International Journal of Solids and Structures 000 (2018) 1–12

Contents lists available at ScienceDirect

International Journal of Solids and Structures

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

Lithiation-induced buckling of wire-based electrodes in lithium-ion batteries: A phase-field model coupled with large deformation

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ARTICLE INFO

Article history:
Received 5 August 2017
Revised 12 April 2018
Available online xxx

Keywords:
Lithium-ion batteries
Phase-field model
Large deformation
Buckling

ABSTRACT

Wire-based electrodes can experience buckling during lithiation, which can lead to the capacity fading of lithium-ion batteries. This work is focused on the buckling behavior of wire-based electrodes induced by a two-phase lithiation reaction process. A Cahn–Hilliard type phase-field model coupled with large deformation is proposed. A modified critical buckling load is proposed as a function of the state of charge, which can be used in the analysis of lithiation-induced instability of wire-based electrodes. The coupling equations are solved by the PDE (partial differential equation) module in the Multiphysics of COMSOL. The numerical results show that the critical buckling time for the onset of buckling decreases with the increase of the wire length and current density. The single-phase reaction case is also studied to compare with the two-phase reaction case. The numerical results reveal that the critical buckling time for a wire with the two-phase reaction is the same as that with the single-phase reaction for the same geometries and the same *C-rate* in accord with the analytical analysis. The constraints to the ends of a wire play an important role in determining the critical buckling time for both cases, and a “stronger” constraint will increase the critical buckling time. Numerical analysis is used to determine the critical length, above which the buckling occurs prior to the onset of phase separation, and reveal the dependence of the critical length on the *C-rate* and the constraint condition. The effect of the wire length on the critical buckling state of charge (*SOC*) is independent of the lithiation mechanism, which is consistent with the analytical solution from the theory of linear elasticity. The larger the aspect ratio, the closer is the interphase position at the onset of the buckling to the outer surface of the wire.

1. Introduction

Lithium-ion battery (LIB) has become the most common choice of energy storage for portable consumer electronics, such as smart phones, laptops, and digital cameras. However, the volumetric change of electrodes during electrochemical lithiation/delithiation, which can lead to mechanical degradation of the electrodes, usually shortens the cycle life of LIBs. To address this issue, wire-based electrodes have been proposed, which exhibit good electrochemical performance with little pulverization, and have a short distance for the lithium insertion (Chan et al., 2008).

The volumetric change due to lithiation or delithiation will introduce local stress in the electrodes of LIBs, which is known as diffusion-induced stress (DIS). For a wire-based electrode, the compressive stress in axial direction will result in the buckling phenomenon if it is equal to or larger than the critical stress. The buckling of wire-based electrodes can cause mechanical degradation and lead to local fracture (Wang et al., 2015; Yang, 2011), formation of dislocations (Huang et al., 2010), and surface cracks (Wang et al., 2012). Studying stresses and their effects on the buckling of wires is of great importance in improving the electrochemical performance or prolonging the cycle life of wire-based electrodes.

It is known that the lithiation or delithiation of electrodes is a complex process, which is a function of the active materials used in electrodes and the operation conditions. Generally, the lithiation or delithiation process can be simply divided into two types; one is associated with a single-phase reaction, and the other is associated with a two-phase reaction.

For the single-phase reaction, the host material is gradually lithiated/delithiated during the insertion/de-insertion of lithium, which does not feature a reaction front and can be simply

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https://doi.org/10.1016/j.ijsolstr.2018.05.014
0020-7683/© 2018 Published by Elsevier Ltd.

Please cite this article as: K. Zhang et al., Lithiation-induced buckling of wire-based electrodes in lithium-ion batteries: A phase-field model coupled with large deformation, International Journal of Solids and Structures (2018), https://doi.org/10.1016/j.ijsolstr.2018.05.014

described by diffusion laws. Many studies have employed the thermal-analogy method proposed by Prussin (1961) to study the stress evolutions in electrodes during the single-phase lithiation. Yang (2010) derived a general relationship among the concentration of solute atoms, local reaction product, and mechanical stress, and studied the effect of local solid reaction on diffusion-induced stress. Cui et al. (2012) used a stress-dependent chemical potential coupled with large deformation theory to investigate the lithiation and delithiation process of a silicon particle. Zhang et al. (2015) developed a theoretical model to probe the effects of composition-gradient on the stress evolution in layered electrodes.

For the two-phase reaction, the host material is electrochemically lithiated to form a lithium compound, and the two phases of the lithiated phase and the un-lithiated phase are separated by a sharp reaction front with the thickness on the nanometer scale. The phase-field model proposed by Cahn and Hilliard (1958) has been widely used to describe the kinetics of the two-phase lithiation/delithiation process. Chen et al. (2014b) developed a phase-field model coupled with large elasto-plastic deformation to study the evolution of phase and stress in crystalline silicon electrodes during Li insertion. Walk et al. (2014) analyzed the stress evolutions in electrode particles by implementing the Cahn–Hilliard equation coupled with small deformation and large deformation theories, respectively. The comparison of the two theories showed that the differences of the results could be significant if both the Young's modulus and the partial molar volume of the electrode material are large. Song et al. (2015) simulated the diffusion of lithium ions and the evolution of stresses in the film electrodes with phase separation under galvanostatic and potentiostatic operations. They compared the stress results to those electrodes with single phase reaction, and showed that the phase separation phenomenon is detrimental to batteries.

