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Abstract
Si is a promising anode material for Li-ion batteries, since it absorbs large amounts of Li. However, insertion of Li leads to 334% of volumetric expansion, huge stresses, and fracture; it can be suppressed by utilizing nanoscale anode structures. Continuum approaches to stress relaxation in $LixSi$, based on plasticity theory, are unrealistic, because the yield strength of $LixSi$ is much higher than the generated stresses. Here, we suggest that stress relaxation is due to anisotropic (tensorial) compositional straining that occurs during insertion-extraction at any deviatoric stresses. Developed theory describes known experimental and atomistic simulation data. A method to reduce stresses is predicted and confirmed by known experiments. Chemical potential has an additional contribution due to deviatoric stresses, which leads to increases in the driving force both for insertion and extraction. The results have conceptual and general character and are applicable to any material systems.

Keywords
Mechanical Engineering, Materials Science and Engineering, coarse-grained models, Batteries, Computational science

Disciplines
Aerospace Engineering | Materials Science and Engineering | Mechanical Engineering

Comments
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Anisotropic Compositional Expansion and Chemical Potential for Amorphous Lithiated Silicon under Stress Tensor

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Si is a promising anode material for Li-ion batteries, since it absorbs large amounts of Li. However, insertion of Li leads to 334\% of volumetric expansion, huge stresses, and fracture; it can be suppressed by utilizing nanoscale anode structures. Continuum approaches to stress relaxation in Li\textsubscript{i}Si, based on plasticity theory, are unrealistic, because the yield strength of Li\textsubscript{i}Si is much higher than the generated stresses. Here, we suggest that stress relaxation is due to anisotropic (tensorial) compositional straining that occurs during insertion-extraction at any deviatoric stresses. Developed theory describes known experimental and atomistic simulation data. A method to reduce stresses is predicted and confirmed by known experiments. Chemical potential has an additional contribution due to deviatoric stresses, which leads to increases in the driving force both for insertion and extraction. The results have conceptual and general character and are applicable to any material systems.
under general tensorial stress states and large strains. Thus, dissipation related to the insertion-extraction is introduced. Generalization of the chemical potential, $\mu$, includes an additional contribution due to deviatoric stresses, which leads to the increase in the driving force both for insertion and extraction and to prediction of unexpected phenomena. A similar approach is applicable to large compositional deformation and stress relaxation for any material systems. Also, such an approach can be applied to other processes, like chemical reactions and melting under nonhydrostatic conditions when anisotropic (tensorial) transformation strain can be introduced and described in a similar thermodynamic way.

The contraction of tensors over one and two indices is designated as $A \cdot B$ and $A : B$; superscripts $-1$ and $t$ denote inverse and transpose operations; subscript $s$ means symmetrization of a tensor, and $I$ the unit tensor.

**Results**

The multiplicative decomposition of the deformation gradient, $F = F_0 \cdot U_0$, into elastic and compositional parts is used: $U_t = U_t'$. This results in the decomposition of the deformation rate $\dot{d}_s = (\dot{F}^{-1}) = (\dot{F}_0^{-1}) + (F_0 \cdot U_0^{-1} \cdot \dot{F}_0^{-1} \cdot F_0^{-1}) = \dot{d}_s + \dot{d}_r$ into elastic and compositional parts. Traditionally, $U_t$ is considered as a spherical tensor describing isotropic volumetric expansion only. However, stresses can induce anisotropy of $Li$ and $Si$ atom distributions in order to minimize the Gibbs energy of the system and lead to tensorial $U_0$ (Fig. 1a).

It is convenient to present $U_t = J_{1/3} U_{0t}$, where $J_{1/3}$ denotes the ratio of the mean volume to the mean volume of $Li$ and $Si$, and $U_{0t}$ describes isochoric change in shape. Then $d_s = J_{1/3} (f_j(I) + d_f^t)$ with $d_f^t = (F_0 U_0^{-1} F_0^{-1})$ represents an additive decomposition of the compositional deformation rate into spherical and deviatoric parts that characterize change in volume and shape.

