + F_{11}N_{,3}^I & F_{23}N_{,1}^I + F_{21}N_{,3}^I & F_{33}N_{,1}^I + F_{31}N_{,3}^I \end{bmatrix}. \quad (64)$$

Here, $N_{,i}^I$ denotes $\partial N^I / \partial X_i$, and F_{ij} are the components of the deformation gradient $\mathbf{F}$.

Thus, the discretized weak form of (59) reads

$$\delta \Pi = (\delta \mathbf{u}^I)^T \mathbf{R}_u^I + \delta c^I \mathbf{R}_c^I + \delta \xi^I \mathbf{R}_\xi^I + \delta \lambda^I \mathbf{R}_\lambda^I = 0, \quad (65)$$

in which the residuals are

$$\mathbf{R}_u^I = - \int_B (\mathbf{B}_u^I)^T \left[(\xi^2 + \eta) \frac{\partial \psi^{e+}}{\partial \underline{\mathbf{E}}} + \frac{\partial \psi^{e-}}{\partial \underline{\mathbf{E}}} \right] \mathrm{d}B, \quad (66a)$$

$$\begin{aligned} \mathbf{R}_c^I = & \int_B \dot{c} N^I \mathrm{d}B + \int_B \xi^2 [1 - 2\chi c(1 - c)] J (\nabla c \cdot \mathbf{F}^{-1} \mathbf{M}^* \mathbf{F}^{-T} \nabla N^I) \mathrm{d}B \\ & + \int_B \xi^2 c(1 - c) J (\nabla \mu^e \cdot \mathbf{F}^{-1} \mathbf{M}^* \mathbf{F}^{-T} \nabla N^I) \mathrm{d}B \\ & + \int_B 2\xi c(1 - c) J (\nabla \cdot \mathbf{K}^* \nabla c) (\nabla \xi \cdot \mathbf{F}^{-1} \mathbf{M}^* \mathbf{F}^{-T} \nabla N^I) \mathrm{d}B \\ & + \int_B \xi^2 (1 - 2c) J (\nabla \cdot \mathbf{K}^* \nabla c) (\nabla c \cdot \mathbf{F}^{-1} \mathbf{M}^* \mathbf{F}^{-T} \nabla N^I) \mathrm{d}B \\ & + \int_B \xi^2 c(1 - c) (\nabla \cdot \mathbf{K}^* \nabla c) (\nabla J \cdot \mathbf{F}^{-1} \mathbf{M}^* \mathbf{F}^{-T} \nabla N^{-1}) \mathrm{d}B \\ & + \int_B \xi^2 c(1 - c) (\nabla \cdot \mathbf{K}^* \nabla c) \Delta N^I \mathrm{d}B \\ & + \int_B \xi^2 c(1 - c) J (\nabla \cdot \mathbf{K}^* \nabla c) [(\nabla \cdot \mathbf{F}^{-1} \mathbf{M}^* \mathbf{F}^{-T}) \cdot \nabla N^I] \mathrm{d}B \\ & + \int_B \xi^2 c(1 - c) J (\nabla \cdot \mathbf{K}^* \nabla c) (\mathbf{F}^{-1} \mathbf{M}^* \mathbf{F}^{-T} : \nabla \nabla N^I) \mathrm{d}B \\ & - \int_B \frac{6\xi^2 (\xi_0 - \xi)^2}{\epsilon^* \xi_0^4} \hat{j}_s N^I \mathrm{d}B - \int_{\partial B} \hat{j}^s N^I \mathrm{d}S \\ & + \int_B \nabla \lambda \cdot \mathbf{K}^* \nabla N^I \mathrm{d}B + \int_B \lambda \nabla \cdot \mathbf{K}^* \nabla N^I \mathrm{d}B, \end{aligned} \quad (66b)$$

$$\begin{aligned} \mathbf{R}_\xi^I = & \int_B \dot{\xi} N^I \mathrm{d}B - \int_B \mathbf{M}_\xi^* \left[2\xi \mathcal{H} + \frac{\mathcal{G}_c^*}{2\epsilon^*} (\xi - 1) \right] N^I \mathrm{d}B \\ & - \int_B \mathbf{M}_\xi^* \cdot 2\mathcal{G}_c^* \epsilon^* \nabla \xi \cdot \nabla N^I \mathrm{d}B \end{aligned} \quad (66c)$$

$$\mathbf{R}_\lambda^I = \int_B \nabla \cdot \mathbf{K}^* \nabla c N^I \mathrm{d}B + \int_B \mathbf{K}^* \nabla c \cdot \nabla N^I \mathrm{d}B - \frac{1}{\alpha} \int_B \lambda N^I \mathrm{d}B. \quad (66d)$$

The construction of the corresponding tangent matrices can be achieved according to the finite element theory.

