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Effect of local velocity on diffusion-induced stress in large-deformation electrodes of lithium-ion batteries

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HIGHLIGHTS

- The effect of local velocity is introduced into the diffusion equation.
- The effect of local velocity on DIS in a spherical electrode is analyzed.
- The immobile surface likely retards mechanical degradation.

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ABSTRACT

In this work, the contribution of local velocity to the resultant flux of lithium in lithium-ion battery is introduced into the diffusion equation to describe the migration of lithium in the active material of electrodes. The effect of the local velocity on the stress evolution in a spherical electrode made of silicon is analyzed, using the derived diffusion equation and nonlinear theory of elasticity. Two boundary conditions at the surface of the electrode, which represent two extreme conditions of real electrode materials, are used in the stress analysis: one is stress-free, and the other is immobile. The numerical results with the stress-free boundary condition suggest that the effect of the local velocity on the distribution of radial stress and hoop stress increases with the increase of time and the effect of the local velocity on the distribution of lithium is relatively small. In comparison with the results without the effect of the local velocity, the effect of the local velocity is negligible for the immobile boundary condition. The numerical result shows that the use of the immobile boundary condition leads to the decrease of von-Mises stress, which likely will retard the mechanical degradation of electrode and improve the electrochemical performance of lithium-ion battery.

1. Introduction

Lithium-ion batteries (LIBs) are being developed to achieve high capacity, fast charging and long life, which can be used in electronic devices or electric cars. One of the most important issues in the applications of lithium-ion batteries is mechanical degradation due to the insertion and de-insertion of lithium during electrochemical cycling. The insertion and de-insertion of lithium into the active materials in lithium-ion batteries will cause local deformation, resulting in crack and cavitation [1]. The stress introduced by the insertion and de-insertion of lithium into the active materials can be referred to as chemical stress or diffusion-induced stress (DIS). Prussin [2] likely was the first one to analyze the diffusion-induced stress, following the concept of linear theory of thermoelasticity. Currently, the concept of diffusion-induced stress has been extensively used in analyzing the stress evolution and mechanical degradation of the electrodes in lithium-ions batteries [3–6].

It is known that there is stress-assisted diffusion under the action of stress (strain energy) gradient according to the theory of irreversible thermodynamics. There exists the coupling effect between diffusion and stress, which determines the deformation state of a material due to the diffusion of solute atoms. There are two approaches to analyze the effect of stress-assisted diffusion: (1) the incorporation of the gradient of hydrostatic stress in the equation of mass transport [6–9], and (2) the incorporation of strain energy in the energy barrier for the diffusion of solute atoms [10,11]. Recently, Yang [12] considered the effects of stress and electric field on the migration of solute atoms from the framework

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of thermal activation process and derived a new relationship between the diffusion flux of solute atoms, hydrodynamic stress, and electric field intensity, which reduces to the linear relationship in the theory of irreversible thermodynamics. Under the action of the gradient of hydrostatic stress, the diffusion of solute atoms is dependent on local stress state. The analysis of diffusion-induced deformation in a material cannot simply follow the approaches used in the analysis of thermoelasticity, as revealed by Yang [12] and Chu and Lee [13].

Zhang et al. [9,14] incorporated the contribution of the gradient of hydrostatic stress in the flux boundary condition in analyzing intercalation-induced stress in an ellipsoidal electrode. Zhao et al. [1] used the gradient of chemical potential for the flux boundary condition in studying plastic deformation of a spherical electrode during charging and discharging. Hao and Fang [15,16] used the gradient of chemical potential for the flux boundary condition at the interface between the core and the shell in studying lithiation-induced stress in a core-shell structure. Guo et al. [7] used the gradient of chemical potential for the flux boundary condition in analyzing layered cylindrical structures.

According to the theory of stress-assisted thermal activation process, local stress at non-hydrostatic stress state can cause the change of the energy barrier for the migration of atoms. Haftbaradaran et al. [10] considered the effect of strain energy on the diffusivity in analyzing the diffusion of lithium during lithiation. Liu et al. [11] examined the stress dependence of diffusivity on the self-limiting lithiation in silicon nanowires. All of these studies reveal the role of the coupling between diffusion and stress in controlling the stress evolution and structural degradation of the electrodes in LIBs.

