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A Cahn-Hilliard-type phase-field theory for species diffusion coupled with large elastic deformations: application to phase-separating Li-ion electrode materials

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Abstract

We formulate a unified framework of balance laws and thermodynamically-consistent constitutive equations which couple Cahn-Hilliard-type species diffusion with large elastic deformations of a body. The traditional Cahn-Hilliard theory, which is based on the species concentration c and its spatial gradient ∇c, leads to a partial differential equation for the concentration which involves fourth-order spatial derivatives in c; this necessitates use of basis functions in finite-element solution procedures that are piecewise smooth and globally $\mathcal{C}^1$-continuous. In order to use standard $\mathcal{C}^0$-continuous finite-elements to implement our phase-field model, we use a split-method to reduce the fourth-order equation into two second-order partial differential equations (pdes). These two pdes, when taken together with the pde representing the balance of forces, represent the three governing pdes for chemo-mechanically-coupled problems. These equations are amenable to finite-element solution methods which employ standard $\mathcal{C}^0$-continuous finite-element basis functions.

We have numerically implemented our theory by writing a user-element subroutine for the widely-used finite-element program Abaqus/Standard. We use this numerically implemented theory to first study the diffusion-only problem of spinodal decomposition in the absence of any mechanical deformation. Next, we use our fully-coupled theory and numerical-implementation to study the combined effects of diffusion and stress on the lithiation of a representative spheroidal-shaped particle of a phase-separating electrode material.

Keywords: Continuum Mechanics; Thermodynamics; Diffusion; Elasticity; Lithium-ion batteries

1 Introduction

Several Li intercalation compounds of interest in battery applications exhibit phase-separation (cf., e.g., Bruce et al., 2008; Tang et al., 2010), and central to the study of coupled diffusion-deformation problems in such electrode materials is the Cahn-Hilliard phase-field theory (Cahn and Hilliard, 1958, 1959; Cahn, 1961). As background, first consider the classical Cahn-Hilliard theory for species diffusion and phase segregation which is *uncoupled* from the mechanical problem. Let $\bar{c} \in [0,1]$ denote a normalized species concentration, $\hat{\psi}_{\mathrm{R}}(\bar{c}, \nabla\bar{c})$ the free energy per unit reference volume, and let the functional

$$\Psi(\bar{c}) = \int_{\mathrm{B}} \hat{\psi}_{\mathrm{R}}(\bar{c}, \nabla\bar{c})\, dv_{\mathrm{R}} \tag{1.1}$$

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