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Finite element analysis of lithium insertion-induced expansion of a silicon thin film on a rigid substrate under potentiostatic operation

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HIGHLIGHTS

- Plastic deformation.
- The coupling between stress and diffusion.
- Diffusion from top and edge surfaces.
- Concentration dependence of material properties.
- Fracture and stress.

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ABSTRACT

Diffusion-induced stress and volumetric expansion under potentiostatic operation are investigated with an axisymmetric finite element model taking account of plastic yielding, coupling effects between diffusion and stress, diffusion from the edge surface, and concentration dependence of material properties. Significant differences on stresses, displacements, and fracture energies between purely elastic and elastic–plastic materials are found. Plasticity based on von-Mises criterion has no effect on concentration variation. The critical regions for fracture are the edge surface, and the regions near the edges on both the top surface and the interface.

1. Introduction

In the past decade, a significant advance has been made for development of lithium-ion (Li-ion) batteries [1], which have become the most widely used secondary battery system [2] due to its highest energy densities of all rechargeable batteries [3]. Although silicon (Si) is the most promising candidate for anode material for Li-ion batteries due to its high capacity of about 4000 mA h/g [4,5] compared to graphite [6,7], its widespread application is obstructed by its massive volumetric expansion of larger than 300% [8–14] after fully lithium insertion, which results in large mechanical stresses, and thus poor cyclic behaviors [15–19] owing to fracture [20,21] and capacity fade [22–24].

Understanding shape evolution of electrodes during lithiation and delithiation is essential to structural design and material selection, and a challenge for development of next-generation Li-ion batteries. The direct investigation on volume variation of active electrodes has been pioneered by Dahn's group [10,25,26]. He et al. [27] studied shape evolution of patterned silicon microarray thin film electrodes under lithium insertion and extraction using ex-situ AFM and SEM. Park et al. [28] investigated morphology change of cylindrical electrodes using in-situ AFM and finite element method. Yang [29] analyzed insertion-induced expansion of an elastic thin film on a rigid substrate, and found the important role of the coupling between diffusion and stress in analyzing diffusion problems.

Many groups [30–37] inspired the investigation on diffusion-induced stress. The coupling between diffusion and stress, which is important for concentrated solutes and large stresses [38], is neglected in most mathematical models [39,40], and only

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considered in a few studies [29,41–43]. Although it is a convention to assume that mechanical properties are independent of concentration [34,44–51], concentration dependence of material properties becomes prominent when new phases [52–56] are formed and material becomes composite [57,58]. Consideration of material properties as a function of concentration is crucial in development of reliable results due to significant effects of the concentration dependence of material properties on stress evolution [59]. Diffusion from side surfaces were neglected in most studies [43,60,61], and concentration was assumed to be independent of radial coordinate [62], although edge effect is expected [63], and neglect of edge diffusion would lead to underestimation of Li-ion concentration [64]. Analytical results cannot be compared with experimental results quantitatively [64], since plastic deformation has not been considered in most theories of insertion-induced deformation, while sufficient evidence has been accumulated that lithiated silicon undergoes plastic deformation when yield stress is reached [27,51,65–68].

Continuum model for diffusion with coupled effects has been validated [42]. The purpose of this work is to study the highly nonlinear behavior of insertion-induced volume variation with finite element method taking into account the coupling effect and the concentration dependence of material properties. Diffusion from both top surface (in vertical direction) and edge surfaces (in radial direction) are considered. Plastic deformation and effects of yielding on stresses and fracture tendency are explored.

2. Physical model

Consider the insertion of solute atoms into a solid. The insertion of solute atoms leads to a distorted lattice, volumetric expansion, stress and fracture under mechanical constraint (e.g. bonded to a substrate).

Extending the 1D relation given by Prussin [69] to 3D, the constitutive equation for diffusion-induced deformation of an elastic solid are expressed [29,70]

$$\varepsilon_{ij} = \frac{1}{E}\left[(1+\nu)\sigma_{ij} - \nu\sigma_{kk}\delta_{ij}\right] + \frac{c\Omega}{3}\delta_{ij} \tag{1}$$

where ε_{ij} ($i,j = 1,2,3$) are components of strain tensor; σ_{ij}, components of stress tensor; c (mol/m^3) is concentration of the diffusing component; Ω (m^3/mol), partial molar volume representing volume expansion caused by concentration of solute atoms; E, elastic modulus; ν, Poisson's ratio. Stresses caused by diffusion of solute atoms are analogous to those caused by gradient of temperature in thermal-mechanical analysis, and $\Omega/3$ in diffusion-induced expansion plays the same role as thermal expansion coefficient in thermal stress.

