BROWN UNIVERSITY

ENGN 2340 Final Project

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Contents

1 Introduction

Recently in response to the need of consumer electronics for longer operation of devices and sustainable energy consumption, battery has been received significant attention. Among them LiFePO4 and graphite emerged as popular cathode and anode materials respectively for their high rate and capability. Despite their wide usage, there's still a lack of understanding for their underlying physics which limit our engineering ability to develop new materials that will surpass them or improve their lifetime/capability. In particular, these material has been discovered to exhibit complex phase-separating behavior during lithiation/delithiation. In addition, there are large stresses. accompany phase-separation lead to mechanical damage and degradation of the battery. In this report, I will attempt to investigate morphology of these materials upon lithiation using FEM.

2 Theory

We employ a coupled chemo-mechanical Cahn-Hilliard-type continuum model with linear elasticity to predict the intercalation in a LixFePO4 and LixC6. The state of each material point is described by a normalized Li concentration field (0<c<1) and strain tensor field ϵ. The free energy of he material in a particle domain B is:

$$F = \int_B (f^c(c) + f^e(\epsilon) + f^{CH}(\nabla c))dV \tag{1}$$

where f^c is homogeneous free energy density, f^e is the elastic energy density, $f^C H$ is the Cahn-Hilliard phase boundary energy. Energy has been normalized with respect to RT, where R is gas constant and T is the temperature. The chemical energy density is typically described by regular solution model in the literature. However, because lithium exhibit complicated phase separation which involves more than 2 phases coexist. It will be quite difficult to employ such model. Therefore, in this work, I will consider homogeneous energy of a polynomial forms:

$$f^c = \sum_{n=0}^{\infty} a_n c^n \tag{2}$$

the exact form (polynomial order and values of coefficients) will be considered as parameters to be tuned in order to capture the physics of these two materials. The elastic energy is taken in the classic linear elasticity form with an additional chemical term:

$$f^e = \frac{1}{2}\left(\epsilon_{ij} - \frac{\Omega}{3}c\delta_{ij}\right)C_{ijkl}\left(\epsilon_{kl} - \frac{\Omega}{3}c\delta_{kl}\right) \tag{3}$$

Finally the Cahn-Hilliard gradient energy which describes the interfacial tension of the diffuse phase boundary, may be written as follows:

$$f^{CH} = \frac{1}{2}\kappa|\nabla c|^2 \tag{4}$$

Taking the variational derivatives of the free energy with respect to concentration leads to the diffusional chemical potential, μ

$$\mu = \frac{\delta F}{\delta c} = \frac{df^c}{dc} - \kappa \nabla^2 c - \frac{\Omega}{3}\sigma_{kk} = f(c) - \kappa \nabla^2 c - \frac{\Omega}{3}\sigma_{kk} \tag{5}$$

where:

$$\sigma_{ij} = C_{ijkl}\epsilon_{kl} \tag{6}$$

Here we will assume our materials are isotropic mechanically for simplicity. This leads to the following constitutive relation:

$$\sigma_{ij} = \frac{E}{(1+\nu)}\left(\epsilon_i j + \frac{\nu}{1-2\nu}\epsilon_{kk}\delta_{ij}\right) - \frac{E}{1-2\nu}\frac{\Omega}{3}c\delta_{ij} \tag{7}$$

where E and ν are Young's modulus and Poisson's ratio respectively. Balance laws yields the following sets of governing partial differential equations:

$$\nabla \cdot \boldsymbol{\sigma} = 0 \tag{8}$$

$$\frac{\partial c}{\partial t} = D\nabla^2 \mu \tag{9}$$

where D is normalized diffusivity of lithium which we're taken as constant. To simulate lithiation/delithiation we will simple prescribed a constant flux on each node of a boundary, which correspond to potentiostatic charging/discharging condition in the battery. Initial condition for this system is taken to be the same as homework 8, 0.01 initial concentration with sinusoidal spatial variation.