The initial part of the continuum thermodynamic derivations is given in the Method Section. We start with the rate of dissipation per unit volume in the reference state $Q_d$ (undeformed Si) $D = \sigma \cdot \dot{\sigma} = \psi + \frac{\mu}{V_s} \dot{\mu} \geq 0$, where $\psi$ is the true Cauchy stress, $V_s$ is the molar volume of Si, and $\mu$ is the chemical potential of Li. Then the independence of $D$ of $F_0$ results in the elasticity rule (see, e.g., Ref. 19) and residual dissipation inequality

$$\sigma = J F_0 \frac{\partial \psi}{\partial \varepsilon} F_0^t; \quad D = \left( \frac{\mu}{V_s} - \frac{\partial \psi}{\partial \varepsilon} \right) \dot{\mu} \geq 0, \quad (1)$$

which can be transformed to

$$D = \left( \frac{\mu}{V_s} - \frac{\partial \psi}{\partial \varepsilon} + p \frac{\partial f_t}{\partial \varepsilon} \right) \dot{\varepsilon} + J S \cdot \dot{d}_s \geq 0, \quad (2)$$

where $p_0$ and $S$ are the mean and deviatoric parts of the stress $\sigma$, and $J_s = \det F_0$ is the ratio of the volumes in the deformed and undeformed states of $Li, Si$ ($J_s = J_s$). If one chooses $p_0$ to make the parenthesis in Eq.(2) equal to zero, then inequality (2), $S \cdot \dot{d}_s \geq 0$, means that $\dot{d}_s$ must depend on $S$, and for isotropic amorphous materials $\dot{d}_s$ is an isotropic function of $S$. To allow change in $U_0$ during insertion-extraction only (otherwise, it would not be a compositional strain but viscous strain), one needs to impose $\dot{d}_s = 0$ when $\dot{\varepsilon} = 0$. We accept the simplest expression

$$\dot{d}_s = \Lambda(x) S \dot{\varepsilon}; \quad \dot{\varepsilon} = \Lambda(x) S \frac{\partial f_t}{\partial \varepsilon} \dot{\varepsilon}; \quad \Lambda > 0 \quad (3)$$

with the kinetic coefficient $\Lambda(x)$. We assumed that $\dot{d}_s$ is scaled with the magnitude of the rate of the volumetric compositional strain, $J_s$, and $\dot{d}_s = 0$ when $\dot{\varepsilon} = 0$. If we assumed that $\dot{d}_s$ is proportional to $\dot{\varepsilon}$ rather than to $\dot{\varepsilon}$, it would violate the dissipation inequality $S \cdot \dot{d}_s = \Lambda(x) S \cdot \frac{\partial f_t}{\partial \varepsilon} \dot{\varepsilon} \geq 0$ for $\dot{\varepsilon} \leq 0$. This means that the deformation rate $\dot{d}_s$ is the same for insertion and extraction if $\Lambda(x)$ and $J_s(x)$ are the same for insertion and extraction. If $\dot{\varepsilon}$ is a linear function of $x$, it does not introduce extra concentration dependence; otherwise, it does. In any case, the multiplier $\frac{\partial f_t}{\partial \varepsilon}$ can be combined with $\Lambda(x)$. A slightly better description of experimental and atomistic results from $^{18}$ with $\Lambda = const$ is achieved (see below) with additional multiplier $\frac{\partial f_t}{\partial \varepsilon}$ in Eq.(3) than without it, which is why it is separated. It should be mentioned that Eq.(3) does not describe traditional viscos relaxation and dissipation, which can be made negligible in an infinitesimally slow process. Indeed, multiplying Eq.(3) by time increment $dt$, one obtains $(F_0 F_0^{-1} U_0^{-1} F_0^{-1}) = \Lambda(x) S \dot{\varepsilon} dt$, i.e., relaxation Eq.(3) is time independent, and the magnitude of the volumetric strain or concentration $|c|$ plays a role of a time-like parameter. This is similar to the flow rule in classical elastoplasticity, which is time-independent, and plastic strain plays a part of a time-like parameter. Thus, even for infinitesimally slow lithiation-delithiation, the problem is thermodynamically nonequilibrium, history-dependent, and cannot be reduced to minimization of the free energy functional.

Traditionally (for $\dot{d}_s = 0$), the compositional dissipation rate is assumed to be zero, which defines an expression for the chemical potential $\mu$. In our more general case with $\dot{d}_s \neq 0$, we postulate

$$D = \zeta J S \cdot \dot{d}_s \leq \zeta \Lambda J S \cdot \frac{\partial f_t}{\partial \varepsilon} \dot{\varepsilon} \geq 0 \quad (4)$$

with the parameter $\zeta (0 \leq \zeta \leq 1)$ and $|\dot{\varepsilon}| = \dot{\varepsilon} \dot{\varepsilon}$ (assuming sign($0) = 0$). Then the remaining part of Eq.(2) is zero, which defines the generalized chemical potential

$$\frac{\mu}{V_s} = \frac{\partial \psi}{\partial \varepsilon} + p_0 \frac{\partial f_t}{\partial \varepsilon} - \Lambda(1 - \zeta) J S \cdot \frac{\partial f_t}{\partial \varepsilon} \dot{\varepsilon} \geq 0 \quad (5)$$

