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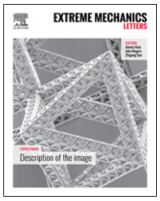

Mechanical interactions regulated kinetics and morphology of composite electrodes in Li-ion batteries

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ABSTRACT

Li-ion batteries are a system that features strong coupling between mechanical stresses and electrochemical reactions. Prior studies on stresses in electrodes are focused on single particles or mono-phase materials. The kinetics and morphology of composite electrodes regulated by the mechanical interactions are much less exploited. We integrate a continuum theory of coupled diffusion and large elasto-plastic deformation into a finite element program. Such a computational tool enables us to explore the intimate coupling between the lithiation kinetics and stresses in three-dimensional electrodes that are composed of multiple components. We find that Li profiles and stress states in multiple particles constrained by a matrix are significantly different from that in a free-standing configuration. The mechanical interactions regulate Li chemical potential in Si nanowires and transform the anisotropic deformation to an isotropic behavior and vice versa. The modeling is in good agreement with a recent experimental report.

1. Introduction

Li-ion batteries are a key technology for portable electronics and electric vehicles [1–3]. The demand of lightweight, high-energy-density batteries has stimulated tremendous efforts from virtually all engineering disciplines [4]. Mechanical degradation has become a limiting factor for the commercialization of high-capacity electrodes. Such effects are exemplified in high-capacity anodes and Li-rich cathodes—large volumetric swelling and shrinking ranging from tens of percent to a few hundred percent occurs repetitively during the charge and discharge cycles [5–7]. Averting the mechanical degradation remains one of the major challenges for the development of high-performance batteries. On the frontier of mechanics, the kinetics of diffusive and interfacial reactions in the electrodes induces a wealth of intriguing phenomena, including cavitation [8–10], reactive plasticity [11,12] and corrosive fracture [13]. The electrochemical processes of Li insertion and extractions modulate large deformation and stress generation in the electrodes. Meanwhile, mechanical stresses significantly influence the thermodynamics and kinetics of lithiation reactions, ion diffusion, and phase transitions [14–18].

Numerical modeling is a common exercise to study the evolution of Li diffusion and the stress field in Li-ion batteries. However, prior research has been extensively focused on single particles or two-dimensional structures [19–25]. Bower and Guduru developed a finite element method to model diffusion, large deformation, and fracture [26], and the method was applied for a thin-film Si electrode [27]. Brassart et al. developed a finite element program to model the cyclic behavior of single spherical particles [28]; similar approach was adopted by Cui et al. [29]. An and Jiang reported a finite element package integrated in ABAQUS, and studied the failure mechanism in Si thin film bonded to a metal current collector [30]. Stein and Xu used isogeometric analysis to model the mechanical behaviors of single particles with different shapes [31]. Yang et al. recently developed a finite element program by manipulating the

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stress effect on Li diffusivity, and studied the lithiation behavior of Si nanowires [32,33]. There are a few attempts in recent studies that incorporate a secondary component in the material model. Higa et al. simulated stresses in a two-dimensional cylindrical model that consists of a well-bonded binder with a cylindrical particle [34]. Rahani et al. studied the role of plastic deformation of binders on the stress evolution in the distributed spherical particles in a porous electrode by using a two-dimensional microstructural resolved model [35]. Nevertheless, the mechanical interactions among the different components and the stress effect on Li transport have not been considered. There has been a lack of computation tools to investigate the fully coupled diffusion and stress in three-dimensional composite configurations. Herein, we develop a finite element program based on a continuum theory of coupled diffusion and large elasto-plastic deformation. It enables us to model the complex behaviors of three-dimensional objects that are composed of multiple components and to explore the kinetics and morphological evolution of composite electrodes coupled with the mechanical interactions.

As pointed out by a recent experimental study on Si nanowires, lithiation often occurs simultaneously in a cluster of active materials in a mechanically confined medium [36]. The mechanical interactions among the individual Si structures in the closed space alter the reaction mechanisms along the various crystallographic orientations and enhance the fracture resistance of lithiated Si by mediating the stress concentrations. Indeed, distinct from the simplified single-particle or free-standing models, a battery electrode usually consists of multiple components with a large variation of mechanical properties [37]. The different components interact with each other during lithiation reactions and raise a complex field of stresses. We demonstrate that single-particle models are unable to capture the mechanical behaviors of a composite electrode due to the strong coupling between Li transport and stresses. In a model of multiple particles embedded in a matrix, we find that Li profiles and the stress field are highly asymmetric due to the matrix confinement and particle interactions. In another example of multiple Si nanowires in a confined space, the mechanical stress regulates the Li chemical potential, redistributes the Li concentration, and transforms the anisotropic deformation of nanowires to an isotropic behavior and vice versa. Such findings are in good agreement with the experimental report [36].

