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REACTIVE FLOW IN LARGE-DEFORMATION ELECTRODES OF LITHIUM-ION BATTERIES

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An electrode in a lithium-ion battery may undergo inelastic processes of two types: flow and reaction. Flow changes the shape of the electrode, preserves its composition and volume, and is driven by the deviatoric stress — a process similar to the plastic flow of a metal. By contrast, reaction changes the composition and volume of the electrode, and is driven by a combination of the mean stress and the chemical potential of lithium in the environment. Both flow and reaction are mediated by breaking and forming atomic bonds. Here we formulate a continuum theory of large-deformation electrodes by placing flow and reaction on the same footing. We treat flow and reaction as concurrent nonequilibrium processes, formulate a thermodynamic inequality and a rheological model, and couple the two processes through a chemomechanical flow rule. Within this theory, the driving force for reaction — the mean stress and the chemical potential — can stimulate flow in an electrode too brittle to flow under a mechanical load alone. For an electrode under vanishingly small stress and current, cyclic lithiation and delithiation can cause hysteresis in the voltage-concentration curve. For a thin-film electrode bonded on a substrate, cyclic lithiation and delithiation can cause hysteresis in both the voltage-concentration curve and the stress–concentration curve.

Keywords: Plasticity; solid-state reactions; hysteresis; lithiation; silicon.

1. Introduction

In a lithium-ion battery, each electrode is a host of lithium. When the battery is charged or discharged, lithium migrates out of one electrode, through the electrolyte, and into the other electrode. Of particular interest are materials capable of absorbing large amounts of lithium [Kasavajjula *et al.*, 2007; Zhang, 2011a, 2011b; Hayner *et al.*, 2012]. On absorbing and desorbing lithium, the electrodes deform, which in turn causes stress when the electrodes are constrained. The stress may cause fracture, and possibly cause the capacity of the battery to fade [Zhao *et al.*, 2010; Xiao *et al.*, 2011; Lee *et al.*, 2012]. It is urgent to gain insight into the solid-state reactions, where mechanics meets chemistry.

Of all materials, silicon can absorb the largest amount of lithium: each silicon atom can host up to 4.4 lithium atoms. By comparison, in the commonly used anodes in lithium-ion batteries made of graphite, each carbon atom can host up to 1/6 lithium atoms. Lithiated silicon swells up to four times the volume of pure silicon [Kasavajjula *et al.*, 2007]. Silicon under mechanical loads is brittle and fractures before reaching its yield strength. During lithiation and delithiation, however, the lithiated silicon can flow [Takamura *et al.*, 2004; Zhao *et al.*, 2011b; Sethuraman *et al.*, 2010a]. First-principles simulation reveals that lithium assists the flow by participating in breaking and forming bonds between silicon atoms [Zhao *et al.*, 2011c, 2012]. Similar behavior is expected in other large-deformation electrodes, such as lithium alloy anodes [Huang *et al.*, 2010; Zhang, 2011b], conversion oxides [Bruce *et al.*, 2012], and sulfur cathodes [Zheng *et al.*, 2011].

When an electrode is lithiated and delithiated, the voltage-concentration curve often exhibits hysteresis, commonly attributed to kinetic processes such as charge transfer at the interface between the electrode and electrolyte and the diffusion of lithium in the electrode. However, hysteresis often persists even under vanishingly small current, when transient phenomena have relaxed [Baggetto *et al.*, 2008; Chevrier and Dahn, 2010; Dreyer *et al.*, 2010]. When the electrode is constrained, such as a thin-film electrode bonded on a substrate, part of the hysteresis results from plasticity due to stress [Sethuraman *et al.*, 2010a, 2010b]. This mechanism, however, is inapplicable when the electrode is stress-free. For example, thin films of silicon and silicon-containing alloys fracture into islands after the first cycle of lithiation and delithiation, and the islands freely expand and contract during many subsequent cycles while hysteresis persists [Beaulieu *et al.*, 2001, 2003]. Hysteresis is also observed in nanostructures specifically designed to accommodate large lithiation-induced strains. Examples include nanowires [Chan *et al.*, 2008], nanotubes [Song *et al.*, 2010], thin films [Cui *et al.*, 2010; Yu *et al.*, 2012], honeycomb structures [Baggetto *et al.*, 2011; Bhandakkar and Johnson, 2012], and porous electrodes [Kim *et al.*, 2008; Yu *et al.*, 2010]. One plausible explanation of hysteresis invokes energy barriers needed to break and reform atomic bounds during lithiation [Zhang, 2011b; Chevrier and Dahn, 2010; Chandrasekaran *et al.*, 2010; Huang and Zhu, 2011]. That is, lithium can be inserted into the host only if the chemical driving force reaches a certain threshold.

