Mechanics of Materials 91 (2015) 372–381

Contents lists available at ScienceDirect

Mechanics of Materials

journal homepage: www.elsevier.com/locate/mechmat

Effects of particle shape and concurrent plasticity on stress generation during lithiation in particulate Li-ion battery electrodes

Yuyang Lu, Yong Ni *

CAS Key Laboratory of Mechanical Behavior and Design of Materials, Department of Modern Mechanics, University of Science and Technology of China, Hefei, Anhui 230026, PR China

ARTICLE INFO

Article history:
Received 1 January 2015
Received in revised form 10 March 2015
Available online 2 April 2015

Keywords:
Phase field method
Stress generation
Elastoplastic
Shape effect
Lithium ion battery

ABSTRACT

A phase field model is developed to investigate the influences of microstructure and concurrent plasticity on the stress development in particulate Li-ion battery electrodes during two-phase lithiation. The model introduces one static order parameter to describe the arbitrary morphology of the particulate electrode and other evolving order parameters governed by the kinetic equations for lithium diffusion and elastoplastic deformation, respectively. The mechanism for the transition from surface hoop compression to surface hoop tension observed in spherical electrodes during lithiation is reexamined using numerical simulations. Our results further show that when the electrode is non-spherical, the combination of large size ratio, large curvature and low yield stress facilitates the transition. In addition, numerical simulations demonstrate that the current model is capable of predicting evolutions of lithium concentration, stress and plastic zone in the electrode with interconnected multi-particle configuration.

1. Introduction

Intensive efforts have been made to explore rechargeable lithium-ion batteries with high energy density (Wang and Kumta, 2007), fast charging or discharging rate (Kang and Ceder, 2009) and long cycle life (Arico et al., 2005) to meet demanding applications (Chiang, 2010; Goodenough and Kim, 2010). One big challenge is to regulate the generated deformation and stress during the electrochemical lithiation and delithiation wherein lithium diffusion is fully coupled to stress. The inhomogeneously distributed lithium usually results in high elastic stresses, which degrade battery performances significantly via mechanical damage of the electrodes (Chon et al., 2011; Gabrisch et al., 2008; Liu et al., 2012b; Ryu et al., 2011), correlated capacity fade or impedance growth (Vetter et al., 2005). In addition, the elastic stresses significantly affect the thermodynamics and kinetics of lithium diffusion especially when a phase transformation is involved (Bower et al., 2011; Wu, 2001; Yang, 2005; Zhang et al., 2014). Thus it is important to understand various causes of the stress development during electrochemical cycling and develop strategies to mitigate the negative impact by the mechanical stress (Mukhopadhyay and Sheldon, 2014).

A number of theoretic works based on the thermal stress model are performed to simulate the stress distribution and evolution in electrodes. It is intuitively accepted that the electrode surface is subject to compressive hoop stress during lithiation (Cheng and Verbrugge, 2009; Christensen and Newman, 2006; Gao and Zhou, 2011; Zhang et al., 2007). However, this intuition contradicts with recent experimental phenomenon, where the observed surface crack during lithiation is believed to be

* Corresponding author.
E-mail address: yni@ustc.edu.cn (Y. Ni).

http://dx.doi.org/10.1016/j.mechmat.2015.03.010
0167-6636/

due to tensile hoop stress close to surface (Liu et al., 2011, 2012b; McDowell et al., 2012). Further experiments indicate that the lithiation in these electrode materials is operated by a moving phase boundary separating Li-rich phase and Li-poor phase in accompany with plastic deformation (Chon et al., 2011; Huang et al., 2010; Lee et al., 2011; Sethuraman et al., 2010). A few papers develop mechanical models taking into account the two-phase lithiation, plasticity and large deformation in a spherical particle or film subject to lithiation (Cui et al., 2012; Drozdov et al., 2013; Huang et al., 2013; Liu et al., 2012a; Zhao et al., 2012). It is found that the anisotropy of the lithiation strain including chemical and plastic parts plays a key role in such tensile hoop stress generation (Cui et al., 2012; Drozdov et al., 2013; Huang et al., 2013; Liu et al., 2012a; Zhao et al., 2012). Since the chemical lithiation strain depends on the process of lithium diffusion while the lithiation induced plastic strain depends on the development of plastic zone, it is valuable tracking concurrent lithium diffusion and plastic flow to evaluate the magnitude and distribution of the tensile hoop stress at the surface especially when the configuration of the electrode is beyond simple geometry as it is in many experiments (Kim et al., 2008; Lee et al., 2012). It is reported that the electrode shape dramatically influences the stress distribution, and then alters the potential failure site and fracture behaviors even during single-phase lithiation in the absence of plasticity (DeLuca et al., 2011; Deshpande et al., 2010). However it remains unclear how the morphological change of such electrode impacts the coupled evolution of lithium concentration and plastic zone in the presence of two-phase lithiation—which determines the magnitude of the tensile hoop stress at the surface— that can induce irreversible mechanical damage.