3 Abaqus Implementation

The implementation of these equations are the same as in homework 8. Turning this set of equations into weak forms along with our usual interpolation function give the following set of discrete equations:

$$M_{ab}\frac{dc^b}{dt} + DK_{ab}\mu^b = 0 \qquad M_{ab}\mu^b - H^a(c^b) + \kappa P_{ab}c^b = 0$$

where

$$M_{ab} = \int_V N^a N^b dV \qquad P_{ab} = \int_V \frac{\partial N^a}{\partial x_i}\frac{\partial N^b}{\partial x_i} dV \qquad H^b = \int_V \frac{df^c}{dc} - \frac{\Omega}{3}\sigma_{kk}N^b dV$$

A generalized mid-point inegration scheme is used to integrate concentration while backward Euler method will be used to integrate μ. This give:

$$M_{ab}\left(\mu^b + \Delta\mu^b\right) - H^a - \kappa P_{ab}(c^b + \Delta c^b) \quad = 0 \tag{10}$$

$$M_{ab}\frac{\Delta c^b}{\Delta t} + DP_{ab}\left[(1-\theta)\mu^b + \theta(\mu^b + \Delta\mu^b)\right] \quad = 0 \tag{11}$$

where $0 < \theta < 1$ is a numerical parameter. In our simulation θ of 0.5 will be used. We will be using a quadratic 8-node element to interpolate the displacement fields while using linear interpolation between the 4 nodes in the corner for concentration fields. Thus:

$$\begin{bmatrix} \varepsilon_{11} \\ \varepsilon_{22} \\ 2\varepsilon_{12} \\ \mu \\ c \\ \partial\mu / \partial x_1 \\ \partial\mu / \partial x_2 \\ \partial c / \partial x_1 \\ \partial c / \partial x_2 \end{bmatrix} = [\mathbf{B}] \begin{bmatrix} u_1^1 \\ u_2^1 \\ \mu^1 \\ c^1 \\ u_1^2 \\ u_2^2 \\ \mu^2 \\ c^2 \\ \vdots \\ u_2^7 \\ u_1^8 \\ u_2^8 \end{bmatrix}$$

$$[\mathbf{B}] = \left[\begin{array}{cccccccc} \partial N^1 / \partial x_1 & 0 & 0 & 0 & & \partial N^5 / \partial x_1 & & \\ 0 & \partial N^1 / \partial x_2 & 0 & 0 & & & \partial N^5 / \partial x_2 & \\ \partial N^1 / \partial x_2 & \partial N^1 / \partial x_1 & 0 & 0 & & \partial N^5 / \partial x_2 & \partial N^5 / \partial x_1 & \\ 0 & 0 & \bar{N}^1 & 0 & & 0 & 0 & \\ 0 & 0 & 0 & \bar{N}^1 & \cdots & 0 & 0 & \cdots \\ & & \partial \bar{N}^1 / \partial x_1 & & & 0 & 0 & \\ & & \partial \bar{N}^1 / \partial x_2 & & & 0 & 0 & \\ & & & \partial \bar{N}^1 / \partial x_1 & & 0 & 0 & \\ & & & \partial \bar{N}^1 / \partial x_2 & & 0 & 0 & \end{array} \right]$$

N_i is the interpolation functions for 8-node elements while $\bar{N}$ for 4-node elements. The element stiffness and residual vector are then:

$$[k^{el}] = \int_V [\mathbf{B}]^T [\mathbf{D}][\mathbf{B}] dV \qquad \underline{r}^{el} = -\int_V [\mathbf{B}]^T \underline{q} dV$$

Where

$$\underline{q} = \begin{bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{12} \\ \mu + \Delta\mu - f(c+\Delta c) - \Omega\sigma_{kk}/3 \\ \Delta c/\Delta t \\ -\kappa\partial(c+\Delta c)/\partial x_1 \\ -\kappa\partial(c+\Delta c)/\partial x_2 \\ D\partial(\mu+\theta\Delta\mu)/\partial x_1 \\ D\partial(\mu+\theta\Delta\mu)/\partial x_2 \end{bmatrix}$$

$$[\mathbf{D}] = \begin{bmatrix} \ddots & & & 0 & -\Omega(D^e_{11}+D^e_{12}+D^e_{13})/3 & 0 & 0 & 0 & 0 \\ & \mathbf{D}^e & & 0 & -\Omega(D^e_{21}+D^e_{22}+D^e_{23})/3 & 0 & 0 & 0 & 0 \\ & & \ddots & 0 & 0 & 0 & 0 & 0 & 0 \\ -\Omega(D^e_{11}+D^e_{12}+D^e_{13})/3 & -\Omega(D^e_{21}+D^e_{22}+D^e_{23})/3 & 0 & 1 & -\frac{df}{dc} - \Omega^2 \sum_{k=1}^{3}\sum_{l=1}^{3} D^e_{kl}/9 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/\Delta t & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\kappa & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\kappa \\ 0 & 0 & 0 & 0 & 0 & \theta D & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \theta D & 0 & 0 \end{bmatrix}$$

