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Evolution of stress within a spherical insertion electrode particle under potentiostatic and galvanostatic operation

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ABSTRACT

Lithium ion battery electrode materials generally experience significant volume changes during charging and discharging caused by concentration changes within the host particles. Electrode failure, in the form of fracture or decrepitation, may occur as a result of a highly localized stress, strain energy, and stress cycles over time. In this paper, we develop analytic expressions for the evolution of stress and strain energy within a spherically shaped electrode element under either galvanostatic (constant current) or potentiostatic (constant potential) operation when irreversible phenomena are dominated by solute diffusion resistance within host particles. We show that stresses and strain energy can evolve quite differently under potentiostatic vs. galvanostatic control. The findings of this work suggest the possibility of developing new battery charging strategies that minimize stress and strain energy and thus prolong battery life.

1. Introduction

Diffusion-induced stress (DIS) can occur as a result of compositional inhomogeneities during solid-state diffusion in many technological situations, including dopant diffusion in semiconductor processing, oxidation of metals, hydrogen transport in solid-state hydrogen-storage media, and lithium diffusion in battery electrodes. Several authors have developed models for DIS. For example, Prussin [1] made an analogy between thermal stress and DIS and analyzed the transverse stresses developed in a thin plate during mass transfer. Li [2] provided a number of analytical solutions to DIS problems in spherical, cylindrical, and thin plate geometry. Lee and co-workers [3–5] have also studied DIS in various systems including thin plates, hollow cylinders, and composites. Yang and Li [6,7] considered the effect of diffusion-induced stresses on the bending of beam and plate structures for sensing applications. Yang also studied the coupled problem of interactions of stress and diffusion [7].

Within the electrochemical energy storage topical area, a number of publications address the modeling of lithium ion batteries [8–15] and are focused on the underlying thermodynamics, interfacial kinetics, and transport phenomena governing electrochemical systems in the context of a volume-averaged treatment of porous media. Recently, García et al. [16], Christensen and Newman [17,18] and Zhang et al. [19] studied stresses generated during Li diffusion under galvanostatic control. The latter authors also investigated linear sweep voltammetry of a single particle as well as heat generation [20]; their investigation included spherical and ellipsoidal particles. The paper by Zhang et al. [21] is devoted to the analysis of a single particle undergoing electrochemical insertion and outlines the motivation for such single particle studies. The aforementioned battery references and this work are motivated by the need to develop high energy and power batteries that are durable over the intended usage profiles [24].

Since batteries are usually charged using sophisticated methods that consist of both galvanostatic and potentiostatic control, we report in this paper stress and strain energy evolution under either purely galvanostatic or potentiostatic condition when the resistance of the cell is governed by solute diffusion limitations within the insertion particles. The analytic solutions developed in this work should improve the current understanding of stress and strain energy evaluation by (1) identifying dimensionless parameters that control stress and strain energy evolution, (2) providing the asymptotic behavior for short- and long-time limits, and (3) rendering order of magnitude estimates for more complicated operating conditions. The results of this work may be used to develop strategies that minimize stress-induced battery failures. Additional information on relevant past works by the present authors can be found in Refs. [22,23]; in these two investigations, surface tension

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Nomenclature

List of symbols

a_s	specific surface (e.g., $cm^2\ cm^{-3}$)
C	molar concentration
C_0	initial (uniform) solute concentration
C_R	surface concentration during constant potential operation
$C_{av}(r)$	average concentration in the spherical volume of radius r
$C_{av}(R)$	average concentration in the spherical particle of radius R
D	diffusion coefficient of the solute
E	Young's modulus
E_T	total elastic energy stored in the sphere of radius R
e	strain energy density
e^-	electron
F	Faraday's constant
H^+	proton
I	current over a spherical particle of radius R
I_{cell}	cell current
$i_{0,ref}$	exchange current based on reference concentration
L	electrode thickness
Li^+	lithium ion
r, θ, ϕ	spherical coordinates
R	radius of spherical particle
S	vacant site in host materials
u	radial displacement
x	dimensionless radial position

