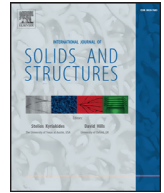




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# Numerical simulation of phase separation in cathode materials of lithium ion batteries

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## ABSTRACT

A nonlinear initial boundary value problem for the lithium ion concentration, the electric potential and the electrode-electrolyte interface currents is introduced on the microscale. The model enables the resolution of porous electrode microstructures. Different exchange current densities for Butler–Volmer interface conditions are evaluated. The Cahn–Hilliard equation is used to describe the phase transition from solid-solution diffusion to two-phase dynamics. The resulting phase-field model is then discretized on a regular mesh. A first-order finite-volume scheme with an adaptive time integration method is applied. The parameters and their effects in the non-convex Helmholtz energy are investigated and explained. Furthermore, the numerical convergence of the scheme is examined. In order to illustrate the method, the charging process of several single-particles and a complex structure is numerically simulated.

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## 1. Introduction

Today lithium ion batteries form an indispensable component for electronic devices or electric vehicles. Even though lithium ion electrodes are very versatile in battery production due to their high energy density, the diverse fields of application require the prediction of life-time and capacity fade. A lot of electrode materials show degradation during usage. If a large current is applied at the poles of the battery during discharge, the diffusion of lithium ions inside the battery from anode to cathode is not fast enough and concentration gradients arise. In some materials the restructuring of the lithium ions inside the crystal structure of the electrode material gives rise to large strains (Brousely et al., 2005). From experiments it is known that the stresses related to these strains can cause mechanical damage effects in materials including lithium tin oxide (Chen et al., 2011), lithium manganese oxide (Huttin, 2014), lithium titanate oxide (Choi et al., 2013) and lithium iron phosphate (Cogswell and Bazant, 2012). The mechanical stresses arising in a

porous electrode made of lithium manganese oxide have been numerically simulated with a model based on diffusive dilute solution theory (Taralov, 2015). In this model a diffusion equation is used to describe the distribution of lithium ions inside the battery.

But especially in lithium iron phosphate, the diffusion of the lithium ions from electrolyte into the active material cannot be modeled by a regular diffusion equation. While in a lot of materials the diffusion leads to an even ion distribution inside the material, for lithium iron phosphate a separation into areas with a maximum concentration of lithium ions and areas where no lithium ions are present (Ebner et al., 2013; Zhu et al., 2013; Chueh et al., 2013; Lim et al., 2016). Even without applied current, the lithium enriched areas do not diffuse. The distribution of the lithium ions inside the material can then be described by two different phases, one phase enriched with lithium ions and one phase devoid of lithium ions. The process of separation into different phases is called spinodal decomposition. The problem of describing the movement of the boundaries between both phases is often called a Stefan problem (Andersson, 2002; Harari and Dolbow, 2010) and can be approached by adaptive meshes and front-tracking methods (Mitchell and Vynnycky, 2009).

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Another approach called phase-field method is introduced in the works of Cahn and Hilliard (Cahn and Hilliard, 1958) and is based on a thermodynamical approach involving a non-convex Helmholtz energy functional. In a general phase-field method, the boundary between two phases is discretized and a fine regular spatial mesh is used. In phase-field models for diffusive processes the constituent fourth-order nonlinear partial differential equation is called the Cahn–Hilliard equation. Recent formulations for lithium iron phosphate particles can be found in Abdellahi et al. (2016); Burch (2009); Singh et al. (2008); Bazant (2013). While those models are restricted to simulations of electrode material, the presented model describes diffusion and electric potentials in both electrodes and the electrolyte. There are simulations for the charging of electrode material for different spherical (Welland et al., 2015; Zeng and Bazant, 2014), ellipsoidal nanoparticles (Huttin, 2014; Leo et al., 2014) or more complex single particle microstructures (Tang et al., 2011; Cogswell and Bazant, 2013). Macroscopic charge-discharge behavior of porous electrodes (Dreyer et al., 2011; Ferguson and Bazant, 2014, 2012; Orvananos et al., 2014; Li et al., 2014) and a focus on effects like hysteresis (Dreyer et al., 2010) are explained without resolving a microstructure but using arguments of homogenization or particle size. In this article a model for the resolution of porous electrode microstructures is introduced.

In Section 2 the electrochemical model for a dilute solution battery on the microscale (Latz and Zausch, 2011) is presented. A phase-field model for phase separation given in Zeng and Bazant (2014) is introduced. A model for a battery with resolved microstructure in the porous electrodes, a phase-field model in the cathode material, and variable Butler–Volmer interface currents are introduced. In Section 3 the spatial discretization is introduced. An adaptive time integration algorithm with small timesteps during initiation of phase-separation and reconfigurations and large timesteps during moving of phase-interfaces is presented. In Section 4 different numerical tests are presented. The well-known process of spinodal decomposition is shown and explained in Section 4.1 on a circular cathode particle. Two different models for the exchange current density in the Butler–Volmer currents are evaluated in Section 4.2, and the interaction of the Butler–Volmer currents with the different phases at the interface is examined. In Section 4.3 the numerical convergence of the battery cell voltage is examined. In Section 4.4 the effect of the size and the shape of the cathode particle on the phase separation process is investigated as already has been reported in Bai et al. (2011). In Section 5 all findings are summarized and possible enhancements as well as extensions of the numerical method are discussed.