5. Simulation results

5.1. Reaction on the particle surface

190 To study the phase segregation under different diffusion and reaction limits,
a sphere with isotropic material is considered, where a homogeneous initial and
boundary setup is furthermore given. Symmetric mechanical constraints are
applied on the planes of symmetry, while the spherical surface is set free from
stresses. The electrochemical reaction takes place on the surface of the sphere,
195 across which a constant voltage drop $\Delta\phi$ is prescribed. It drives the reaction,
such that the neutral Lithium is produced (consumed) until the particle is fully
(dis-)charged. The reaction rate is controlled by the single reaction step time
 τ_0 which is given as 0.01 s for a fast reaction and 1 s for a slow reaction. The
parameters for the simulation are given in Table 1.

Gas constant (R)	$8.32 \text{ J mol}^{-1} \text{ K}^{-1}$
Absolute temperature (T)	283 K
Diffusivity (D)	$7.08 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$
Faraday's constant (F)	96 485 C mol ⁻¹
Partial molar volume (Ω)	$3.497 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$
Maximum concentration (c_{max})	$2.29 \times 10^4 \text{ mol m}^{-3}$
Phase parameter (χ)	2.5
Interface parameter (κ)	$1.0 \times 10^{-10} \text{ J mol}^{-1} \text{ m}^2$
Length scale (L_0)	1 μm
Bulk modulus slope (K_0)	100 MPa
Shear modulus slope (G_0)	100 MPa
Concentration intercept (c_{in})	10.0
Surface site concentration (c_s)	$6.78 \times 10^{-6} \text{ mol m}^{-2}$
Single reaction step time (τ_0)	0.01 s (fast)/1 s (slow)
Voltage drop electrode/electrolyte ($\Delta\phi$)	-4.88 mV
Initial normalized concentration (c_0)	0.25

Table 1: Parameters for the simulation of the spherical particle.

200 The state of charge (SOC) with respect to time is measured in the simulation
by integrating all the Lithium inside the particle at each current time compared
with the amount in a full lithiation ($c_R = c_{\text{max}}$). The results are shown in
Figure 6. The solid lines describe the simulated SOC with respect to time.

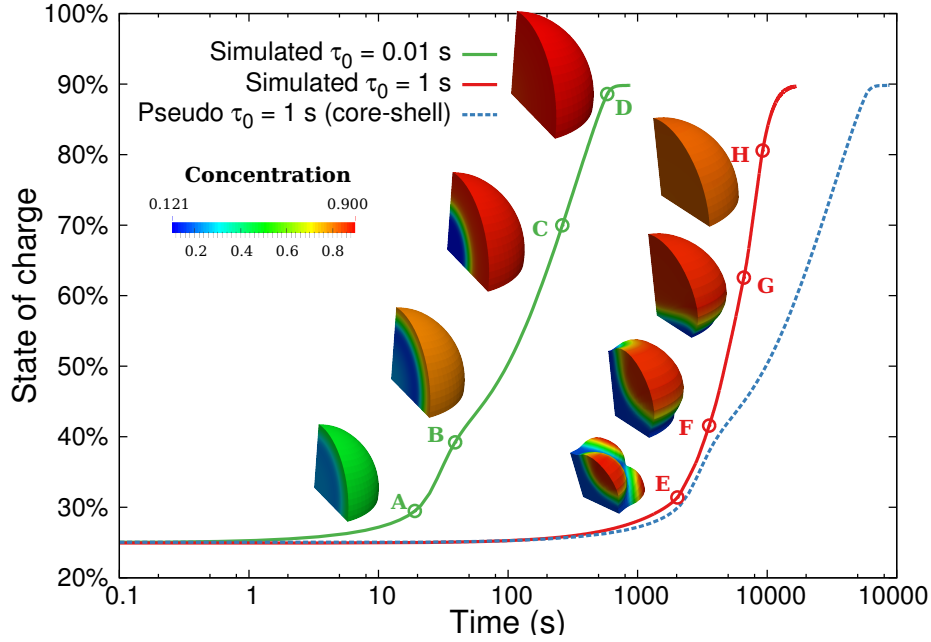


Figure 6: The SOC and the corresponding concentration profile of the particle at different charge rate. A fast reaction (green line) can give a core-shell structure while a slow reaction (red line) will not preserve the core-shell. However, the latter can give a more robust reaction after the phase segregation occurs. The pseudo plot is the curve when the core-shell structure is enforced when $\tau_0 = 1$ s.

