A Phase Field Model for Lithium Ion Battery Particles

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Abstract

Lithium iron phosphate (LiFePO$_4$) is the most commonly used phosphate based cathode material for lithium ion batteries. LiFePO$_4$ has a strong tendency to separate into stable high Li$^+$ concentration and low Li$^+$ concentration phases, resulting in the batteries characteristic wide voltage plateau at room temperature. The COMSOL model equations consist of the Cahn-Hilliard Reaction equation for evolution of Li$^+$ concentration in a spherical nanoparticle, and Butler-Volmer kinetics for charge conservation. The mathematical complexities of the Cahn-Hilliard Reaction model and especially the discontinuities associated with spinodal phase decomposition make 3-D solutions of the system difficult and consequently rare in application. In this study, a 3-D phase field model was developed to better understand the parameters impacting the LiFePO$_4$ cathode material in lithium ion batteries. The COMSOL model is an adaptation and a generalization of a 1-D in radius isotropic model and is based on recent developments in nonequilibrium thermodynamics [1, 2]. Enthalpies of mixing per site producing repulsive behavior resulted in no phase change. Battery voltage profiles for these conditions were similar to simple diffusion or shrinking core model results. Battery voltage plateauing was observed and two wave spinodal phase decomposition was demonstrated for enthalpies in the attractive regime. Our 3-D solution and COMSOL's postprocessing capabilities resulted in greater insight into the phase separation behavior of LiFePO$_4$ cathode material. For example, the model indicates that the separate phase regions extend to the surface of the particle. Consequently, while the global rate of intercalation of Li$^+$ remains constant during phase separation, the ion flux varies significantly over the surface of the particle while two phase behavior persists.

Keywords: COMSOL, nanoparticles, Cahn-Hilliard Reaction model, non-equilibrium thermodynamics, lithium batteries, LiFePO^4, spinodal phase decomposition.

Introduction

Fossil fuels play a major role in the world economy since automobiles, trains, airplanes and a majority of the power plants use fossil fuels. The continued demand for fossil fuels leads to serious problems like environmental pollution, climate change and economic dependence on other nations. Renewable energy sources alleviate this problem to a certain extent but they are not capable of generating large quantities of electricity relative to fossil fuels and their supply can be unpredictable and inconsistent. Therefore, there is a need to develop new technologies which are consistent, have high energy density and have minimum effects on the environment. Emerging battery technologies are addressing these problems of renewable and fossil fuel energy sources since they can store and release energy on demand. In recent years significant strides have been made in the field of lithium battery technology. Lithium batteries are the primary sources of power in modern day applications, such as portable consumer electronics, hybrid electric vehicles, implantable electronic medical devices and space vehicles [3-5].

Theory/Parameterization

The phase-field model, as presented here, grows out of the work of Cahn and Hilliard. A phase field model is necessary for modeling systems in which the diffuse interface is essential to the problem, such as spinodal phase decomposition. Traditionally mathematical models of two-phase intercalation dynamics in LiFePO$_4$ cathodes was based on a spherical diffusion or shrinking core concept [6-7]. However, recent experimental and theoretical advances indicate a more realistic particle model must account for two-phase thermodynamics. Such a model was first proposed by Singh, Ceder, and Bazant [8], represents bulk phase separation driven by heterogeneous reactions, 2008. Our model is a 3D adaptation of a 1D model in radius by Zeng and Bazant, 2013 for an isotropic spherical LiFePO$_4$ nanoparticle [1]. We used their basic parameters and similar dimensionless variables. Charge conservation for the model is achieved via Butler Volmer kinetics.

In our model, we assumed the particle was spherical and isotropic. The basic evolution equation for mass conservation is,

$$\frac{\partial c}{\partial t} = -\nabla \cdot F, \qquad \text{Eq. 1}$$

where c is the ion concentration and F is the ion flux. The ion flux is driven by the gradient of the bulk chemical potential μ as,

$$F = -\frac{D_0(c_m - c)c}{k_m T c_m}\nabla\mu. \qquad \text{Eq. 2}$$

where D_0 is the ion diffusivity and c_m is the maximum possible ion concentration. The bulk chemical potential derived from the Cahn-Hillard free energy functional is,

$$\mu = -k_b T \ln\frac{c}{cm - c} + \frac{\Omega(cm - c)}{cm} - \frac{K V_s}{cm}\nabla^2 c, \qquad \text{Eq. 3}$$

where T is the absolute temperature, k_b is Boltzmann's constant, Ω is the enthalpy of mixing per site, K is the gradient energy penalty coefficient, and $V_s = 1/c_m$.