4 Parameters to Investigate

Here the main parameters we will be investigating are the functional form of chemical free energy, values of Ω, rate of lithiation, and particle geometry. Before focusing on the chemical free energy, we will first discuss the other parameters. Values of Ω, which signifies the impact of mechanical effects, will be between 0 (no coupling) to 0.06 (strong mechanical effects). Rate of lithiation will be 0.1C, 1C, and 10C.I will consider a 0.6x0.6 squared particle and 1/4 of a 0.3 radius spherical particle.

4.1 Chemical Free Energy

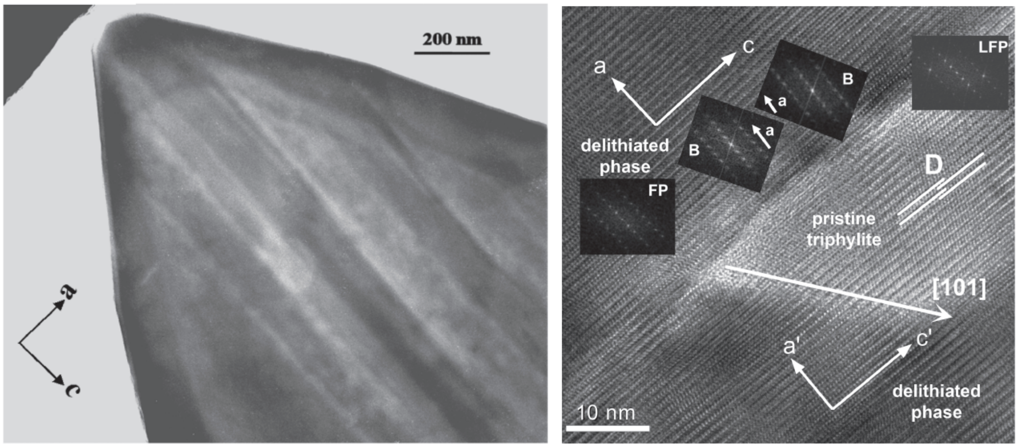

Figure 1: TEM of (100) phase boundary in LiFePO4 and HRTEM image of (101) phase boundary. Darker region is the lithiated phase and brighter region is the lithium-depleted phase

Motivated by experimental result from Figure 1. We can clearly see that there are 2 phases coexist during lithiation of LiFePO4. This mean our free energy must consist of two minima with a energy barrier in between. Because the two phases corresponding to lithium-rich and lithium-poor regions LiFePO4, we could represent $f^c = W * c^2(c-1)^2$. Even though a regular-solution-model-based free energy has been proposed, $f^c = (clog(c) + (1-c)log(1-c)) + Wc(1-c)$. We can see from Figure 2 that for appropriate parameters (7 and 4.52 for the respective W), their behavior is indistinguishable. Moreover, polynomial form will be much easier extending to complicated material like graphite.

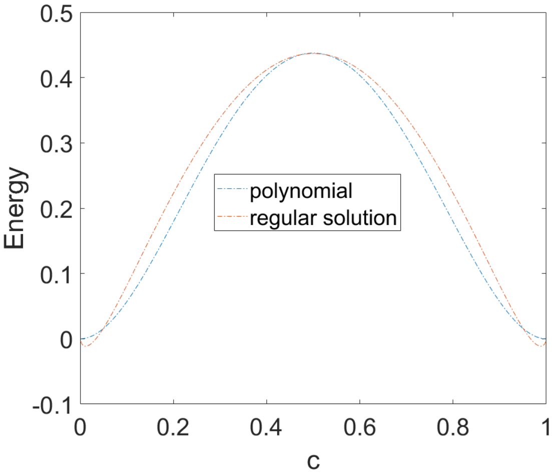

Figure 2: Comparison between polynomial and regular solution chemical free energy

Graphite is a complicated material due to that fact that it has been reported to exhibit at least 5 phases during lithitation. For simplicity, we will assume there are 3 dominated phases coexist during lithiation. This assumption has been supported by experimental evidences as indicated in Figure 3 below.