Both curves show the same tendency of the reaction, which is fairly fast at the beginning and slows down towards the end of the charge. Both of them show an acceleration of reaction when the particle is charged at roughly 30% (A, E), because in both cases the phases start to form and the overpotential η^s increases rapidly as the concentration increases, which can be seen in Figure 4 (a).

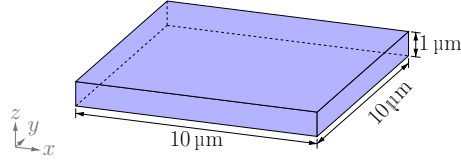
However, the phase segregation is very different in the two cases. The green line shows that, when the reaction is fast enough, a core-shell structure can be achieved. This is in agreement with the predictions in the work of Singh et al. [32], which stated that in an isotropic bulk-transport-limited case, where the bulk diffusion is much slower than the reaction, the phase boundary is driven largely by the incoming flux, thus a shrinking-core profile being formed. On the

215 other hand, as shown by the red line, when the surface reaction is slow enough,
 the species can be always equilibrated by the bulk transport. In this case,
 the spinodal decomposition, or nucleation, initiates from the surface, where the
 dynamics of reaction can cause strong fluctuations in the species concentration.
 They are very unstable inside the spinodal region. The reaction in the core-
 220 shell structure slows down as the two phase region is finally formed (B, C),
 because the outer shell approaches a full lithiation. However, in the other case,
 the reaction maintains its rate (F, G) until the phase segregation is suppressed.
 Based on the simulation results of the case $\tau_0 = 0.01$ s, one can predict the state
 of charge curve for $\tau_0 = 1$ s when the core-shell structure is enforced, simply
 225 by scaling the time of the fast case by a factor of 100. For comparison, this
 predicted result is shown by the curve in blue color in Fig. 6. It shows that
 if the core-shell structure is maintained, the lithiation process becomes slower
 than that in the case when the particle is free to adjust the phase pattern for a
 more robust reaction.

230 5.2. Reaction inside the interface

To investigate the reaction in different phases and in the phase interface,
 a square plate with isotropic and anisotropic chemical properties is studied in
 this section. The geometry is given in Figure 7. No preferred direction for the
 reaction is assumed. Therefore, in the simulation, the reaction will take place
 235 on all six surfaces of the plate and the reaction rate is governed by the chemical
 state at each position on the surface. The anisotropic interfacial parameter κ
 and diffusivity D in different directions are given in Table 2. In this model, the
 mechanical part is disregarded.

In the isotropic case, as shown in Figure 8, the flux is marching towards the
 240 interior from all four sides and the phase segregation of a Li-rich frame and a
 Li-deficient center forms. As more flux comes in, there arises an island of Li-rich
 phase in the middle of the Li-poor phase. This can be explained by the dynamics
 of diffusion and reaction, where the whole system is perturbed strongly and it
 is easy to achieve a phase segregation once the magnitude of fluctuation is large



Interfacial Parameter	κ_x	$1.0 \times 10^{-10} \text{ J mol}^{-1} \text{ m}^{-2}$
	κ_y	$1000 \kappa_x$
	κ_z	$1000 \kappa_x$
Diffusivity	D_x	$7.08 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$
	D_y	$1000 D_x$
	D_z	$1000 D_x$
Sing. reac.	τ_0	1 s

Figure 7: Sketch and measurements of the square plate problem. All six surfaces of the plate are exposed to the electrolyte. Therefore electrochemical reaction can take place on all sides.

Table 2: Anisotropic interface and diffusivity parameters for the plate problem. For the isotropic case, the parameters for x direction are used for all three directions. All other parameters are given in Table 1.

245 enough. As for the reaction, by comparing the concentration profile and the reaction rate, one can observe that the reaction peaks at the interface front, where the concentration gradient is very high. In the two homogeneous phases, the reaction is relatively slow, especially in the Li-rich phase, where the reaction almost stops. This low efficiency of reaction in the Li-rich phase explains again
250 why the core-shell structure is lithiated much slower than the other, studied in the last subsection.

