A Phase Field Model for Lithium Ion Battery Particles

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Abstract

In this study, a three-dimensional (3-D) phase field model was developed to better understand the parameters impacting the LiFePO4 cathode material in lithium ion batteries. LiFePO4 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. 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. The Cahn-Hilliard Reaction equation is a fourth-order partial differential equation, so casting it directly in the weak form results in second-order spatial derivatives, and could not be solved by COMSOL. 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 chemical potential respectively. 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. Enthalpies of mixing 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 decomposition was demonstrated for enthalpies in the attractive regime. In this regard, 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. Our 3-D solution and COMSOL's postprocessing capabilities resulted in greater insight into the phase separation behavior of LiFePO4 cathode material. For example, and contrary to other interpretations, 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 throughout, the ion flux varies significantly over the surface of the particle while two phase behavior persists.
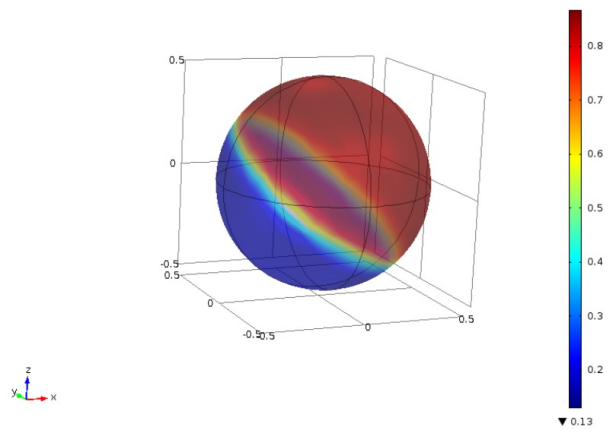
Figures used in the abstract

Figure 1: High Density and Low Density Phases for Filling Fraction (X) =0.55 with Current Density 500 (A/m^2)