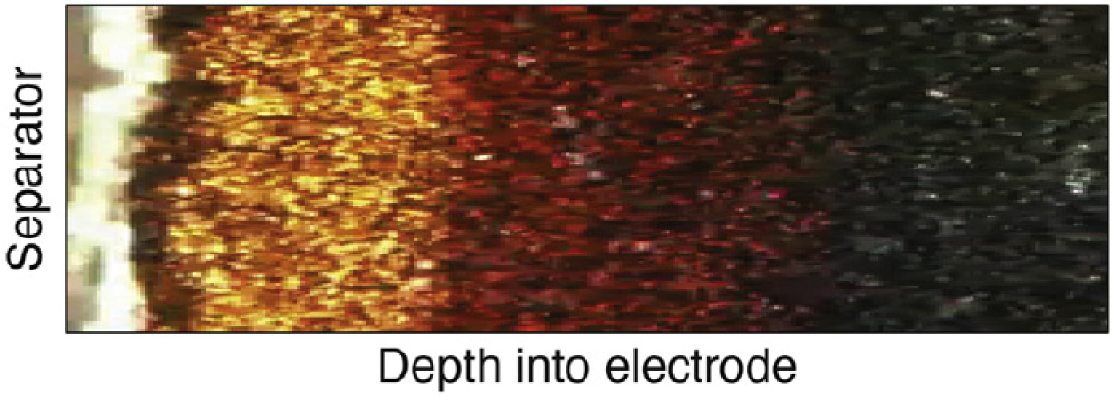

Figure 3: Experimental observation of coexistence of three phases (indicated by the three colors) during lithiation of graphite.

With this we would need to have three minima along with two energy barriers. While a simple extension of the form $f^c = c^2(c-0.5)^2(c-1)^2$ might be tempting, one would find through simulation/reasoning that, the metastable phase (c=0.5) would not appear during lithiation due to no energetic differences between its minimum and the other two minima which is direct consequence of the lever rule. Moreover curvature of each minima and the relative height of the two energy barriers are also of great importance. For those reasons we will consider these three potential (Figure 4) to see which one would represent the most accurate physics. They are: $f_1^c = c^4(c-1)^2(c-0.5)^2$,$f_2^c = 0.4(2.391c^6 - 7.009c^5 + 7.344c^4 - 3.231c^3 + 0.515c^2 - 0.007603c + 0.001834)$, and $f_3^c = 1.664c^7 - 4.951c^6 + 5.19c^5 - 2.117c^4 + 0.1484c^3 + 0.06731c^2 - .000115c - 5.136e - 5$.Also it would be instructive to consider their second derivatives (Figure 10). Here the potentials are constructed to reveal whether the curvature of minima or absolute values of minima would be critical for coexistence of three phases. While f_c^1 does not have any differences in values of minima, the higher c_{eq} has higher stability (more positive values in second derivative). f_c^2 is constructed to favors the appearance of $c = 0.5$ phase in term of energy, but such phase is not as stable as compared to the other two phases. f_c^3 essentially gave a staging potential where higher c_{eq} is less energetically favorable but having higher stability.

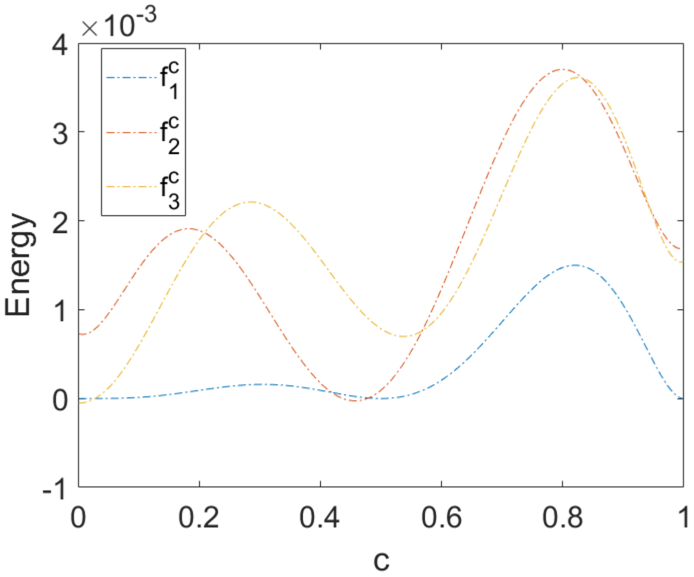

Figure 4: Comparison between the three potential functions for graphite chemical free energy. Here we see that f_c^1 make all three minima to have the same energy, but their stability is different. f_c^2 favors the c = 0.5 over the other two minima. f_c^3 represents a staging potential with values of the minima increase along with their stability (indicated in Figure 10) as c_{eq} = 0, 0.5, 1 gets larger