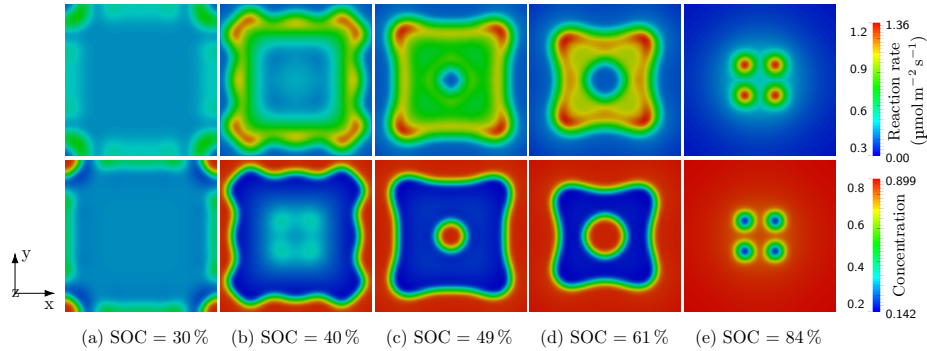


Figure 8: Contour plot of the reaction rate and the concentration SOC in an isotropic diffusion process. The peak of the reaction will always take place near the interface.

Figure 9 shows the case of an anisotropic diffusion. As explained in the section 2.3, the interfacial parameter is chosen in such a way that $\kappa_x/D_x =$

$\kappa_y/D_y = \kappa_z/D_z$. In the simulation, the diffusion in x direction is set to be
 255 slowest. Note that even though the diffusivity in y, z direction is the same,
 in z-direction lithium sites are filled faster than in y-direction. This is due to
 the fact that the dimension in z-direction is smaller than that in y-direction.
 In contrast to the isotropic case, phase segregation initiates from the two ends
 although the reaction takes place in all six sides of x axis. As time goes on,
 260 the phase interface marches towards the center. A third Li-rich phase appears
 in the middle when SOC is approximately 50 %, thus the formation of stripes
 appears. This result supports the domino-cascade model of LiFePO_4 , which was
 proposed in the work of Delma et al. [33]

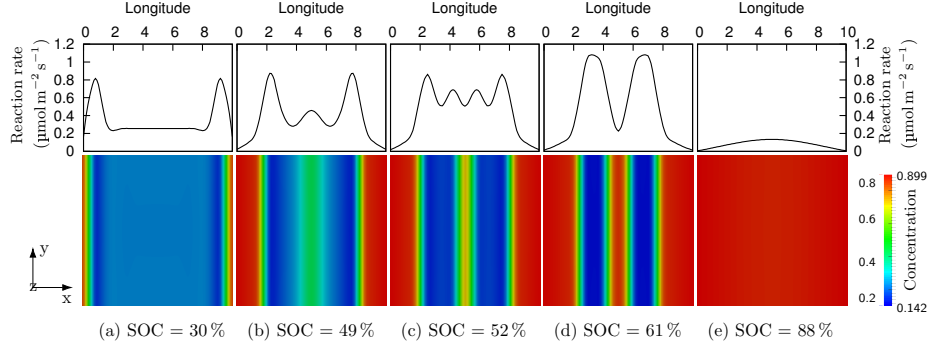


Figure 9: Contour plot of the concentration and plot of the reaction rate along the direction of the slowest diffusion (x direction) at different SOC in an anisotropic diffusion process.

These two cases are extreme. However, with a proper implementation of
 265 crystal anisotropy, by filling the diffusion matrix also in the off-diagonal entries,
 one can also achieve a core-shell structure with a polygonal core, as observed in
 the work of Liu et al. [34].

5.3. Reaction on the crack surface

As final example, we simulate an infinitely long cylinder with two initial
 parallel longitudinal cracks on its exterior. The problem is illustrated in Fig-
 ure 10, and the corresponding parameters are given in Table 3. The elec-

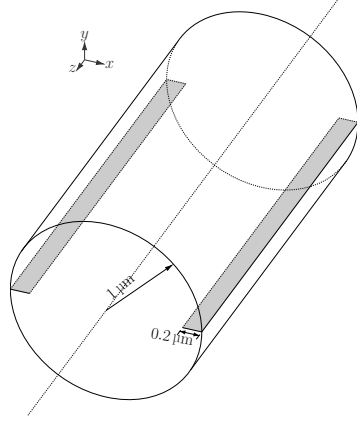


Figure 10: Illustration and dimensions of an infinite cylinder with initial cracks. One quarter of a disc with a thickness of $1\text{ }\mu\text{m}$ under plane strain assumption is simulated.

