

Stress simulation in lithium-ion batteries

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Micro Abstract

Phase separation during the intercalation of lithium ions can lead to degradation effects in some cathode materials. A model describing lithium ion diffusion, electric potentials and small deformations is introduced on the microscale. The Cahn-Hilliard equation is used in an electrochemical model, coupled to linear elasticity of small strains in the electrode material. An immersed boundary method is used with adaptive time steps. Charging of porous microstructures is numerically simulated.

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Introduction

Some cathode materials in lithium-ion batteries show phase-separation during usage. The imbalanced intercalation of the lithium ions into the lattice causes large concentration gradients. The stresses resulting from these gradients can damage and destroy the battery cell. The computer simulation of the stresses during charging and discharging can support the development of battery cell structures.

A micromodel coupling lithium-ion diffusion to the electric potential and Butler-Volmer interface currents and linear elasticity is applied [3]. It is extended by a phase-field model for the phase-separation of lithium-rich and lithium-poor phases in lithium iron phosphate [2]. This enables the resolution of a complex three-dimensional porous microstructure of the anode and cathode material in the liquid electrolyte. Additionally mechanical stresses resulting from strains depending on the concentration are computed [6].

The Cahn-Hilliard equation resulting from the phase-field model requires fine spatial resolutions. A domain decomposition algorithm is introduced that allows for an efficient numerical solution in each of the domains separately such that extensive numerical effort is constricted to the cathode domain. The immersed interface method, first introduced in [4], is extended for diffusion equations and the Cahn-Hilliard equation. By this, large, adaptive time steps are possible in arbitrary complex domains [1].

Numerical examples demonstrate the coupling effects between the electro-chemical model and the mechanical model. The lithium ion concentration results in an isotropic expansion of the cathode material and stress residuals in the material. Also, the hydrostatic stress changes the Nernst overpotential and the cell voltage is changed. Stress invariants and their maxima are calculated depending on the microstructure during a charge cycle. Based on this, the damage inside the electrode domain is predicted.

1 Electro-chemo-mechanical model

A cuboid domain $\Omega = (0, L_1) \times (0, L_2) \times (0, L_3) \subset \mathbb{R}^3$ denotes the microstructure of a battery cell and consists of the two solid electrodes, anode Ω_a and cathode Ω_c , and the liquid electrolyte Ω_e . A time-dependent problem is posed on the domain $T = (0, t_0)$. For concentration, electric potential and displacement, partial differential equations are given on each of the

three domains anode, cathode and electrolyte.

Transport equations in the electrolyte domain, the anode domain, and the cathode domain are introduced separately based on [3] and [5]. The transport equations for ion concentration c_e and the electric potential ϕ_e in a liquid electrolyte, see [3], are considered as

$$\begin{aligned}\partial_t c_e &= \text{div} \left[\left(\frac{D_e}{RT} c_e + \frac{\kappa_e t_+ (t_+ - 1)}{F^2} \right) \nabla \mu_e(c_e) + \frac{\kappa_e t_+}{F} \nabla \phi_e \right], \\ 0 &= \text{div} \left[\kappa_e \frac{(t_+ - 1)}{F} \nabla \mu_e(c_e) + \kappa_e \nabla \phi_e \right].\end{aligned}\quad (1)$$

Depending on the transference number t_+ , the transport of positive lithium ions is coupled to the transport of additional negative anions. Inside the anode material the lithium ion diffusion and the electric potential are decoupled by the equations

$$\begin{aligned}\partial_t c_a &= \text{div} \left[\frac{D_a}{RT} c_a \left(1 - \frac{c_a}{c_{\max,a}} \right) \nabla \mu_a(c_a) \right], \\ 0 &= \text{div} (\kappa_a \nabla \phi_a).\end{aligned}\quad (2)$$

The stress-strain relationship model presented in this work is based on a linear-elastic model [6]. The strain $\boldsymbol{\varepsilon}$ is modified to include a chemical part, $\boldsymbol{\varepsilon}_{\text{el}} := \boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_{\text{ch}}$. The stress-strain relationship is then given as

$$\begin{aligned}\boldsymbol{\varepsilon}_{\text{el}} &= \frac{1}{2} (\nabla \mathbf{u} + \nabla \mathbf{u}^T) - \frac{\theta}{3} c \mathbf{I}, \\ \boldsymbol{\sigma} &= \lambda \text{Tr}(\boldsymbol{\varepsilon}_{\text{el}}) \mathbf{I} + 2\mu \boldsymbol{\varepsilon}_{\text{el}},\end{aligned}\quad (3)$$