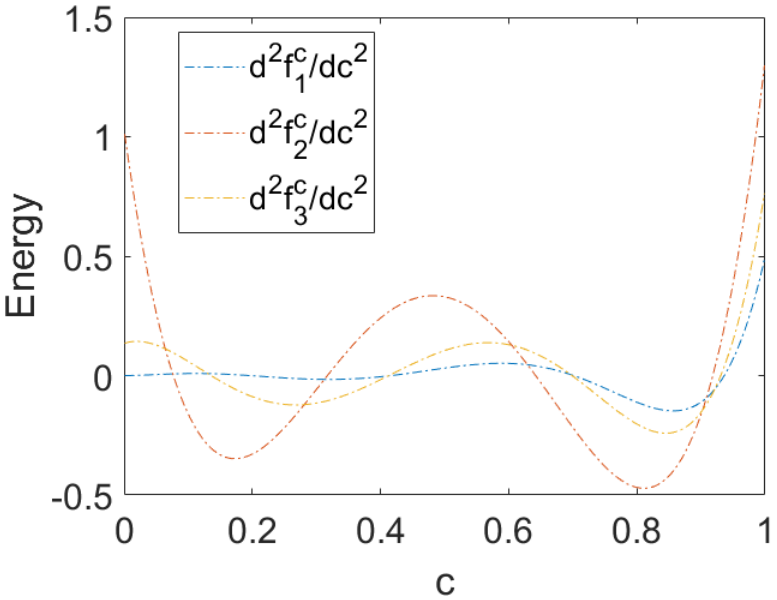

Figure 5: Comparison between the second derivatives of the three potential. Here we see that f_c^2 despite having c = 0.5 as the global minimum, that minimum is not as stable as compared to the ones at c = 0 and c = 1 indicated by the lower positive values.

5 Result

5.1 Olivine (LiFePO4)

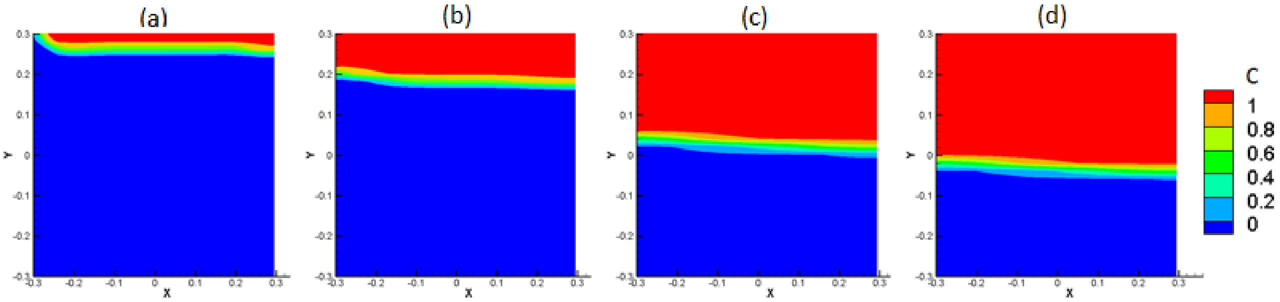

Figure 6: Lithiation of square particle. Lithium is intercalating from the top edge. No stress effect. Time increases from (a)-(d)

First we will consider the case where lithium is diffusing through the top edge of a square domain. In this case, there is no effect of stresses. As seen below (Figure 6), we are seeing that, instead of homogeneously diffusing in, lithium phase-separated into two regions and propagate like a wave. Moreover because of the κ term in the functional, phase boundary is kept straight to minimize the total area of phase boundary. However in the picture taken experimentally, we see stripes appears instead of straight interface. When the size of particle is enlarged, such stripes still does not appear. Thus we can infer that the current model is missing some important physics, mechanics.