Voltage drop eld./ely. ($\Delta\phi$)	4.88 mV
Single reac. step time (τ_0)	0.01 s
Initial concentration (c_0)	0.8
Fracture resistance ($\mathcal{G}_c$)	$6 \times 10^{-2} \text{ N m}^{-1}$
Crack length scale (ϵ)	0.05 μm
Crack mobility (M_c)	$1.3 \times 10^{-3} \text{ J m}^{-3} \text{ s}^{-1}$

Table 3: Simulation parameters for the crack propagation problem. Others parameters can be found in Table 1.

trode/electrolyte voltage drop is given such that Li is extracted from the cylinder. The reaction only takes place on the cylindrical surface and the crack surface. As it is explained in section 3.2, the reaction on the crack surface is approximated by the weighted source in the phase-field theory. The initial crack is imposed through the strain history field $\mathcal{H}_R$ such that an initial fracture order parameter ξ is determined. $\mathcal{H}_R$ is given at initialization as

$$\mathcal{H}_R(\bar{\mathbf{X}}, 0) = 10^3 \times \frac{\mathcal{G}_c^*}{4\epsilon^*} \left(1 - \frac{d}{\epsilon^*}\right) \quad \text{with} \quad d = \min \{ \text{dist}(\bar{\mathbf{X}}, \Gamma_f), \epsilon^* \} \quad (67)$$

where $\text{dist}(\bar{\mathbf{X}}, \Gamma_f)$ is the closest distance of a material point $\bar{\mathbf{X}}$ to the crack Γ_f .

For more details the readers are referred to the work of Borden et al. [30]. In order to reach the diffusive profile for the initial crack, the reaction is set to be zero for the first 3 seconds.

The results of the crack propagation is shown in Figure 11. Initially, the concentration field is homogeneous. As the outer layer loses more lithium, a two-phase profile appears. It should be noted that at the crack tip lithium can be supplied quickly from the unbroken material. In fact, due to the large

tensile stresses at the crack tip, the drift effect of the mechanical field towards the crack tip becomes prominent. The phase interface overtakes the crack tip and the fracture branching occurs at the interface, where there are intensified stresses.

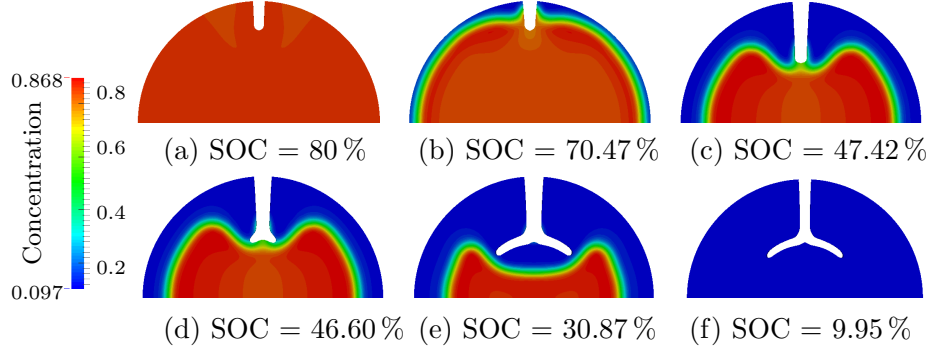


Figure 11: Crack propagation under delithiation and phase segregation. a) Initial homogeneous state. b) Formation of phase segregation initiates the crack propagation. c) Intermediate stage when the phase interface catches up with the crack tip. d) Stage when the crack tip starts to branch at the phase interphase. e) Stage when phase interface leaves crack tip and moves towards center, the crack is perpendicular to the phase interface. f) Final stage when the reaction stops.

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On the other hand, due to the loss of lithium, the outer layer turns to shrink. Because of this mismatch with the interior Li-rich phase, tensile circumferential stresses arise in the outer layer, which drive the crack to propagate. At the first stage, the crack propagates faster than the interface. It then slows down, until the phase interface runs over the crack tip. After the phase interface leaves the crack, the propagation of crack turns to stop, due to the decrease of the driving force. However, the phase interface continues to move. At the end of the simulation, the whole material is almost fully delithiated, and the reaction stops. It should be mentioned that the interplay between the phase segregation and the crack propagation can strongly depend on the choice of the kinetics parameters. A more comprehensive study on this topic will be carried out in the future.