Chemical potential can be expressed as [41]

$$\mu = \mu_0 + RT\ln c - \sigma\Omega \tag{2}$$

where μ_0 is a constant, R is the gas constant, T is the absolute temperature, c is concentration, and σ is the hydrostatic stress. For a film being firmly adherent to the substrate [29]

$$\sigma = \frac{\sigma_{11}+\sigma_{22}+\sigma_{33}}{3} = -\frac{2E}{1-\nu}\frac{c\Omega}{9} \tag{3}$$

The diffusion flux is proportional to the gradient of chemical potential [29,47]

$$\vec{J} = -MC\vec{\nabla}\mu = -D_0\left(\vec{\nabla}C - \frac{\Omega c}{RT}\vec{\nabla}\sigma\right) \tag{4}$$

where D_0 is the diffusivity of the solute atoms in a stress-free solid,

Substituting Eq. (3) into Eq. (4) gives an effective diffusion coefficient taking account of effect of stress on diffusion [29,41], and the flux of solute atoms, $\boldsymbol{J}$ (mol m^{-2} s^{-1}), is

$$\boldsymbol{J} = -D\nabla c, \quad D = D_0(1+\alpha c), \quad \alpha = \frac{2E\Omega^2}{9(1-\nu)RT} \tag{5}$$

where D is the effective diffusion coefficient depending on concentration.

The governing equation for mass conservation is

$$\int_V \frac{dc}{dt}dV + \int_S \boldsymbol{n}\cdot\boldsymbol{J}dS = 0 \tag{6}$$

where V is any volume whose surface is S, $\boldsymbol{n}$ is the outward normal to the surface, and $\boldsymbol{n}\cdot\boldsymbol{J}$ represents flux of concentration leaving S. The equation for mass conservation in diffusion problem is analogous to equation for energy balance in heat transfer problem under the condition that the product of density term and specific heat term is 1.

3. Finite element modeling

Cracking and interface debonding are not considered, although they have attracted much attention recently [64,71–78]. Body forces and inertia effects are neglected, and mechanical deformation is quasi-static compared to the much slower diffusion process. Because mechanical response under concentration loading is analogous to that under temperature loading due to the analogy between thermal stresses and diffusion-induced stresses [79–83], fully coupled diffusion-stress analysis is performed using the fully coupled thermal-mechanical transient analysis procedure in ABAQUS/Standard [84], where the diffusion equations are integrated using a backward-difference scheme, and the computed system is solved using Newton's method. A “line search” algorithm with maximum 5 iterations is used in order to improve convergence of the strongly nonlinear problem. Only lithium-insertion is modeled. The convention of a homogeneous isotropic electrode [85] is followed.

Because low-dimensional electrodes such as thin films are extensively studied due to their structural stability and good performance [64,86–90], consider a thin film electrode, which is a host of lithium [7], and surrounded by an invariant Li-ion concentration. An axisymmetric finite element model with a cylindrical polar coordinate system (r, θ, z) and a uniform quadrilateral mesh is used. The film is assumed to be perfectly bonded to a rigid substrate. Reduced integrated elements, which effectively eliminate shear and volumetric locking, are used, since the constraint of the rigid substrate can cause overly stiff behavior due to volumetric locking if fully integrated elements are used. First-order elements are used due to the highly nonlinear problem. Fine mesh is used due to stress concentration, and element size is set to equal 1% of film

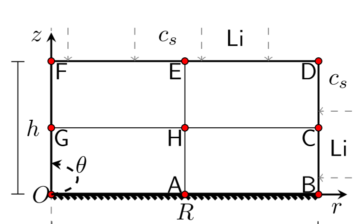

Fig. 1. Schematic of a thin film subject to insertion of Li-ion.