We have proposed a continuum model for concurrent flow and reaction in high-capacity hosts [Brassart and Suo, 2012]. A host can undergo either elastic or inelastic deformation. An elastic deformation corresponds to small distortions of atomic bonds, preserving the identity of neighbors. An inelastic deformation corresponds to changes of neighboring atoms by breaking and forming atomic bonds. We further distinguish inelastic processes of two types: flow and reaction (Fig. 1). Flow changes the shape of the electrode, preserves its composition and volume, and is driven by the deviatoric stress — a process similar to the plastic flow of a metal. Reaction changes the composition and volume of the electrode, and is driven by a combination of the mean stress and the chemical potential of lithium in the environment.

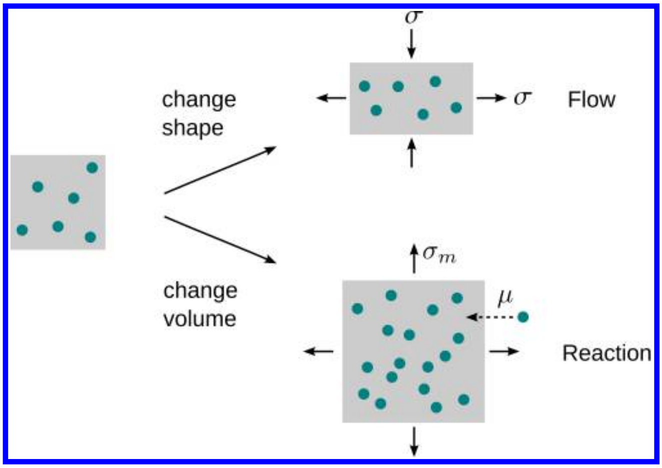


Fig. 1. A host can undergo inelastic processes of two types: flow and reaction. Flow changes shape of the host, preserves its volume and composition, and is driven by the deviatoric stress. Reaction changes the composition and the volume of the host, and is driven by the hydrostatic stress and the chemical potential of lithium in the environment.

Our previous paper was restricted to infinitesimal deformation [Brassart and Suo, 2012]. In the present paper, we consider reactive flow in large-deformation electrodes. We formulate the thermodynamic inequality of reactive flow, as well as a rheological model consistent with the inequality. Because flow and reaction are mediated by similar atomic processes — breaking and forming of atomic bonds, we treat both flow and reaction as concurrent nonequilibrium processes. The two processes are coupled through the introduction of an equivalent chemomechanical stress and a chemomechanical flow rule. When the host is subject to purely deviatoric stress, flow will proceed when the deviatoric stress reaches a certain threshold, and the model recovers the conventional theory of plasticity. When the host is subject to a purely hydrostatic stress and is connected with a reservoir of lithium, the host will absorb lithium when a combination of the mean stress and chemical potential reaches another threshold. Under combined stress and the chemical potential, the driving force for reaction enables the host to flow under low deviatoric stress. We illustrate the theory with two examples: cyclic lithiation and delithiation of an electrode under no constraint and that of a thin-film electrode bonded on a substrate.

2. Thermodynamics of Reactive Flow

Consider a setup of a host, a reservoir, and a set of applied forces (Fig. 2). Both the host and the reservoir may contain many species of atoms, but the host and the reservoir only exchange one species of atoms: lithium. To focus on main ideas, we consider deformation in principal coordinates — that is, a cube deforms into a rectangular block. We further assume that the host is sufficiently small so that

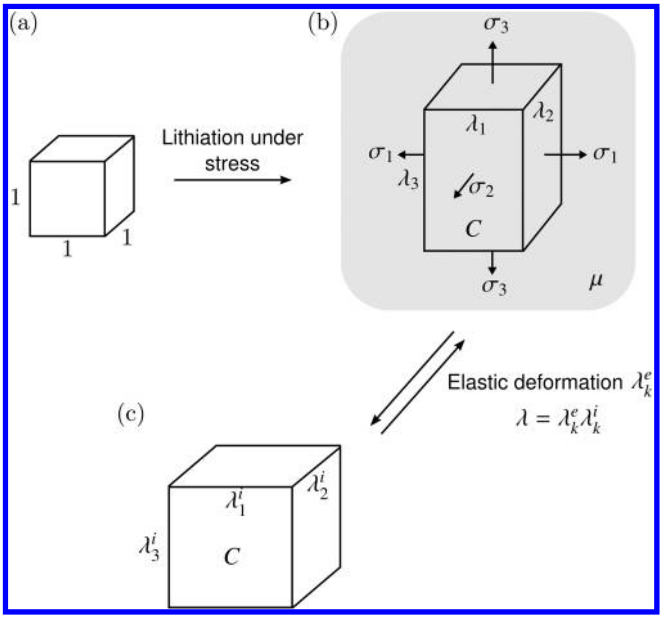


Fig. 2. (a) In the reference state, the host is a unit cube, stress-free and lithium-free, and is disconnected from the reservoir. (b) In an actual state at a particular time, subject to stresses and in contact with a reservoir of lithium, the host absorbs a certain amount of lithium and becomes a rectangular block. (c) In an intermediate state, the elastic stretches in the actual state are removed, but the inelastic stretches remain, along with the absorbed lithium.

both the distribution of lithium and deformation in the host are homogeneous. Inhomogeneous fields will be considered elsewhere.