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During the whole process, lithium can indeed be released on the crack surface. To check the approximated reaction on the crack surface, the reaction and the corresponding concentration profile on the circular plate at SOC = 46.60 %
 295 are demonstrated in Fig. 12. At this state, the phase interface overtakes the crack tip and the crack starts to branch. By comparing the contour plots of concentration and reaction, it can be seen that near the crack surface the reaction is very strong in the neighborhood of the phase interface, with peaks at the crack tip.

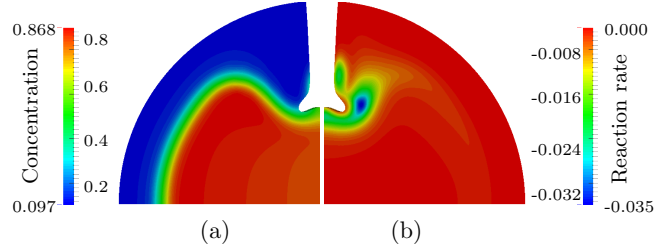


Figure 12: Reaction rate at the crack interface. a) The concentration profile when SOC = 46.60 %. b) The simulated reaction rate around the crack interface.

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6. Conclusion

In this paper, the electrochemical reaction in the lithium ion batteries is studied by using phase-field modeling of fracture coupled with anisotropic Cahn-Hilliard-type diffusion in the large deformation regime.

305 The reaction on the surface is modeled through a modified Butler-Volmer equation, taking into account the influence of phase separation on the surface. The reaction on the crack surface is considered as a source term within the volume, weighted by a damage-variable-related term to constrain the reaction to take place only on the transition zone between the unbroken and broken
 310 state.

Three examples are carried out to study different aspects. The first example of an isotropic sphere shows that the ratio of the timescale of the reaction and

diffusion strongly influences the phase segregation of the material: a fast reaction gives a “shrinking core”, while for a slow reaction the nucleation initiated from the surface early on. In turn, the phase segregation also influences the real reaction rate through the electrochemical potential on the surface. When a core-shell structure is formed, the highly homogeneous concentration on the surface prevents the lithium from further inserting into the particle. However, an uneven distribution of the concentration, although accompanied by a highly distorted surface, can give a much more robust reaction in the long run. In the second example, the reaction on the interface of two phases in an isotropic diffusion case and an anisotropic diffusion case is studied. The results show that, both in isotropic and anisotropic cases, the reaction rate peaks near the interface, where there exists a large concentration gradient. Orthotropic diffusion as in the example has been observed in many cathode materials such as LiFePO_4 [2, 33]. The last example shows the reaction on the crack surface. It is shown that the crack evolution can be driven by an outflow of the species when the material exhibits a phase segregation behavior. The electrochemical reaction on the newly created crack surfaces has been discussed, along with the interaction between the crack propagation and the phase segregation process.

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References

- [1] U. Kasavajjula, C. Wang, A. J. Appleby, Nano- and bulk-silicon-based insertion anodes for lithium-ion secondary cells, *Journal of Power*