5.1.1 Rate of Lithiation and Stress

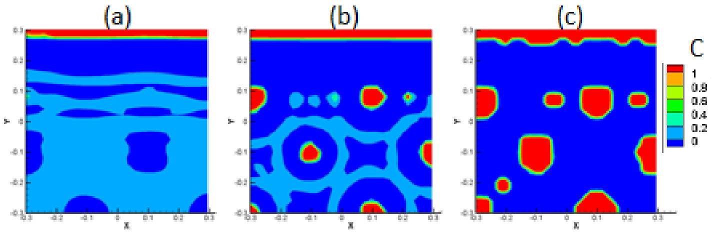

Figure 7: Lithiation of square particle. Lithium is intercalating from the top edge. $\Omega = 0.02$. Rate of lithiation 0.1C. Time increases from (a)-(c)

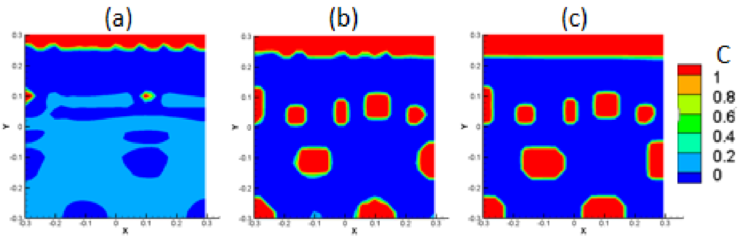

Figure 8: Lithiation of square particle. Lithium is intercalating from the top edge. Ω = 0.02. Rate of lithiation 1C. Time increases from (a)-(c)

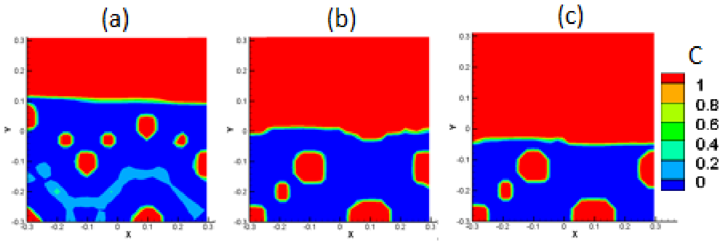

Figure 9: Lithiation of square particle. Lithium is intercalating from the top edge. Ω = 0.02. Rate of lithiation 10C. Time increases from (a)-(c)

Here we see that stress has significant impact on the morphology of the particle. As we see here there are many small lithium-rich island formed while the straight interface advancing (Figure 7-9). The rate of lithiation, to my surprise, did not have much significant impact on the morphology of the particles as evidence by the Even though this still does not constitute the stripes that we see but one can imagine that if the number of islands increases and merged we perhaps would see our expected result. Therefore I proceed to increase the value of Ω to 0.03 and 0.06.

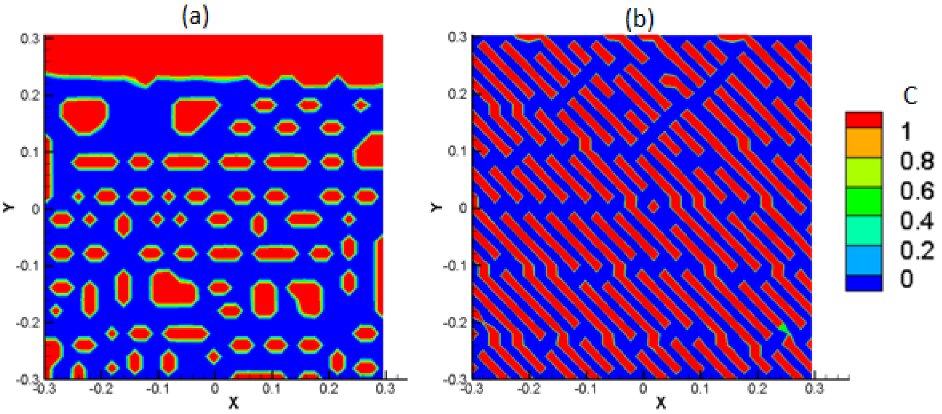

Figure 10: Lithiation of square particle. Lithium is intercalating from the top edge. Ω = 0.03 (a) and 0.06 (b). Rate of lithiation 1C.

As our expectation, higher values of Ω leads to formations of many islands and ultimately when $\Omega = 0.06$, this induces the formations of many stripes of poor and rich lithium regions. Such morphology confirms the ability of phase field model with Cahn-Hilliard functional to capture physics of lithium-ion battery. Moreover, it also emphasizes the importance of mechanics in getting all the important phase behavior.

