



Phase-field modeling of Li-insertion kinetics in single LiFePO₄-nanoparticles for rechargeable Li-ion battery application



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ABSTRACT

We develop a continuum phase-field model for the simulation of diffusion limited solid-solid phase transformations during lithium insertion in LiFePO₄-nano-particles. The solid-solid phase boundary between the LiFePO₄ (LFP)-phase and the FePO₄ (FP)-phase is modeled as a diffuse interface of finite width. The model-description explicitly resolves a single LiFePO₄-particle, which is embedded in an elastically soft electrolyte-phase. Furthermore, we explicitly include anisotropic (orthorhombic) and inhomogeneous elastic effects, resulting from the coherency strain, as well as anisotropic (1D) Li-diffusion inside the nano-particle. In contrast to other related research work, we employ an Allen-Cahn-type phase-field approach for the diffuse interface modeling of the solid-solid phase boundary. The model contains an extra non-conserved order parameter field to distinguish the two different phases. The evolution of this order parameter field is controlled by an extra kinetic parameter independent from the Li-diffusion. Further, the effect of the nano-particle's size on the kinetics of FP to LFP phase transformations is investigated by means of both model. Both models predict a substantial increase in the steady state transformation velocity as the particle-size decreases down to dimensions that are comparable with the width of the interface between the FP and the LFP-phase. However, the extra kinetic parameter of the Allen-Cahn-type description may be used to reduce the strength of the velocity-increase with the decreasing particle size. Further, we consider the influence of anisotropic and inhomogeneous elasticity on the lithiation-kinetics within a rectangularly shaped LiFePO₄-particle embedded in an elastically soft electrolyte. Finally, the simulation of equilibrium shapes of LiFePO₄-particles is discussed. Within a respective feasibility study, we demonstrate that also the simulation of strongly anisotropic particles with aspect ratios up to 1/5 is possible.

1. Introduction

LiFePO₄ powder is widely considered to be a promising novel cathode material for the application in rechargeable Li-ion batteries. The reasons are high energy storage, low cost and electrochemical stability [1,2]. A recent trend in the design of LiFePO₄-cathodes is to synthesize particles of smaller and smaller sizes. For LiFePO₄-nanoparticles excellent performance parameters such as high charge rates have been reported [3]. However, for designing next generation Li-ion battery cathodes materials, based on LiFePO₄-nano-particles, a thorough understanding of the kinetics of the lithiation process in this novel battery material is highly desired. Here, we aim to contribute to this topic from the perspective of a continuum materials science simulation approach. Within the present article, we focus on the issues that are placed around the model development, whereas subsequent detailed simulation studies and related results will be part of future work.

The true physical mechanism of the Li insertion process in cathodes made of LiFePO₄-nano-powders is in due to the underlying complexity still a matter of an ongoing scientific debate, and for recent reviews on this issue, we refer to [4,5]. In this article, the charge and discharge process in the bulk LiFePO₄-material is regarded to proceed via a coherent solid-solid phase transformation between LiFePO₄ (LFP-phase) and FePO₄ (FP-phase). During this first order phase transformation lithium is inserted into the olivine bulk material. The diffusion of Li inside the orthorhombic olivine lattice is strongly anisotropic along 1D channels in (010) crystallographic direction [6–8]. Important for the modeling of the Li insertion process in single LiFePO₄-nano-particles is of course the thermodynamics of the bulk LiFePO₄-system: At room temperature the two stable phases are separated by a miscibility gap, generally providing a strong tendency for the material to phase separate into FP and LFP phase. It is quite interesting that for small LiFePO₄-particles, a size dependence of the miscibility gap has been observed

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experimentally [9–11], whereas a relation to the excellent rate capabilities of nano-sized LiFePO_4 -powders is conceivable. It is interesting to note that, such a size dependence of the miscibility gap can result from a gradient energy contribution within diffuse interphase models, where the interface width is on the same order of magnitude than the size of the nano-particle [12–14].

For the development of a respective diffuse-interface description, we apply the so-called phase-field method. This approach has already been applied to model electrochemical reaction kinetics in electrode materials in a number of other research work [13,15–20]. Within the phase-field method, moving phase boundaries between different phases are treated as diffuse interfaces of finite width. Then, the evolution of the diffuse phase boundary is driven by the mechanics and the thermodynamics of the adjacent bulk phases. In turn, the motion of the diffuse interface strongly influences the bulk properties such as mechanical or thermodynamical degrees of freedom. Already on microscopic length-scale problems, such as solidification or solid-state reactions in metallic alloys, the diffuse interface approach provides an elegant way to dynamically incorporate complex effects, such as multi-component diffusion of refractory elements, chemical reactions at the phase boundary or stress and strain effects due to the lattice mismatch between the phases [21–26]. On the nano-scale, such as in novel LiFePO_4 cathode materials, the width of the diffuse interface can be chosen in accordance with corresponding experimental observations. In contrast to phase-field descriptions on the micrometer scale, then, the diffuse interface of finite width can carry physical information, which means that the respective nonlinear model behavior has an actual physical meaning [11–14,27].