As discussed above, the lithiation or de-lithiation during electrochemical cycling will introduce mechanical strain in electrodes due to diffusion-induced strain or reaction-induced strain. Local velocity (strain rate) depends on the rates of lithiation and de-lithiation, and likely contributes to the deformation of the active materials in electrodes. Here, the local velocity is referred to as the local deformation velocity in solid, which has been observed in the experimental study of lithium-ion batteries, especially for the electrodes made of silicon [17]. It is expected that there exists coupling between the local velocity and the migration of lithium, which plays a role in the stress evolution especially for large deformation of electrodes. In this work, the contribution of the local velocity to the resultant flux of lithium is introduced into the diffusion equation for the description of the migration of lithium in the active material of the electrodes in a lithium-ion battery. The effect of the local velocity on the stress evolution in a spherical electrode made of silicon is analyzed, using the derived diffusion equation and the theory of nonlinear elasticity. Numerical analysis of the coupled partial differential equations is performed to obtain the diffusion-induced stress in the spherical electrode. Two boundary conditions at the surface of the electrode, which represent two extreme boundary conditions of real electrode materials, are used in the stress analysis: one is stress free, and the other is immobile.

2. Problem formulation

2.1. Mechanical equations

The insertion of solute atoms into host material can cause volumetric change. For large deformation, there are two approaches to describe the deformation behavior, including Lagrangian description and Eulerian description. The Lagrangian description is based on initial configuration as the reference state, and the coordinates in the Lagrangian description are written as **X**; the Eulerian description is based on current configuration as the reference state, and the coordinates in the Eulerian description are written as **x**. The Lagrangian description and Eulerian description are related by a vector field χ as

$$\mathbf{x} = \chi(\mathbf{X}, t), \tag{1}$$

$$\mathbf{X} = \chi^{-1}(\mathbf{x}, t), \tag{2}$$

where χ is referred to as the motion of the material and is assumed to be uniquely invertible. The Lagrangian coordinates **x** are a function of the Eulerian coordinates **X** and time t, and is expressed as **x** (**X**,t). The Eulerian coordinates **X** are a function of the Lagrangian coordinates **x** and time t, and is written as **X** (**x**,t).

From the definition, the velocity field, **V** (**X**,t), in the Lagrangian description is the first derivative of χ as

$$\mathbf{V}(\mathbf{X}, t) = \frac{\partial \chi(\mathbf{X}, t)}{\partial t}. \tag{3}$$

Substituting Eq. (2) into (3) yields

$$\mathbf{V}(\mathbf{X}, t) = \mathbf{V}\left(\chi^{-1}(\mathbf{x}, t), t\right) = \mathbf{v}(x, t), \tag{4}$$

where **v** (**x**,t) is the velocity in the Eulerian description. The displacement vector, **U**, in the Lagrangian description is

$$\mathbf{U}(\mathbf{X}, t) = \mathbf{x}(\mathbf{X}, t) - \mathbf{X}. \tag{5}$$

Substituting Eqs. (1) and (5) into Eq. (3), one obtains

$$\mathbf{V}(\mathbf{X}, t) = \frac{\partial \mathbf{U}(\mathbf{X}, t)}{\partial t} = \dot{\mathbf{U}}. \tag{6}$$

The deformation gradient tensor, **F**, can be calculated as

$$\mathbf{F} = \mathrm{Grad}\mathbf{x} = \mathbf{I} + \mathrm{Grad}\mathbf{U}(\mathbf{X}, t), \tag{7}$$

where Grad is the gradient operator in the Lagrangian description, and **I** is a unit second order tensor. The deformation gradient tensor consists of two contributions: elastic deformation, $\mathbf{F}^e$, and diffusion-induced deformation, $\mathbf{F}^i$, i.e.

$$\mathbf{F} = \mathbf{F}^e\mathbf{F}^i. \tag{8}$$

Assume that the diffusion-induced deformation is isotropic and is caused by the insertion or de-insertion of solute atoms [1]. The deformation gradient tensor for the diffusion-induced deformation is [18].

$$\mathbf{F}^i = (1 + \Omega_1 C)^{1/3}\mathbf{I}, \tag{9}$$

where C is the concentration of solute atoms in the Lagrangian description, and Ω_1 is the volumetric strain per unit mole fraction of the solute atoms.

The Green-Lagrange strain tensor, **E**, is used and can be expressed as

$$\mathbf{E} = \frac{1}{2}\left(\mathbf{F}^T\mathbf{F} - \mathbf{I}\right). \tag{10}$$

The elastic strain tensor of the Green-Lagrange strain tensor, $\mathbf{E}^e$, and diffusion-induced strain tensor of the Green-Lagrange strain tensor, $\mathbf{E}^i$, are

$$\mathbf{E}^e = \frac{1}{2}\left((\mathbf{F}^e)^T\mathbf{F}^e - \mathbf{I}\right), \tag{11}$$