5.1.2 Particle Geometry

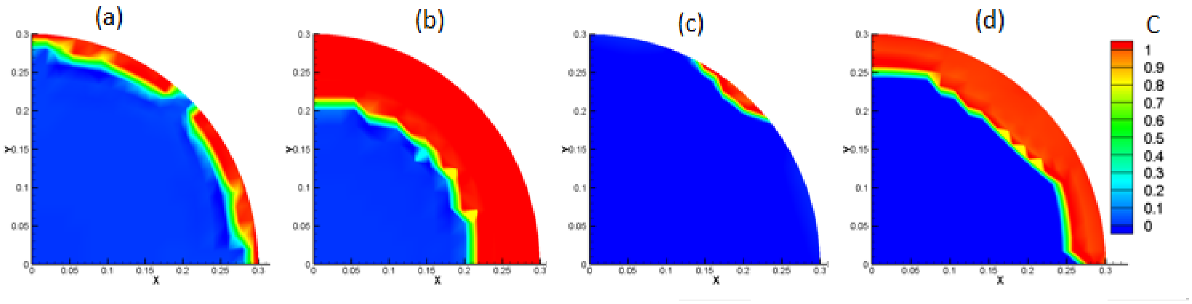

Figure 11: Lithiation of spherical particle. Lithium is intercalating from radial edge. $\Omega = 0$ (a) & (b) and 0.01 (c) and (d) (b). Rate of lithiation 1C.

It's interesting here that having a spherical geometry would make lithium nucleates first before forming an interface and propagates as before. Moreover, stress seems to suppress the amount of nucleations. Also the interface aren't as straight as before, this could just be attributed to the fact that the elements aren't exactly uniform as in the case of a square particle.

5.2 Graphite

Despite many simulations of different C-rate potentials of the form of f_2^c could not form any c = 0.5 phases. This confirms that the absolute value of the minimum does not control appearance of its corresponding phase during lithation even if it's the global minimum. I was able to form some c = 0.5 with f_1^c but it quickly got absorbed into c=1 and does not lead to 3 phases coexisting while intercalation wave pushing in. However that problem got solved when switching to f_2^c as shown below (Figure 12-14). This confirms that even though the curvature is the critical factor for having metastable phase, the relative differences in the minima also important in leading to coexistence of the three phases. In the square geometry, we clearly see the metastable phase (c = 0.5) form an interface initially. As lithiation continues, small regions of lithium-rich (c=1) nucleates and quickly expand into an interface. Then the three phases coexist while the intercalation wave pushing in.

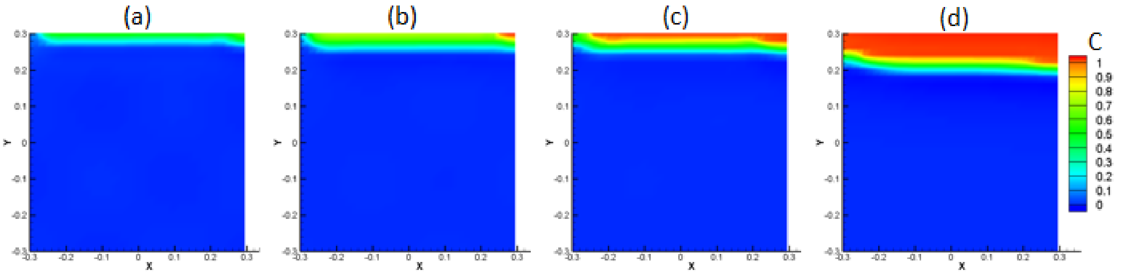

Figure 12: Lithiation f_2^c potential. Lithium is intercalating from top edge. $\Omega = 0$ (a) & (b) and 0.01 (c) and (d) (b). Rate of lithiation 0.1C.Time increase from (a)-(d)