Let us consider a $Li$ reservoir with a chemical potential $\mu$, in contact with a small $Li, Si$ sample (i.e., heterogeneities of all parameters can be neglected) with the chemical potential of $Li$ $\mu$. Let the magnitude of the flux of $Li$ to the sample in the reference state be described by experimentally determined function $j = b V_s \dot{\mu} / \Delta y$, with size $\Delta y$ of the order of magnitude of the size of a $Li, Si$ sample, $\Delta \mu = \mu_s - \mu$, and with mobility coefficient $b$. An unusual feature of Eq.(5) is that the last term due to the deviatoric stresses always increases the magnitude of the driving force, $|\Delta \mu|$, for the $Li$ transport both for insertion and extraction, i.e., it decreases $\mu$ for insertion and increases $\mu$.
Figure 2 | Calculated biaxial stress during lithiation-delithiation is in remarkable good correspondence with experimental results and density functional theory (DFT) simulations from Ref. 15, with just one fitted material parameter \( \Lambda \). For delithiation, two options were used: with volumetric strain \( \varepsilon_0^d \) and with the same \( \varepsilon_0^s \) as for lithiation.
dissipation due to insertion-extraction are advanced for an arbitrary material system.

Methods
The large strain continuum thermodynamic approach under general nonhydrostatic conditions is utilized. Kinematics of large deformations with multiple intermediate configurations is described in Ref. 19. Here, kinematics is based on the multiplicative decomposition of the deformation gradient into elastic and compositional parts. Compositional part includes change in volume and shape, i.e., it represents a second-rank tensor. Plastic deformation is neglected because stresses are below the yield strength. We accepted the expression for the free energy per unit volume of the unloaded configuration, which allowed us to directly use results of atomistic simulations for elastic moduli. The initial part of the continuum thermodynamic derivation will be considered: the reference configuration 

\[ \Omega_0 \]

and unloaded configuration \( \Omega_u \), which corresponds to the undeformed Si state; actual configuration \( \Omega_c \), which corresponds to the actual deformed state of Li,Si and unloaded configuration \( \Omega_u \), obtained after release of external stresses after deformation of Li,Si without change in x. All derivations will be performed in the reference configuration \( \Omega_0 \). For the molar fraction of Li per mole of Si, x, the following mass balance equation is valid in \( \Omega_0 \):

\[ x + V_0 \psi_j = 0, \]

where \( V_0 \) is the molar volume of Si and \( x \) is the flux of the Li defined as a number of moles per unit reference area per unit time; \( V \) and \( V' \) are the gradient and divergence operators in \( \Omega_0 \), respectively. The first and second laws of thermodynamics for the reference volume \( V_0 \) for neglected volumetric forces, heat supplies and kinetic energy are:

\[ \int_{\Omega_0} [ (v \cdot P - h n - \mu j_1 j_1) dS_0 - \frac{d}{dt} \int_{V_0} U dV_0] = 0, \]

\[ \frac{d}{dt} \int_{\Omega_0} \psi_0 V_0 + \int_{\Omega_0} h n dS_0 \geq 0. \]

Here \( v \) is the material velocity, \( h \) the heat flux, \( n \) the unit normal to the external surface \( \Omega_0 \), \( U \) is the specific (per unit volume of Si) internal energy, \( s \) is the specific entropy, \( T \) the temperature, \( \mu \) the chemical potential of Li, and \( P \) is the first nonsymmetric Piola-Kirchoff (nominal) stress tensor (the force per unit area in the undeformed state). Using the Green-Gauss theorem to transform surface to volume integrals, \( V' = F \), as well as the equilibrium equation \( \nabla \cdot \mathbf{P} = 0 \), we transform Eqs. (9) and (10) to volumetric integrals and then to the local form

\[ \mathbf{P}' = \mathbf{F} - U - h - \mu j - j \mu v = 0. \]

Combining Eq. (11) and Eq. (12) multiplied by the temperature, we obtain the dissipation inequality

\[ \psi_j + \frac{1}{\beta} \nabla h - \frac{\psi h}{\beta} \geq 0. \]
Additional information
Competing financial interests: The authors declare no competing financial interests.
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