Further, we also include anisotropic and inhomogeneous elastic effects, resulting from the lattice misfit between the LFP and the FP-phase. Primarily, these effects are considered to be very important to reproduce experimental observations with regard to favored LFP/FP-interface orientations [16,28]. Furthermore, it is also interesting to access the micro-mechanical states during the charging of LiFePO_4 -particles, since frequent cracking along the FP/LFP-interface upon electro-chemical shock is observed and discussed [29–31]. However, a realistic consideration of the elastic effects requires the modeling of the whole particle, which can have strongly anisotropic shapes [32,33].

Therefore, here, we develop a phase-field model, which combines the following mechanisms for a description of the lithiation-reaction in single LiFePO_4 -particles:

- The introduction of anisotropic bulk diffusion along 1D channels in (010) crystallographic direction.
- The incorporation of anisotropic coherency strains arising from the lattice-mismatch between the two joining solid phases with different elastic constants.
- The implementation of strongly anisotropic interfacial energies that give rise to the anisotropic particle-shapes.
- The introduction of the anisotropic particle-shape, which act as a free-surface guaranteeing realistic strain energy contributions.

A major difference of the present model, as compared to other models of similar purpose is that the diffusion limited phase transformations are reformulated in terms of two strongly coupled but still independent kinetic equations: one for the Li diffusion and one for the solid-solid phase transformations. This leads to two coupled 2nd order partial differential equations of parabolic type, instead of one equation of forth order. Within the present article, we focus on the model development and discuss the relations and differences to other phase field models for the simulation of charge and discharge in LiFePO_4 cathodes. Moreover, first interesting results on the size dependent kinetics of diffusion limited phase transformations are presented. Since, an electrolyte phase is explicitly included, it might be also possible to study the complex dynamics of multi-particle interaction [17,34–36]. However, this is beyond the scope of the present work.

The article is structured as follows: In Section 2 the development of the phase-field model for the simulation of Li-insertion kinetics in single LiFePO_4 particles is described. It is subdivided into the description of the energetics and the subsequent derivation of the evolution equations. Then, in Section 3, the simulation results are presented. First, we present the results on the size-dependent kinetics of diffusion limited phase transformations, second the influence of anisotropic and inhomogeneous elastic effects is discussed and finally a feasibility study on the formation of strongly anisotropic particle shapes is presented. Finally, in Section 4, a small summary is given.

2. Phase field modeling of LiFePO_4 particles

Here, we describe the development of the continuum phase field model for the simulation of lithium insertion kinetics in single LiFePO_4 nano-particles. In contrast to conventional Cahn-Hilliard-type descriptions, the lithium transport is considered to be independent from the solid-solid phase transformation from the FP-phase to the LFP-phase. The conservative lithium transport is described by a continuous concentration field c . In order to locally distinguish between the LFP and the FP-phase, we introduce the non-conserved phase field parameter ϕ , with $\phi = 1$ denoting the LFP phase and $\phi = 0$ denoting the FP-phase. At the FP/LFP-interface a smooth transition about the phase field width ξ_ϕ between the two bulk values of the phase field ϕ is enforced. Furthermore, in the model, we resolve individual nano-particles with the potential possibility to study multi-particle interaction [17,34–37]. This is realized by the inclusion of an extra phase field φ for the particle, which takes the value $\varphi = 1$ at the places where a LiFePO_4 -particle is located and the value $\varphi = 0$ in the area that surrounds the particles. Finally the elastic deformations, which result from the lattice-misfit between two the coherently connected phases are contained in the displacement vector-field \mathbf{u} . All these field are defined in the entire (rectangular) simulation domain. The full 3D-setup of the model for the simulation of lithium insertion in a single anisotropically shaped LiFePO_4 -particle is illustrated in Fig. 1.

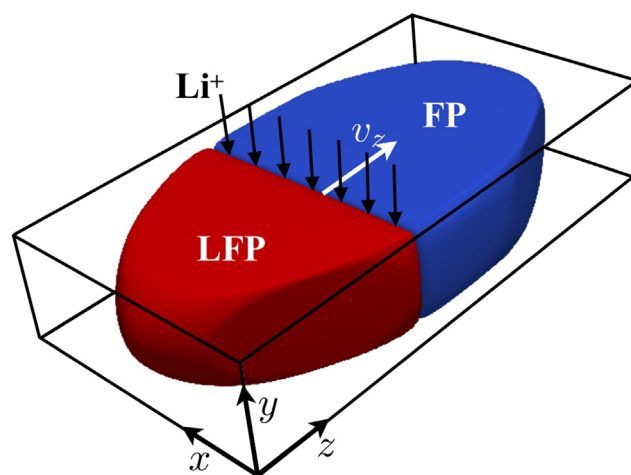


Fig. 1. The setup of a partially lithiated, plate-like particle for 3D phase field simulation of the lithiation-reaction inside single LiFePO_4 nano-particles. The LiFePO_4 -phase is shown in red and the FePO_4 -phase in blue. The particle is surrounded by an electrolyte phase, not shown in the picture. Li-diffusion inside the particle is restricted to one-dimensional channels oriented along the (010)-crystallographic orientation as indicated by black arrows. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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