By this, the electrochemical model and the mechanical model are coupled as

$$\mu_{\text{el}} = \frac{\theta}{3} \text{tr}(\boldsymbol{\sigma}) \Leftrightarrow \boldsymbol{\varepsilon}_{\text{ch}} = \frac{\theta}{3} c \mathbf{I}, \quad (4)$$

where θ is the partial molar volume coefficient.

In the cathode, a phase-field model for the concentration c_c is considered. The phase-field parameter is here the normalized lithium ion concentration $p = \frac{c}{c_{\max,c}}$. A free energy with a penalty gradient term is assumed as

$$F(p, \nabla p) = \alpha L_0^2 \frac{G}{L} F_0(p) + \frac{\beta GL}{2} (\nabla p)^2, \quad (5)$$

where the parameters G and L are used to describe the phase-field model. They represent energy density and the width of the interface region, respectively. The chemical potential μ is now given as the variational derivative by

$$\frac{\mu(c_c)}{RT} = \alpha L_0^2 \frac{G}{L} F_0' \left(\frac{c_c}{c_{\max,c}} \right) - \beta GL \Delta \left(\frac{c_c}{c_{\max,c}} \right). \quad (6)$$

Combining (2) and (6), the equations governing the lithium ion concentration c_c , the electric potential ϕ_c and the chemical potential μ in the cathode material are given by

$$\begin{aligned}\partial_t c &= \text{div} \left[\frac{D_c}{RT} c_c \left(1 - \frac{c_c}{c_{\max,c}} \right) \nabla \mu \right], \\ 0 &= \text{div} (\kappa_c \nabla \phi_c), \\ \mu &= RT \alpha L_0^2 \frac{G}{L} F_0' \left(\frac{c_c}{c_{\max,c}} \right) - RT \beta GL \Delta \left(\frac{c_c}{c_{\max,c}} \right).\end{aligned}\quad (7)$$

On the electrode-electrolyte interfaces, interface conditions are defined by the Butler-Volmer conditions as

$$i_{\text{se}} = i_0(c_s, c_e) \sinh \left(\frac{F}{2RT} \eta \right). f_{\text{se}} = \frac{i_{\text{se}}}{F} \cdot \eta = \phi_s - \phi_e - \frac{\mu_s}{F} + \bar{U}_s, \quad (8)$$

The function i_0 is called the exchange current density, possibly defined as

$$i_0(c_s, c_e) = 2k\sqrt{c_e c_s \frac{c_{\max,s}}{2}}. \quad (9)$$

The electric current i_{se} is used to define Neumann boundary conditions for the Poisson equations for the electric potential while the concentration flux f_{se} is used to define Neumann boundary conditions for the diffusion equations of the lithium ion concentration. The Faraday constant F acts as a coupling factor. By the positive lithium ion charge, diffusion is coupled to the electric current. A fixed electric current is defined by the C-rate, usually specified in the unit per hour, $\frac{1}{3600s} = \frac{1}{h}$. C-rate 1 defines a charging current i_{in} such that it takes one hour to charge the battery cell from empty to full state of charge. For the diffusion equations and the elastic equations valid boundary conditions are considered. A discharged battery is considered for the numerical simulation test case.

2 Numerical methods

First the governing equations of the electro-chemical model are separated into six smaller initial-boundary-value-problems (IBVPs). The focus is on the coupling of those six different IBVPs in anode, cathode and electrolyte for both lithium ion concentration and electric potential. The coupling by the non-linear Butler-Volmer equations is solved by iteration. The convergence order of the domain decomposition algorithm is one.

Next the immersed interface method (IIM) is introduced for the Poisson equation, the diffusion equation, and the Cahn-Hilliard equation. For the solution finite difference stencils and implicit Runge-Kutta schemes are applied. Methods with convergence order two, four and six are defined for the periodic Poisson equation and the periodic diffusion equation. For the periodic Cahn-Hilliard equation a method with convergence order two is defined.