2. Theory and finite element modeling

As the first attempt to model the composite electrodes, we consider three-dimensional material models consisting of two components—active and inactive materials, where Li diffusion only occurs in the active material while the inactive material provides mechanical confinement. This is an assumption based on the fact that the kinetics in batteries is often limited by the diffusion in the active materials while Li transport through the porous matrix is usually a faster process. In the reference state, both components are free of Li and stresses. Lithiation is induced by imposing a nominal influx J_0 of Li on the surface of the active material. The concurrent diffusion and large elasto-plastic deformation is described by a previous developed theory by Zhao et al. [38]. In brevity, the mechanical equilibrium is represented as follows,

$$\nabla \cdot \mathbf{S} + \mathbf{F_b} = 0 \tag{1}$$

where $\mathbf{S}$ is the nominal stress calculated as $\mathbf{S} = \mathbf{K} : \boldsymbol{\varepsilon}_\mathbf{e}$, $\mathbf{K}$ the stiffness matrix, $\boldsymbol{\varepsilon}_\mathbf{e}$ the elastic strain, $\mathbf{F_b}$ the body force. The total deformation of a representative material element is treated to follow the kinematic multiplicative decomposition $F = F_e F_l F_p$, where F represents the deformation gradient, F_e the reversible elastic distortion of the material, F_l lithiation-induced volumetric deformation, and F_p the irreversible plastic deformation that dictates the shape change of the body. The elastic strain is computed as $\boldsymbol{\varepsilon}_\mathbf{e} = \frac{1}{2}(\mathbf{F_e^T F_e} - \mathbf{I})$. The volumetric change due to Li insertion is $1 + \Omega C$, where Ω and C are the partial molar volume and concentration of Li, respectively. The material element yields under the von Mises conditions and the plastic deformation follows the J_2 flow theory. For the inactive material, the deformation and stresses are caused by the mechanical interactions with the active material. Its constitutive behavior is described by a Neo-Hookean material model [39].

The kinetics of Li diffusion is described as follows. Let C be the nominal concentration of Li (i.e., the number of Li atoms per unit volume of active materials in the reference state). Let $\boldsymbol{J}$ be the nominal flux of Li (i.e., the number of Li atoms per unit reference area per unit time). Conservation of the number of Li atoms requires that

$$\frac{\partial C}{\partial t} + \nabla \cdot \boldsymbol{J} = 0, \tag{2}$$

where ∇ represents the gradient with respect to the material (or Lagrangian) coordinate. Let $\boldsymbol{j}$ be the true flux of Li (i.e., the number of Li atoms per unit area per unit time in the spatial (or Eulerian) coordinate). It is taken to depend on the spatial gradient of the chemical potential μ, $\boldsymbol{j} = -\frac{cD}{kT}\nabla_{x_i}\mu$, where D is a constant diffusion coefficient, kT the temperature in the unit of energy, c the true concentration of Li in the spatial coordinate, and the ∇_{x_i} gradient with respect to the spatial coordinate. Using the standard transformation rules of continuum mechanics, the relationship between the nominal flux and the chemical potential in the Lagrangian coordinate can be obtained as $\boldsymbol{J} = -\frac{CD}{kT}F^{-1}F^{-T}\nabla\mu$. The boundary conditions are prescribed as follows. We prescribe a zero displacement condition at the center of the active materials during Li insertion to prevent the rigid motion, $\mathbf{u}(0, t) = 0$. For the diffusion boundary condition, we assume good ionic and electronic conductivities of the inactive materials such that each active material experiences the same current. We impose a nominal flux $\boldsymbol{J}$ on the surface of the particles with a constant value J_0.

The governing equations for the kinematics of deformation and the kinetics of diffusion are both strongly nonlinear. We integrate their weak formulations into the finite element program within a Lagrangian setting. The coupled equations for stress equilibrium and Li diffusion are solved simultaneously at every time step. The weak form for the

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