Greek symbols

ε_r	radial strain
ε_θ	tangential strain
θ_1	volume fraction of active material in porous electrode
σ_r	radial stress
σ_θ	tangential stress
σ	mean stress
$\sigma_{r,\max}$	maximum radial stress
$\sigma_{\theta,\max}$	maximum tangential stress
$\sigma_{shear,\max}$	maximum shear stress
ν	Poisson's ratio
Ω	partial molar volume of the solute
ζ_r^V	dimensionless stress in the radial direction for potentiostatic operation
ζ_θ^V	dimensionless stress in the tangential direction for potentiostatic operation
ζ_r^I	dimensionless stress in the radial direction for galvanostatic operation
ζ_θ^I	dimensionless stress in the tangential direction for galvanostatic operation
τ	dimensionless time
$\prod^V$	dimensionless total elastic energy in the sphere for potentiostatic operation
$\prod^I$	dimensionless total elastic energy in the sphere for galvanostatic operation

and surface modulus were shown to play a significant role in the determination of the stress amplitude and distribution for small particles. For the purposes of this work, we shall not include the surface phenomena, allowing us to streamline the exposition and focus on the distinguishing differences between potentiostatic and galvanostatic operation.

2. Analysis and results

2.1. Mechanics of composition induced stresses

We consider stress caused by diffusion within a spherical particle of radius R. The bulk of the spherical particle is assumed to be an isotropic linear elastic solid. Using the analogy between thermal and DIS [1–7,17–20,22,23,25], the stress–stain relationships, expressed in the spherical coordinate system, for the radial and tangential components, are

$$\varepsilon_r = \frac{1}{E}(\sigma_r - 2\nu\sigma_\theta) + \frac{1}{3}\Omega C, \qquad \varepsilon_\theta = \frac{1}{E}[(1-\nu)\sigma_\theta - \nu\sigma_r] + \frac{1}{3}\Omega C, \tag{1}$$

where E is Young's modulus, ν is Poisson's ratio, C is molar concentration, and Ω is the partial molar volume of the solute. We further assume that the elastic properties are independent of the concentration C.

Because of spherical symmetry, the radial and tangential strains, in the infinitesimal formulation of deformation, are given by $\varepsilon_r = du/dr$ and $\varepsilon_\theta = u/r$, where u is the radial displacement. Since atomic diffusion in solids is a much slower process than elastic deformation, mechanical equilibrium is established much faster than that of diffusion. Mechanical equilibrium is, therefore, treated as a static equilibrium problem. In the absence of any body-force, the equation for static mechanical equilibrium in the bulk of a sphere is given by Ref. [25]:

$$\frac{d\sigma_r}{dr} + 2\frac{\sigma_r - \sigma_\theta}{r} = 0. \tag{2}$$

The solutions for the normal and tangential stresses that satisfy the boundary condition $\sigma_r(R) = 0$ and remain finite at $r = 0$ are given by:

$$\sigma_r(r) = \frac{2E\Omega}{9(1-\nu)}[C_{av}(R) - C_{av}(r)],$$

$$\sigma_\theta(r) = \frac{E\Omega}{9(1-\nu)}[2C_{av}(R) + C_{av}(r) - 3C(r)], \tag{3}$$

where $C_{av}(r) \equiv (3/r^3)\int_0^r r^2 C(r)\,dr$ is the average concentration in the spherical volume of radius r within the particle of radius R. Since $\lim_{r\to 0} C_{av}(r) = C(0)$, Eq. (3) shows that the stress-state at the center of the sphere is purely hydrostatic, i.e., $\lim_{r\to 0}\sigma_r(r) = \lim_{r\to 0}\sigma_\theta(r)$, which is true for any physically admissible concentration profile.

Recognizing that $\sigma_\theta(r) = \sigma_\phi(r)$, we can write the "mean" stress as

$$\sigma(r) = \frac{\sigma_r(r) + 2\sigma_\theta(r)}{3} = \frac{2E\Omega}{9(1-\nu)}[C_{av}(R) - C(r)]. \tag{4}$$

Because of the spherical symmetry, one principal shear stress is zero and the other two are both equal to $(\sigma_r - \sigma_\theta)/2$. Eq. (3) shows that the principal shear stress is

$$\frac{\sigma_r(r) - \sigma_\theta(r)}{2} = \frac{E\Omega}{6(1-\nu)}[C(r) - C_{av}(r)]. \tag{5}$$

Hence, the stresses at any given location and time can be obtained once composition profile is known.

From the stresses, we can calculate the strain energy per unit volume or strain energy density $e(r)$ accumulated as a result of the elastic deformation for the isotropically deformed sphere [25]:

$$e(r) = \frac{\sigma_r^2(r) + 2\sigma_\theta^2(r) - 2\nu\sigma_\theta(r)[2\sigma_r(r) + \sigma_\theta(r)]}{2E}. \tag{6}$$

The total elastic energy stored in the sphere, E_T, which provides the driving force for fracture, can then be obtained by integrating the strain energy density over the entire volume of the spherical