- 340 Sources 163 (2) (2007) 1003–1039. doi:<http://dx.doi.org/10.1016/j.jpowsour.2006.09.084>.
- [2] G. K. Singh, G. Ceder, M. Z. Bazant, Intercalation dynamics in rechargeable battery materials: General theory and phase-transformation waves in LiFePO_4 , *Electrochimica Acta* 53 (26) (2008) 7599–7613. doi:[10.1016/j.electacta.2008.03.083](http://dx.doi.org/10.1016/j.electacta.2008.03.083).
345
- [3] P. Bai, D. A. Cogswell, M. Z. Bazant, Suppression of Phase Separation in LiFePO_4 Nanoparticles During Battery Discharge, *Nano Letters* 11 (11) (2011) 4890–4896. doi:[10.1021/nl202764f](http://dx.doi.org/10.1021/nl202764f).
- [4] S. Dargaville, T. W. Farrell, The persistence of phase-separation in LiFePO_4 with two-dimensional Li^+ transport: The Cahn-Hilliard-reaction equation and the role of defects, *Electrochimica Acta* 94 (2013) 143–158. doi:[10.1016/j.electacta.2013.01.082](http://dx.doi.org/10.1016/j.electacta.2013.01.082).
350
- [5] C. V. Di Leo, E. Rejovitzky, L. Anand, A Cahn-Hilliard-type phase-field theory for species diffusion coupled with large elastic deformations: Application to phase-separating Li-ion electrode materials, *Journal of the Mechanics and Physics of Solids* 70 (2014) 1–29. doi:[10.1016/j.jmps.2014.05.001](http://dx.doi.org/10.1016/j.jmps.2014.05.001).
355
- [6] H. Dal, C. Miehe, Computational electro-chemo-mechanics of lithium-ion battery electrodes at finite strains, *Computational Mechanics* 55 (2) (2014) 303–325. doi:[10.1007/s00466-014-1102-5](http://dx.doi.org/10.1007/s00466-014-1102-5).
360
- [7] J. Christensen, J. Newman, Stress generation and fracture in lithium insertion materials, *Journal of Solid State Electrochemistry* 10 (5) (2006) 293–319. doi:[10.1007/s10008-006-0095-1](http://dx.doi.org/10.1007/s10008-006-0095-1).
- [8] X. Zhang, W. Shyy, A. M. Sastry, Numerical simulation of intercalation-induced stress in Li-ion battery electrode particles, *Journal of The Electrochemical Society* 154 (10) (2007) A910–A916. doi:[10.1149/1.2759840](http://dx.doi.org/10.1149/1.2759840).
365

- [9] P. Stein, B. Xu, 3D Isogeometric Analysis of intercalation-induced stresses in Li-ion battery electrode particles, *Computer Methods in Applied Mechanics and Engineering* 268 (2014) 225–244. doi:10.1016/j.cma.2013.09.011.
- [10] S. Huang, F. Fan, J. Li, S. Zhang, T. Zhu, Stress generation during lithiation of high-capacity electrode particles in lithium ion batteries, *Acta Materialia* 61 (12) (2013) 4354–4364. doi:10.1016/j.actamat.2013.04.007.
- [11] M. Huttin, M. Kamlah, Phase-field modeling of stress generation in electrode particles of lithium ion batteries, *Applied Physics Letters* 101 (13) (2012) 133902. doi:10.1063/1.4754705.
- [12] A.-C. Walk, M. Huttin, M. Kamlah, Comparison of a phase-field model for intercalation induced stresses in electrode particles of lithium ion batteries for small and finite deformation theory, *European Journal of Mechanics - A/Solids* 48 (2014) 74–82. doi:10.1016/j.euromechsol.2014.02.020.
- [13] J. Rohrer, K. Albe, Insights into Degradation of Si Anodes from First-Principle Calculations, *The Journal of Physical Chemistry C* 117 (37) (2013) 18796–18803. doi:10.1021/jp401379d.
- [14] J. Rohrer, A. Moradabadi, K. Albe, P. Kaghazchi, On the origin of anisotropic lithiation of silicon, *Journal of Power Sources* 293 (2015) 221–227. doi:10.1016/j.jpowsour.2015.05.057.
- [15] G. Chen, X. Song, T. J. Richardson, Electron Microscopy Study of the LiFePO_4 to FePO_4 Phase Transition, *Electrochemical and Solid-State Letters* 9 (6) (2006) A295–A298. doi:10.1149/1.2192695.
- [16] C. V. Ramana, A. Mauger, F. Gendron, C. M. Julien, K. Zaghib, Study of the Li-insertion/extraction process in $\text{LiFePO}_4/\text{FePO}_4$, *Journal of Power Sources* 187 (2) (2009) 555–564. doi:10.1016/j.jpowsour.2008.11.042.
- [17] D. Schneider, M. Selzer, J. Bette, I. Rementeria, A. Vondrous, M. J. Hoffmann, B. Nestler, Phase-Field Modeling of Diffusion Coupled Crack Prop-