In this paper, we develop a phase field model to study the influences of microstructure and plastic deformation on the stress development in Li-ion battery electrodes during two-phase lithiation in the case of small deformation. It is well-known that phase field method has an advantage to investigate various evolution kinetics coupled with mechanical stresses avoiding the need to trace the arbitrarily moving interface (Chen, 2002; Wang and Li, 2010). The method has been successfully applied to simulate the effect of various factors on the thermodynamics and kinetics of lithium-ion batteries, such as size-dependent phase separation (Burch and Bazant, 2009; Tang et al., 2009), intercalation dynamics (Han et al., 2004; Singh et al., 2008), electrode boundary reaction (Bai et al., 2011; Burch and Bazant, 2009) and anisotropic lithiation. So far, only a few phase field models (Cogswell and Bazant, 2012; Hu et al., 2013; Huttin and Kamlah, 2012; Liang et al., 2014; Tang et al., 2009; Zuo and Zhao, 2015) have accounted for the effect of stress on above phenomena, let alone the effect of complex electrode geometry. In the current phase field model one static order parameter is introduced to describe arbitrarily-shaped particulate electrodes. The lithium diffusion involving phase transformation is driven by minimizing the Gibbs free energy using the Cahn–Hilliard model where the stress-coupled diffusion is automatically taken into account (Cogswell and Bazant, 2012). In addition, the evolution of the plastic zone is assumed by solving a modified time-dependent Ginzburg–Landau equation (Guo et al., 2005), which is consistent with the classic J_2 flow theory (Asaro and Lubarda, 2006). We consider the electrode and the surrounding electrolyte as a computational system. The phase field microelasticity model (Wang et al., 2002) based on the Eshelby's equivalent inclusion theory (Eshelby, 1957) is adapted to calculate the elastic field which includes the combined contributions of chemical lithiation strain, plastic zone and elastic inhomogeneity.

The remainder of this paper is organized as follows. In Section 2 we present the phase field modeling. In Section 3 we discuss when and why the transition from surface hoop compression to surface hoop tension in a nanowire electrode with circular cross section occurs during lithiation by performing numerical simulations based on the current model. In Section 4 we present numerical simulations to discuss how the size ratio, the curvature and low yield stress influence evolutions of lithium concentration, elastic stress and plastic zone in the electrode with non-spherical or interconnected multi-particle configuration.

2. Phase field model

As sketched in Fig. 1(a), we consider an electrode surrounded by the electrolyte undergoing lithiation. In the framework of phase field model, the morphology of the electrode is described by a static order parameter $\eta(\mathbf{r})$ defined as $\eta(\mathbf{r}) = 1$ in the electrode and $\eta(\mathbf{r}) = 0$ in the electrolyte. During two-phase lithiation, the lithium inserts into the electrochemical active compound forming a moving phase boundary separating Li-rich phase and Li-poor phase. In addition, we assumed such lithiated electrode is a binary solid solution, and its two-phase feature can be described by the bulk chemical free energy as a double-well function with respect to lithium concentration c. The evolution of the lithium concentration driven by minimizing the total free energy is governed by the Cahn–Hilliard equation (Cahn and Hilliard, 1958)

$$\frac{\partial c}{\partial t} = \nabla \cdot \left(\frac{D}{N_v k_B T} \nabla \frac{\delta E^{tot}}{\delta c} \right), \tag{1}$$

where D is the diffusion coefficient that is assumed to be constant for simplification. N_v is the number of atoms per volume, k_B is Boltzmann's constant, T the is absolute temperature. The total free energy of the system can be expressed as

$$E^{tot} = \int_V \left\{ N_V [\Omega c(1-c) + k_B T(c \ \ln \ c + (1-c)\ln(1-c)) + \frac{\kappa}{2} |\nabla c|^2] + \frac{1}{2} \sigma_{ij}^{el} \varepsilon_{ij}^{el} \right\} dV, \tag{2}$$

where the first two terms in the square bracket are the bulk chemical free energy per molecule based on the regular solution model, Ω is a constant respect to the nearest-neighbor interaction strength between lithium atoms, the third term is the gradient energy with κ the gradient energy coefficient and ∇ the gradient operator, the last term is the elastic energy density with σ_{ij}^{el} and $\varepsilon_{ij}^{el} = \varepsilon_{ij} - \varepsilon_{ij}^{*}$ the elastic stress and strain tensors,