Assume the diffusion equation on an arbitrary domain Λ . Then a discretization in time with an implicit Euler method and in space with a symmetric finite difference stencil results in the equation

$$(I_h + \tau \Delta_h) c_h = \check{c}_h, \quad (10)$$

where c_h and \check{c}_h denote the concentration field for the current and previous timestep, respectively. This equation is extended to include additional jump variables g_h on the boundary $\partial\Lambda$ that allow for an embedding of the equation onto a larger cuboid domain Ω ,

$$\begin{pmatrix} I_h + \tau \Delta_h & \Psi \\ D & I_h \end{pmatrix} \begin{pmatrix} c_h \\ g_h \end{pmatrix} = \begin{pmatrix} \check{c}_h \\ f_h \end{pmatrix}, \quad (11)$$

where f_h denotes arbitrary Neumann boundary conditions on $\partial\Lambda \subset \Omega$. The enlarged block system is then reduced by Schur's complement to

$$(I_h - D(I_h + \tau \Delta_h)^{-1} \Psi) = f_h - D(I_h + \tau \Delta_h)^{-1} \check{c}_h. \quad (12)$$

This allows for an efficient numerical solution as the number of variables is significantly reduced. Given a regular voxel mesh discretization with width h , the number of degrees of freedom inside Λ is in $O(\frac{1}{h^3})$, while the number of degrees of freedom on the boundary domain $\partial\Lambda$ is in $O(\frac{1}{h^2})$. For the Poisson and the diffusion equation, second-order formulation for the immersed interface methods can be given. For the Cahn-Hilliard equation, the linear operator resulting from the discrete partial differential equation is more complex and only a first-order convergence can be achieved.

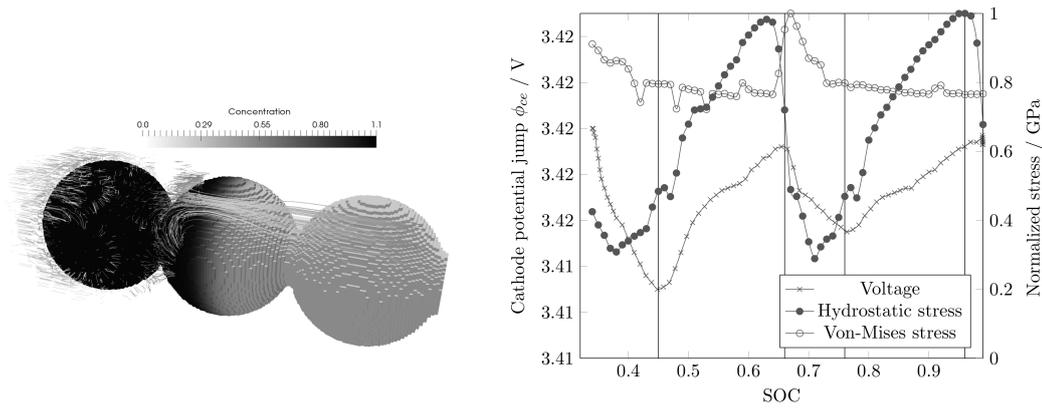


Figure 1. Left: Phase-separating cathode microstructure of three spherical particles. Depicted is the concentration inside the electrode and the lithium ion current in the electrolyte. Right: Cell voltage and maximum non-dimensionalized stress invariants occurring in the electrode during a charge cycle.

3 Numerical examples

Figure 1 shows on the left the phase separation in a cathode microstructure made from three spherical particles. On the right, the cell voltage and non-dimensionalized maximum stress invariants occurring in the electrode during a charge cycle are depicted. The simulation results of the phase separation are interpreted to allow for qualitative and quantitative prediction of damage and fracture resulting from multiple charge cycles by extension of the linear elastic model to e.g. include large deformations.

Conclusions

Currently, the evaluation of maximum stress invariants inside the battery electrode particles allow only for rough qualitative prediction of time and point of failure. Different microstructures can be analyzed and their advantages compared. Depending on material parameters the maximum C-rate and cycling effects can be evaluated. In the future, additional damage or fracture models allow for a more precise prediction of the aging under realistic load cases.

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