The system was driven by constant current for all parameter studies. Parameter studies were conducted for conditions producing enthalpies of mixing resulting in repulsive and attractive forces between ions and vacancies. Details for the nondimensionalization of model variables and parameters are provided in Table 1 and the values of model parameters used in this study are provided in Table 2.

Table 1: Parameter Nondimensionalization				
$\bar{c} = \frac{c}{c_m}$, $\bar{t} = \frac{D_0}{R_p^2}$, $\bar{r} = \frac{r}{R_p}$, $\bar{\nabla} = R_p\nabla$, $\bar{F} = \frac{R_p}{c_m D_0}$				
$\bar{\mu} = \frac{\mu}{k_B T}$, $\bar{\Omega} = \frac{\Omega}{k_B}T$, $\bar{k} = \frac{k}{R_p^2 c_m k_B}$, $\bar{V^\theta} = \frac{eV^\theta}{k_b}$				
$\bar{V} = \frac{eV}{k_b}$, $\bar{I} = \frac{R_p I}{c_m n e D_0}$, $\bar{I_0} = \frac{R_p I_0}{c_m n e D_0}$,				
$\bar{\gamma_s} = \frac{\gamma_s}{R_p c_m k_b T}$, $\beta = \frac{d\bar{\gamma_s}}{d\bar{c}}$, $\bar{\eta} = \frac{e}{k_b T}$				

Where $\bar{c}$ is the local filling fraction of ions, $\frac{\Omega}{2}$ is the ratio of the critical temperature (T_c) to the current temperature (T). Phase separation is expected when $\frac{\Omega}{2} > 1$. $\frac{\bar{k_0}}{2}$ is the nondimensional exchange current density when the particle is uniformly half filled and the particle and the surface area is normalived to

4π. β is related to surface wetting and de-wetting as per (Zeng and Bazant, 2013).

Table 2: Parameter Settings	
$R_p = 1x10^{-7} m$	$\Omega = 0.115$ eV
$k = 3.13x10^9 \frac{eV}{m}$	$D_0 = 1x10^{-14} \frac{m^2}{s}$
$n = 1$	$c_m = 1.379x10^{28} m^{-3}$
$V^\theta = 3.42V$	$\alpha = 0.5$
$k_0 = 1000$	

COMSOL Implementation

The Cahn-Hilliard Reaction equation is a fourth-order partial differential equation in $\bar{c}$, so casting it directly in the weak form results in second-order spatial derivatives in the weak formulation. Our model resolves this by rephrasing the problem in COMSOL's standard PDE format as a system of two fully coupled second-order partial differential equations in Li$^+$ concentration and bulk chemical potential respectively. The details of the general form implementation are given below in COMSOL input notation.

$$e_a\frac{\partial^2 u}{\partial t^2} + d_a\frac{\partial u}{\partial t}$$

$$u = [\bar{c}, \bar{\mu}]^T$$

$$\nabla = [\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}]$$

$$\underline{\Gamma}$$

$$(\bar{c}^2 - \bar{c})\bar{\mu}x$$
$$(\bar{c}^2 - \bar{c})\bar{\mu}y$$
$$(\bar{c}^2 - \bar{c})\bar{\mu}z$$

$$\bar{k}\bar{c}x$$
$$\bar{k}\bar{c}y$$
$$\bar{k}\bar{c}z$$

$$\underline{f}$$

$$0$$

$$\bar{\mu} - \log\frac{\bar{c}}{(1 - \bar{c})} - \bar{\Omega}(1 - \bar{c})$$

$$\underline{d_a}$$

$$1$$
$$0$$

$$\varrho_a$$

$$0$$
$$0$$

Note: In order to facilitate the recovery of the COMSOL solver after the sudden change in $\overline{\mu}$ associated with spinodal phase decomposition, the time step had to be driven small by setting both the relative and absolute tolerances to 10^{-6}.

Discussion and Results

When the particle repulses the added ion or when the ion is attracted but $T > T_c = \frac{\Omega}{2\,k_b}$ phase separation is not expected to occur. For these cases, the intercalation process is a simple nonlinear diffusion of the ion. We will only address the lithiation process here (discharging). A more in-depth treatment involving lithiation as well as delithiation is provided by Zeng and Bazant, 2013.

Note in Figure 1 that $\overline{\mu}$ is always 0 for $\overline{c} = 0.5$ and thus (as per Equation 7) $\overline{i}_0$ is simply $\frac{\overline{k}_0}{2}$. Here we maintain $\overline{i} = 500\ \frac{A}{m^2}$ or $\frac{\overline{i}}{\overline{i}_0} = 1$ throughout.

Enthalpies of mixing producing repulsive behavior resulted in no phase change. Battery voltage profiles for this condition ($\Omega = -2$) shown in Figure 2 were similar to simple diffusion or shrinking core model responses.