There are only a few works focused on the effect of diffusion-induced stresses on the buckling of electrode structures. Chakraborty et al. (2015) presented a general framework to study the mechanical behavior of a cylindrical silicon particle and observed the occurrence of buckling due to the compressive axial stress under axially-restrained condition, and obtained a critical length below which the cylinder will never buckle. Zhang et al. (2017) studied the effect of diffusion paths, including radial diffusion and axial diffusion, on the onset of buckling, and gave the analytical solution of the critical length for wire-based electrodes. Li et al. (2016b) implemented a shear-lag model to investigate the diffusion-induced buckling of core-shell nanowires. These studies are based on the single-phase reaction. As mentioned above, the phase separation phenomenon is detrimental to batteries (Song et al., 2015). It is of great importance to analyze the buckling of wire-based electrodes during lithiation with the two-phase reaction.

In this work, we focus on the lithiation-induced buckling of wire-based electrodes, and incorporate the two-phase reaction in the analysis. A Cahn–Hilliard type phase-field model coupled with large deformation is established. The coupling equations are solved by the PDE (partial differential equation) module in the Multiphysics of COMSOL. The effects of the aspect ratio of a wire, electric current density and constraint conditions on the onset of buckling and the interphase position are investigated. The differences of the critical bucking time between the single-phase reaction and the two-phase reaction are also discussed.

2. Methodology

2.1. Mechanical equations

The insertion/de-insertion of lithium into or out of a host material will lead to the volumetric change of the host material, resulting in local deformation. Consider a wire-based electrode of an initial radius, R_0, in a cylindrical coordinate system (R, Θ, Z). With axisymmetric characteristic, the deformation gradient, **F**, which is due to the volumetric change, is written as

$$\mathbf{F} = \begin{bmatrix} F_R & 0 & 0 \\ 0 & F_\Theta & 0 \\ 0 & 0 & F_Z \end{bmatrix} = \begin{bmatrix} 1+\partial u/\partial R & 0 & 0 \\ 0 & 1+u/R & 0 \\ 0 & 0 & 1+\partial w/\partial Z \end{bmatrix}, \tag{1}$$

where u and w are the radial displacement and the axial displacement, respectively.

Using multiplicative decomposition for the diffusion-induced deformation in the framework of large deformation, the deformation gradient can be expressed as

$$\mathbf{F} = \mathbf{F}^e\mathbf{F}^i, \tag{2}$$

where $\mathbf{F}^e$ is the elastic deformation tensor, and $\mathbf{F}^i$ is the inelastic deformation tensor. Assuming that the inelastic part of deformation induced by the insertion or de-insertion of solute atoms is purely volumetric, the inelastic deformation tensor (Cui et al., 2012) can be written as

$$\mathbf{F}^i = \left(1+\Omega_1^*\hat{c}\right)^{1/3}\mathbf{I}, \tag{3}$$

where $\hat{c} = c/c_{\max}$ is the normalized concentration, and Ω_1^* $(= \Omega_1 c_{\max})$ is the corresponding normalized volumetric strain per mole fraction of the solute atoms with Ω_1 being the molar volume and $c_{\max}$ being the maximum solubility of lithium in the wire-based electrode.

The Green–Lagrange strain tensor, **E**, is then defined as

$$\mathbf{E} = \frac{1}{2}\left(\mathbf{F}^T\mathbf{F} - \mathbf{I}\right), \tag{4}$$

from which the components of the elastic strain tensor, $\mathbf{E}^e$, are calculated as

$$E_R^e = \frac{1}{2}\left[\frac{(1+\partial u/\partial R)^2}{\left(1+\Omega_1^*\hat{c}\right)^{2/3}} - 1\right], \tag{5}$$

$$E_\Theta^e = \frac{1}{2}\left[\frac{(1+u/R)^2}{\left(1+\Omega_1^*\hat{c}\right)^{2/3}} - 1\right], \tag{6}$$

$$E_Z^e = \frac{1}{2}\left[\frac{(1+\partial w/\partial Z)^2}{\left(1+\Omega_1^*\hat{c}\right)^{2/3}} - 1\right]. \tag{7}$$

Assuming that the constitutive relation for the deformation can be determined from the strain energy density, the first Piola–Kirchhoff stress, **P**, is then introduced as

$$\mathbf{P} = \frac{\partial W}{\partial \mathbf{F}} = \frac{\partial W}{\partial \mathbf{E}^e}\frac{\partial \mathbf{E}^e}{\partial \mathbf{F}^e}\frac{\partial \mathbf{F}^e}{\partial \mathbf{F}}, \tag{8}$$

where W is the strain energy density, which is expressed as a quadratic function of the Green–Lagrange strain tensor as

$$W = \det\left(\mathbf{F}^i\right)\frac{E_h}{2(1+\nu)}\left[\frac{\nu}{(1-2\nu)}\left[tr(\mathbf{E}^e)\right]^2 + tr(\mathbf{E}^e\mathbf{E}^e)\right], \tag{9}$$

with E_h being Young's modulus and ν being Poisson's ratio. Substituting Eqs. (5)–(7) and Eq. (9) into Eq. (8) gives the components of the first Piola–Kirchhoff stress as

$$P_R = \left(1+\Omega_1^*\hat{c}\right)^{1/3}\frac{\nu}{(1+\nu)(1-2\nu)} \times E_h\left(\frac{1-\nu}{\nu}E_R^e + E_\Theta^e + E_Z^e\right)\left(1+\frac{\partial u}{\partial R}\right), \tag{10}$$

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