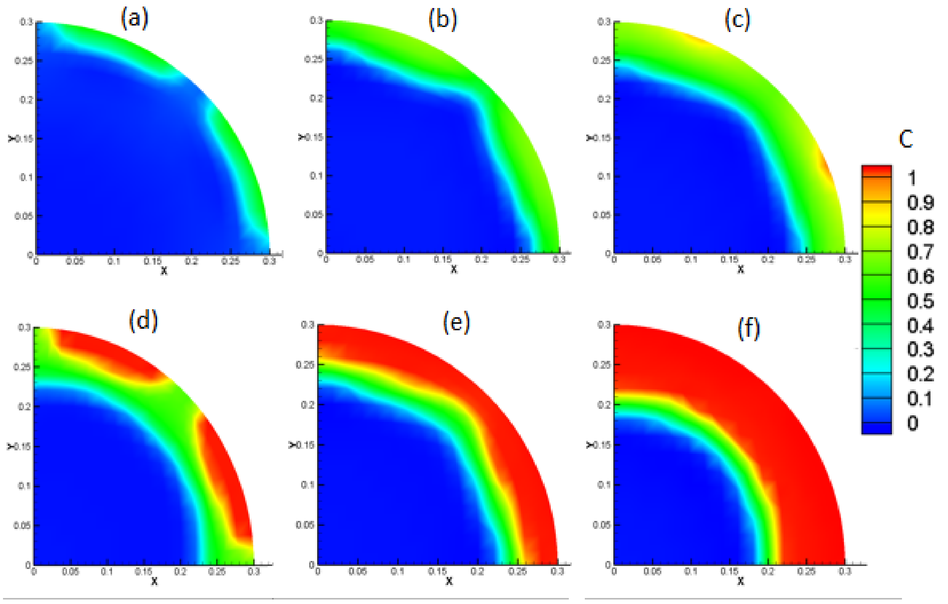

Figure 13: Lithiation f_2^c potential. Lithium is intercalating from radial edge. $\Omega = 0$. Rate of lithiation 0.1C. Time increase from (a)-(f)

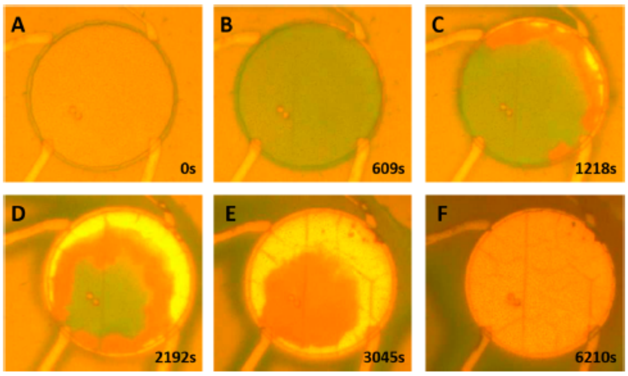

Figure 14: Experimental result of lithiation in spherical graphite particle

It is interesting to see that in spherical geometry, due to the initial nucleation we could see the metastable phases very clearly. Compared to experimental result, it seems like our model is still missing some important physics. As shown the metastable phases will dominate the lithium-poor phase before being dominated by the lithium-rich phase. In our simulation such result is not observed. Toward the end of the simulation, both c = 0 and c = 0.5 phases almost got dominated simultaneously by c = 1 phase. Therefore, it is true that refinement of the model will need to be done for it to completely capture all the important physics.

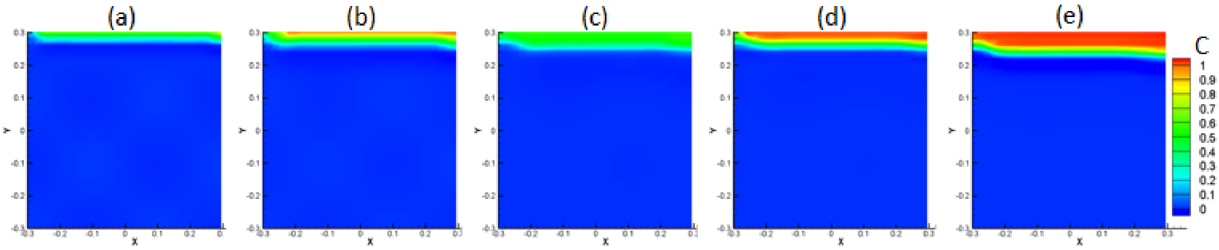

Figure 15: Lithiation with f_2^c potential. Lithium is intercalating from top edge. After 10 time steps of lithiation, the particle is rest for 20 time steps and then lithiation starts again. $\Omega = 0$. Rate of lithiation 1C.

When I try to speed up lithiation, the metastable phase got very quickly dominated by the lithium-rich phase. However, when I allow the particle to rest a for 20 time step (1hr) after getting lithiated for 10 time steps, the same morphology as slow lithiation follows.

6 References

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