Enthalpies in the attractive range, result in much different results from the simple diffusion behavior shown in Figure 2. Figure 3 shows discharge curves for the attractive cases $\overline{\Omega} = 1$ and 2. For these values there is no phase change but there is significant plateauing of the discharge response. For mixing enthalpies > 2 phase separation may occur. This behavior is shown in Figure 4 for $\overline{\Omega} = 2.5$. Spinodal phase decomposition results in a sudden increase in voltage at the onset of two phase behavior. Thereafter the voltage is effectively constant until the solution once again becomes a single high concentration phase. Based on these results, it is clear that the complex phase field model is superior to simple diffusion and shrinking core models for modeling the behavior of lithium ion batteries.
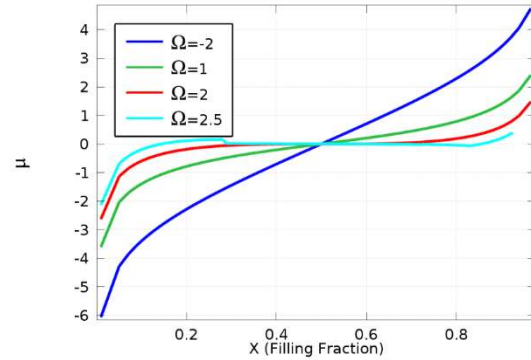

Figure 1: Chemical potential vs. filling fraction for solid solution with mixing enthalpies ranging from -2 to 2.5.
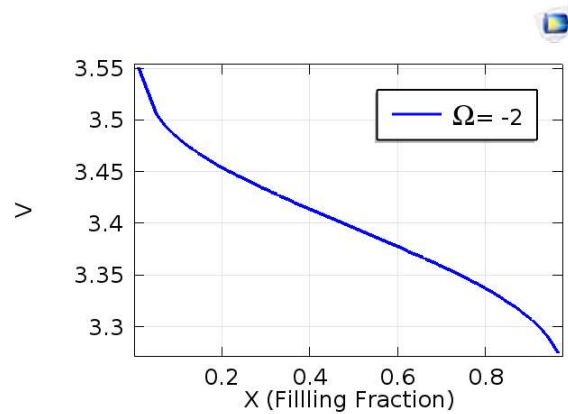

Figure 2: Voltage vs. filling fraction for a solid solution with mixing enthalpy -2. The response is similar to a pure diffusion process.
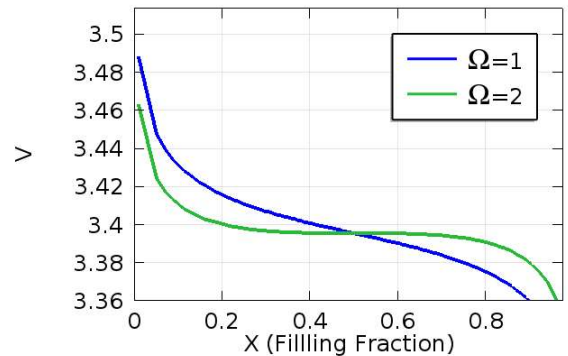

Figure 3: Voltage vs. filling fraction for a solid solution with mixing enthalpies 1 and 2. There is significant voltage plateauing compare to Figure 3.
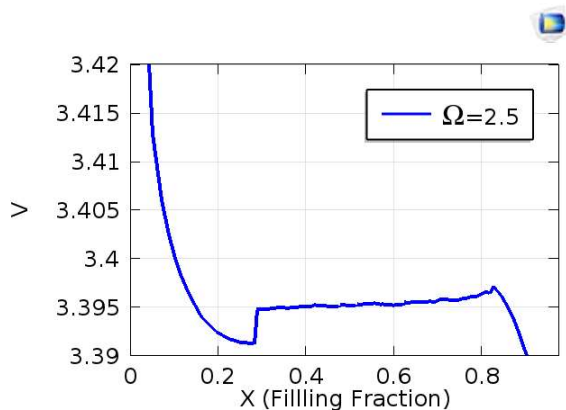
Figure 4: Voltage vs. filling fraction for solid solution with mixing enthalpy 2.5. Resulting in spinodal phase decomposition.

The ion concentration is depicted as hyperplanes through the particle's equator. Figure 5 shows the ion concentration profiles for X = 0.6 and Ω = -2. The lithiation process is uniform in this case for moderate currents. Figure 6 shows the filling faction profiles for X = 0.6 and $\overline{\Omega}$ = 2.5. In this case two phase behavior is apparent. Figure 7 is a surface plot of ion concentration on the particle surface.