2. Electrochemical model

In this section the equations for a lithium ion battery model on the microscale are presented. After introducing the spatial domains involved the transport equations (Latz and Zausch, 2011) for the lithium ions and electric charges in each domain are proposed in anode and electrolyte. The transport in the cathode domain is given in Bazant (2013); Zeng et al. (2013). Current conditions on the interface between the domains are taken from established models and boundary and initial conditions complete the model. In this paper the spatial two dimensional case is considered. The extension to a three dimensional model is possible.

A rectangular domain  $\Omega = (0, L_x) \times (0, L_y) \subset \mathbb{R}^2$  in Fig. 1 denotes the micro-structure of a battery cell and consists of the two solid electrodes, anode  $\Omega_a$  and cathode  $\Omega_c$  and the liquid electrolyte  $\Omega_e$ , i.e.  $\Omega = \Omega_a \cup \Omega_e \cup \Omega_c$ . A domain for a separator is not included in the model. The union  $\Omega_s = \Omega_a \cup \Omega_c$  is called the solid domain. Fig. 1 also introduces a domain decomposition with interface domains  $\Gamma_{ae}$ ,  $\Gamma_{ce}$  and  $\Gamma_{se} = \Gamma_{ae} \cup \Gamma_{ce}$ .

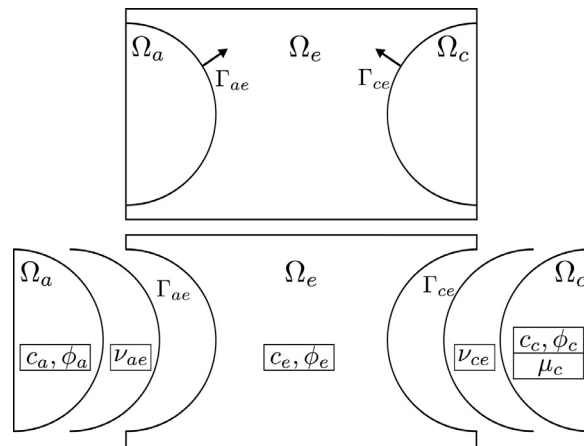


Fig. 1. Decomposition of a battery cell into anode  $\Omega_a$ , electrolyte  $\Omega_e$ , cathode  $\Omega_c$  and the interfaces  $\Gamma_{ae}$  and  $\Gamma_{ce}$ .

2.1. Governing equations

First the transport equations in the three domains  $\Omega_a$ ,  $\Omega_e$ ,  $\Omega_c$  are introduced separately.

Electrolyte

In Latz and Zausch (2011) the transport equations for ion concentration  $c_e$  and the electric potential  $\phi_e$  in an electrolyte are given as

$$\partial_t c_e - \text{div} \left( D_e \nabla c_e - \frac{t_+}{z_+ F} (\kappa_e \nabla \phi - \kappa \frac{t_+ - 1}{z_+ F} \left( \frac{\partial \mu_e}{\partial c} \right) \nabla c_e) \right) = 0, \quad (x, y, t) \in \Omega_{e,T}, \tag{1}$$

$$- \text{div} \left( \kappa_e \frac{1 - t_+}{z_+ F} \left( \frac{\partial \mu_e}{\partial c} \right) \nabla c_e - \kappa_e \nabla \phi_e \right) = 0, \quad (x, y, t) \in \Omega_{e,T}. \tag{2}$$

Table 1 gives numerical values for the electrolyte diffusion coefficient  $D_e$ , the electrolyte conductivity  $\kappa_e$ , the charge coefficient  $z_+$ , the lithium transference number  $t_+$  and the Faraday constant  $F$ .

A logarithmically scaled chemical potential  $\mu_e(c_e) = RT \log \frac{c_e}{c_m}$  is used to rewrite Eq. (1). This gives the final governing equations in terms of the concentration  $c_e$  and the electric potential  $\phi_e$  in the electrolyte as

$$\partial_t c_e - \text{div} \left( \left( \frac{D_e}{RT} c_e + \frac{\kappa_e t_+ (t_+ - 1)}{F^2} \right) \nabla \mu_e(c_e) + \frac{\kappa_e t_+}{F} \nabla \phi_e \right) = 0, \quad (x, y, t) \in \Omega_{e,T}, \tag{3}$$

$$- \text{div} \left( \frac{\kappa_e (t_+ - 1)}{F} \nabla \mu_e(c_e) + \kappa_e \nabla \phi_e \right) = 0, \quad (x, y, t) \in \Omega_{e,T}.$$

This system of two equations consists of a parabolic equation and an elliptic equation (Evans, 1996).

Anode

An electrochemical model for the transport of lithium ions inside electrode material is taken from Latz and Zausch (2011) as

$$\partial_t c_a + \text{div} (D_a(c_a) \nabla \mu_a(c_a)) = 0, \quad (x, y, t) \in \Omega_{a,T}. \tag{4}$$

The anode diffusion coefficient  $D_a(c_a)$  is chosen depending on the local lithium ion concentration  $c$  as

$$D_a(c_a) = \frac{D_0}{RT} c_a \left( 1 - \frac{c_a}{c_m} \right) \tag{5}$$

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