- 395 agation Processes, *Advanced Engineering Materials* 16 (2) (2014) 142–146.
 doi:10.1002/adem.201300073.
- [18] L. Liang, M. Stan, M. Anitescu, Phase-field modeling of diffusion-induced
 crack propagations in electrochemical systems, *Applied Physics Letters*
 105 (16) (2014) 163903. doi:10.1063/1.4900426.
- 400 [19] P. Zuo, Y.-P. Zhao, A phase field model coupling lithium diffusion and stress
 evolution with crack propagation and application in lithium ion batteries,
 Physical Chemistry Chemical Physics 17 (1) (2014) 287–297. doi:10.1039/
 C4CP00563E.
- [20] C. Miehe, H. Dal, L.-M. Schänzel, A. Raina, A phase-field model for chemo-
 mechanical induced fracture in lithium-ion battery electrode particles, In-
 405 ternational Journal for Numerical Methods in Engineering 106 (9) (2016)
 683–711. doi:10.1002/nme.5133.
- [21] M. Z. Bazant, Theory of Chemical Kinetics and Charge Transfer based on
 Nonequilibrium Thermodynamics, *Accounts of Chemical Research* 46 (5)
 410 (2013) 1144–1160. doi:10.1021/ar300145c.
- [22] J. W. Cahn, J. E. Hilliard, Free energy of a nonuniform system. I. interfacial
 free energy, *The Journal of Chemical Physics* 28 (26) (1958) 258–267. doi:
 10.1016/j.electacta.2008.03.083.
- [23] B. Bourdin, G. A. Francfort, J.-J. Marigo, The Variational Approach
 to Fracture, *Journal of Elasticity* 91 (1-3) (2008) 5–148. doi:10.1007/
 415 s10659-007-9107-3.
- [24] Y. Zhao, P. Stein, B.-X. Xu, Isogeometric analysis of mechanically coupled
 Cahn–Hilliard phase segregation in hyperelastic electrodes of Li-ion batter-
 ies, *Computer Methods in Applied Mechanics and Engineering* 297 (2015)
 420 325–347. doi:10.1016/j.cma.2015.09.008.

- [25] C. Kuhn, R. Müller, A continuum phase field model for fracture, *Engineering Fracture Mechanics* 77 (18) (2010) 3625–3634. doi:10.1016/j.engfracmech.2010.08.009.
- [26] C. Kuhn, A. Schlüter, R. Müller, On degradation functions in phase field fracture models, *Computational Materials Science* 108, Part B (2015) 374–384. doi:10.1016/j.commatsci.2015.05.034.
- [27] A. Schlüter, A. Willenbücher, C. Kuhn, R. Müller, Phase field approximation of dynamic brittle fracture, *Computational Mechanics* 54 (5) (2014) 1141–1161. doi:10.1007/s00466-014-1045-x.
- [28] C. Miehe, M. Hofacker, F. Welschinger, A phase field model for rate-independent crack propagation: Robust algorithmic implementation based on operator splits, *Computer Methods in Applied Mechanics and Engineering* 199 (45-48) (2010) 2765 – 2778. doi:http://dx.doi.org/10.1016/j.cma.2010.04.011.
- [29] C. Miehe, L.-M. Schänzel, H. Ulmer, Phase field modeling of fracture in multi-physics problems. Part I. Balance of crack surface and failure criteria for brittle crack propagation in thermo-elastic solids, *Computer Methods in Applied Mechanics and Engineering* 294 (2015) 449 – 485. doi:http://dx.doi.org/10.1016/j.cma.2014.11.016.
- [30] M. J. Borden, C. V. Verhoosel, M. A. Scott, T. J. R. Hughes, C. M. Landis, A phase-field description of dynamic brittle fracture, *Computer Methods in Applied Mechanics and Engineering* 217–220 (2012) 77–95. doi:10.1016/j.cma.2012.01.008.
- [31] R. L. Taylor, FEAP - finite element analysis program (2014).
URL <http://www.ce.berkeley.edu/projects/feap>
- [32] G. K. Singh, G. Ceder, M. Z. Bazant, Intercalation dynamics in rechargeable battery materials: General theory and phase-transformation waves in

LiFePO₄, *Electrochimica Acta* 53 (26) (2008) 7599–7613. doi:10.1016/j.
electacta.2008.03.083.

450 [33] C. Delmas, M. Maccario, L. Croguennec, F. Le Cras, F. Weill, Lithium
deintercalation in LiFePO₄ nanoparticles via a domino-cascade model, *Nature Materials* 7 (8) (2008) 665–671. doi:10.1038/nmat2230.

[34] X. H. Liu, L. Zhong, S. Huang, S. X. Mao, T. Zhu, J. Y. Huang, Size-
Dependent Fracture of Silicon Nanoparticles During Lithiation, *ACS Nano*
455 6 (2) (2012) 1522–1531. doi:10.1021/nm204476h.