Figure 8 compares the overall filling fraction to the local filling fraction at a random probe point on the surface of the particle. This demonstrates that local and average filling fractions remain the same for single phase intercalation. The figure further shows that while the overall filling remains steady during phase separation. On the other hand, the local ion concentration at points on the particle's surface varies significantly for two phase intercalation.
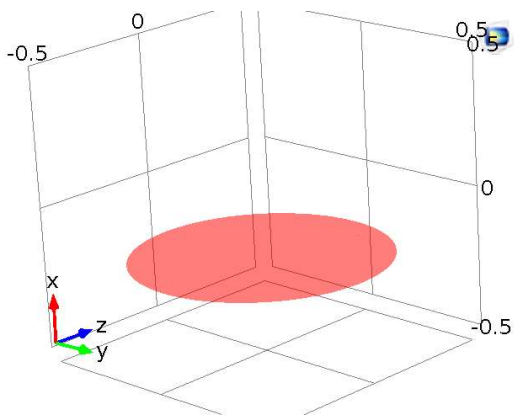

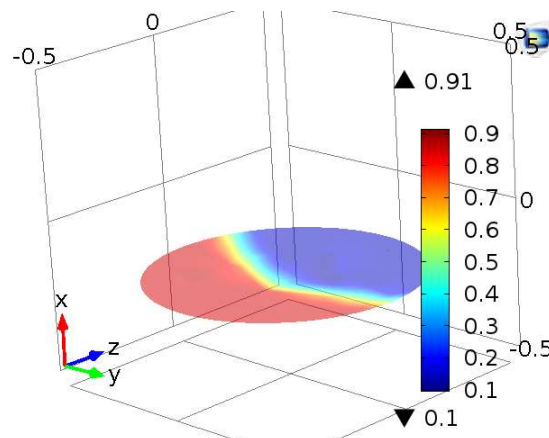Figure 5: Ion concentration profile for solid solution with repulsive forces (Ω = - 2.0) for X = 0.6

Figure 6: Ion concentration profile for solid solution with attractive forces (Ω = 2.5) for X = 0.6
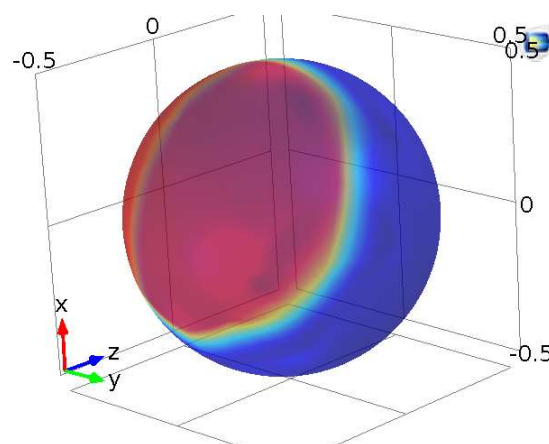

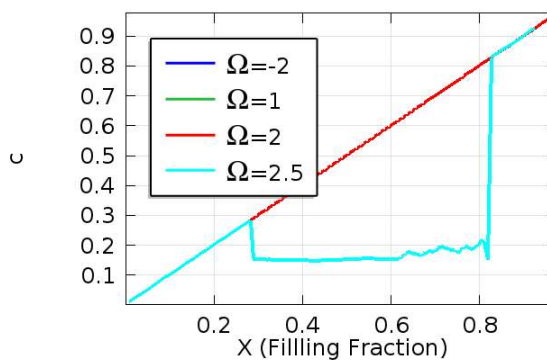Figure 7: Ion concentration on the surface of the particle.

Figure 8: Comparison of the local filling fraction at a probe on the particle to the overall average filling fraction.

Conclusions

We studied the ion intercalation of isotropic, spherical LiFePO₄ particles based on Cahn-Hillard

reaction kinetics. Charge conservation entered the model via Bulter-Volmer kinetics. The model exhibited results similar to simple nonlinear diffusion or phase seperation depending on the thermodynamics as reflected by the enthalpy of mixing per site. In this regard, it is clear that the phase field model derived from the principles of nonequilibrium thermodynamics is superior to simple diffusion and shrinking core models. This is apparent from our study in spite of the simplifying assumptions of spherical symetry and isotropy. We did not adress solid phase surface wetting and de-wetting here but the model is capable of adressing surface wetting with a simple change of the boundary condition assumptions.

This simple 3-D spherical Cahn-Hilliard Equation model is an improvement of a 1-D in radius model for visualization purposes. The major utility of our finite element model, though, is the ease of its adaptation to address more realistic particle geometry, anistropy, and surface wetting. These improvements of our model will provide a robust simulation of the complex physics needed for calculations and interpretation of experimental results. One area that we plan to address is the impact of extreme temperature environments on the physics and more practically on the operation of LiFePO$_4$ batteries in extreme conditions.

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