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Anisotropic compositional expansion in elastoplastic materials and corresponding chemical potential: Large-strain formulation and application to amorphous lithiated silicon

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ABSTRACT

A general large-strain thermodynamic approach with anisotropic (tensorial) compositional expansion/contraction in elastoplastic material under stress tensor is developed. The dissipation rate due to compositional expansion/contraction is introduced. Adapting and utilizing a previously formulated postulate of realizability, we derived a simple equation for the deviatoric part of the compositional deformation rate. This leads to a nontrivial generalization of the concept and expression for the chemical potential. It receives a contribution from deviatoric stresses, which leads to an increase in the driving force for both the compositional expansion and contraction and to some new phenomena. Our model provides a remarkable description of the known experimental and atomistic simulation data on the biaxial stress evolution during lithiation–delithiation of Li_xSi on a rigid substrate with just one constant kinetic coefficient. In contrast to known approaches, it does not involve plasticity, because the yield strength is higher than the stresses generated during lithiation–delithiation. This allowed us to suggest a method for reduction in internal stresses by cyclic change in *Li* concentration with a small amplitude, and our simulations were in qualitative agreement with known experiments. The coupled diffusion and mechanical model was applied to lithiation and delithiation of thin-film, solid, and hollow spherical nanoparticles. The importance of the contribution of the deviatoric stress on the diffusion is demonstrated.

1. Introduction

Starting with the celebrated work by Larche and Cahn (1973, 1978), the concept of the chemical potential of multicomponent materials with diffusion under nonhydrostatic stresses received significant development. More recent large-strain formulations have been presented in Grinfeld (1991), Wu (2001), Bower et al. (2011), Cui et al. (2012), and Levitas (2000b). Practical motivation for large-strain formulations was recently received from the development of lithium-ion batteries. In particular, *Si* is a promising anode material for *Li*-ion batteries since it is able to absorb a large amount of *Li* (Tarascon and Armand, 2001; Sethuraman et al., 2010b). The maximum insertion of *Li* corresponds to $Li_{4.4}S$, which possesses

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Nomenclature

$\boldsymbol{F}$	deformation gradient
$\boldsymbol{U}$	right stretch tensor
$\boldsymbol{R}$	rotation tensor
$\boldsymbol{E}_e$	Lagrangian elastic strain
J	Jacobian
$\boldsymbol{p}_0$	traction vector
$\boldsymbol{P}$	Piola–Kirchof stress
$\widehat{\boldsymbol{\sigma}}$	second Piola–Kirchof stress
$\boldsymbol{\sigma}$	Cauchy stress
p_0	mean stress
$\boldsymbol{S}$	deviatoric Cauchy stress
$\overline{\boldsymbol{S}}$	generalized deviatoric stress
$\boldsymbol{v}$	particle velocity
$\boldsymbol{l}$	velocity gradient
$\boldsymbol{d}$	deformation rate
ϵ_0	volumetric strain
η_c	linear coefficients of compositional expansion
b	mobility coefficients
D_0	pre-exponential factor
α	activation volume
D	diffusion coefficient
x	molar fraction of A per mole of B
c	molar concentration
x_{max}	maximum solubility
$\overline{V}_i$	partial molar volume of i
$\boldsymbol{j}$	diffusive flux
μ	chemical potential
μ_r	chemical potential of reservoir
μ_0	standard chemical potentials
U	internal energy per unit reference volume
s	entropy per unit reference volume
ψ	Helmholtz free energy per unit reference volume
$\mathcal{D}$	dissipation per-unit reference volume
ψ_m^{exc}	concentrational part of the free energy
ψ_m	molar excess energy per mole of B
θ	temperature
$\boldsymbol{X}$	generalized thermodynamic forces
$\boldsymbol{h}_0$	heat flux
λ	thermal conductivity
Λ	relaxation parameter
$\boldsymbol{C}$	fourth-rank tensor of (isotropic) elastic moduli
K	bulk moduli
G	shear moduli
E	Young's moduli
ν	Poisson's ratio

Subscripts

c	compositional part
e	elastic part
p	plastic part

a theoretical *Li* capacity of 4200 mAh/g, an order of magnitude larger than for a graphite anode (Tarascon and Armand, 2001; Sethuraman et al., 2010b). However, insertion of such an amount of Li is accompanied by a 334% volumetric expansion, which under constraint conditions lead to huge stresses that may cause fracture of an Li_xSi anode (Bhandakkar and Gao, 2010, 2011; Hu et al., 2010; Haftbaradaran and Gao, 2012; McDowell et al., 2012). This is one of the main problems that prevents industrial application of *Si* anodes, and it is why understanding of the stress development and relaxation during lithiation–delithiation is of great applied and basic importance. For nanoscale anodes (nanowires, particles, and films Arico et al., 2005; Wu et al., 2012; Chan et al., 2008; Liu et al., 2012), fracture is suppressed, and large compositional volumetric deformations of Li_xSi under constrained conditions are believed to be accommodated by plastic flow (Bower et al., 2011; Zhao et al., 2012, 2011a; Cui et al., 2012). All continuum approaches to stress relaxation in Li_xSi anodes are based on classical viscoplasticity theory (Bower et al., 2011; Zhao et al., 2012, 2011a; Cui et al., 2012), but recent density functional theory (DFT) simulations (Zhao et al., 2012) have demonstrated that the yield strength of Li_xSi is at least two times higher than the stresses generated during lithiation–delithiation in a thin film on a rigid substrate for all x. This practically excludes plasticity as a relaxation mechanism and requires approaches different from those in Bower et al. (2011), Zhao et al. (2012, 2011a), and Cui et al. (2012). The fact that atomistic simulations for crystalline materials without defects (for example, dislocations and grain boundaries) usually overestimate the yield strength cannot be used as an excuse. For amorphous nanomaterial, the same atomistic calculations (Zhao et al., 2012) describe satisfactory experimental data on biaxial stress relaxation in Si film during insertion-extraction. In the most recent model (Brassart and Suo, 2012a,b), the flow (change in shape) and reaction (change in composition) are assumed to be the concurrent non-equilibrium processes that are coupled thermodynamically. It has two fitting material parameters, but it was not checked against atomistic calculations or experiments. One of our goals in this paper was to suggest and develop a different approach in which stress relaxation in Li_xSi anodes occurs not due to classical plasticity when the yield condition is satisfied but due to anisotropic (tensorial) compositional straining that occurs during insertion–extraction reaction at any deviatoric stresses (i.e., below the yield strength). The anisotropic swelling in nanowires was observed and modeled in Liu et al. (2011) and Yang et al. (2012). The source of anisotropy is orientation-dependent mobility of the core/shell interface, where the core is the crystalline Si and the shell is the amorphous Si, which is much different from the model considered here. Also, plasticity is the active mechanism for the stress relaxation in Liu et al. (2011) and Yang et al. (2012). Here, we derive constitutive equations for anisotropic compositional expansion in a material point–i.e., without involving interfaces. McDowell et al. (2013) and Wang et al. (2013) showed that the first lithiation of amorphous Si thin film and nanoparticles is an interface-controlled process rather than diffusion-controlled. However, after the first cycle, the amorphous–amorphous interface disappears, and diffusion becomes