



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 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.

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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 Fig. 1. The current

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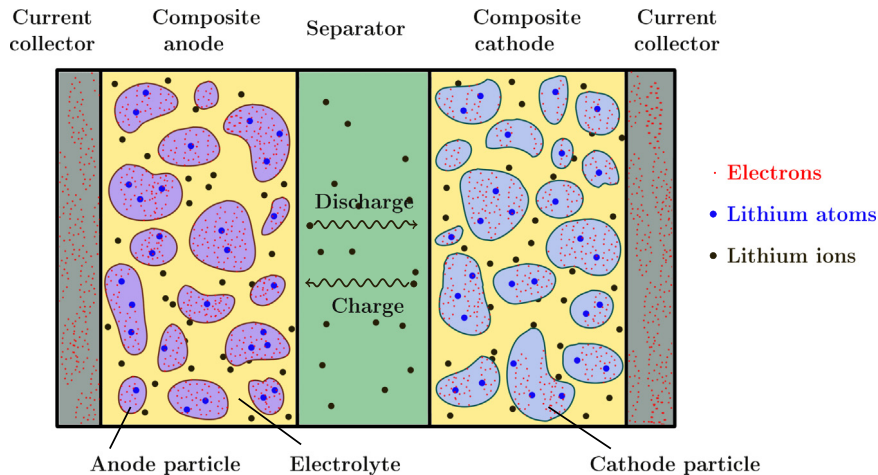


Fig. 1. Schematic of a lithium-ion battery cell.

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 on this model, Bai et al. [3] discussed the suppression of the phase segregation 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 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 intensively studied in various chemo-mechanical coupled models [7–10]. However, those models mainly treat the diffusion process as in a dilute solution, where the concentration smoothly changes with the incoming/outgoing flux, accompanied 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 employed 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 cannot 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

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