In the reference state, the host is a unit cube, stress-free and lithium-free [Fig. 2(a)]. In the current state at a particular time, in contact with the reservoir and subject to the applied forces, the host absorbs C number of lithium and becomes a rectangular block of sides λ_1, λ_2 and λ_3 [Fig. 2(b)]. Because the host in the reference state is a unit cube, C is the nominal concentration of lithium in the host (i.e., the number of lithium atoms in the host in the present state divided by the volume of the host in the reference state), and λ_1, λ_2 and λ_3 are the stretches (i.e., each side of the host in the present state divided by the side in the reference state). Write $J = \lambda_1\lambda_2\lambda_3$, the ratio of the volume of the host in the current state to that in the reference state. The logarithmic strains is defined by $\varepsilon_k = \log \lambda_k$.

Let the stresses applied on the faces of the rectangular block be σ_1, σ_2 and σ_3 — that is, the forces applied on faces of the rectangular block are $\sigma_1\lambda_2\lambda_3, \sigma_2\lambda_3\lambda_1$ and $\sigma_3\lambda_1\lambda_2$. These forces can be represented by hanging weights. Associated with small changes in the stretches, $\delta\lambda_1$, $\delta\lambda_2$ and $\delta\lambda_3$, the potential energy of the weights changes by $-\sigma_1\lambda_2\lambda_3\delta\lambda_1 - \sigma_2\lambda_3\lambda_1\delta\lambda_2 - \sigma_3\lambda_1\lambda_2\delta\lambda_3$. This quantity can also be written as $-J(\sigma_1\delta\varepsilon_1 + \sigma_2\delta\varepsilon_2 + \sigma_3\delta\varepsilon_3)$. Let μ be the chemical potential of lithium in the reservoir. When the host gains δC number of lithium atoms, the reservoir loses the same number of lithium atoms, and the Helmholtz free energy of the reservoir changes by $-\mu\delta C$. Let W be the Helmholtz free energy of the host in the current state. Because the host in the reference state is a unit cube, W is the nominal density of the free energy — that is, the free energy of the host in the current state divided by the volume of the host in the reference state.

The host, the weights and the reservoir together form a composite thermodynamic system. The composite exchanges energy with the rest of the world by heat, and the composite conserves matter. The Helmholtz free energy of the composite is the sum of the Helmholtz free energy of the host, the Helmholtz free energy of the reservoir, and the potential energy of the weights. We restrict our analysis to isothermal processes. Thermodynamics dictates that the Helmholtz free energy of the composite should never increase:

$$\delta W - \mu\delta C - J(\sigma_1\delta\varepsilon_1 + \sigma_2\delta\varepsilon_2 + \sigma_3\delta\varepsilon_3) \leq 0. \tag{1}$$

The variation means the value of a quantity at a time minus that at a slightly earlier time. As usual in thermodynamics, this inequality involves the direction of time, but not the duration of time. The equality holds when the composite is in a state of equilibrium, while the inequality holds when the composite is not in equilibrium.

3. Rheology of Reactive Flow

The quantities σ_1, σ_2, σ_3 and μ represent external loads applied on the host, while the quantities λ_1, λ_2, λ_3 and C represent kinematic variables. When the external loads are known, we wish to predict how the kinematic variables evolve in time. We do so by specifying a rheological model. The following rheological model generalizes a previous one [Zhao *et al.*, 2011a] by treating reaction and flow as concurrent nonequilibrium processes.

The total stretches are taken to be the products of elastic and inelastic stretches (Fig. 2):

$$\lambda_1 = \lambda_1^e\lambda_1^i, \quad \lambda_2 = \lambda_2^e\lambda_2^i, \quad \lambda_3 = \lambda_3^e\lambda_3^i. \tag{2}$$

The elastic stretches λ_k^e represent distortion of atomic bonds with no rearrangement of atoms. The inelastic stretches λ_k^i represent rearrangements of atoms, including both flow and the change of composition. The products in (2) can also be written as the sums, $\log\lambda_k = \log\lambda_k^e + \log\lambda_k^i$. Defining the logarithmic elastic strains by $\varepsilon_k^e = \log\lambda_k^e$, and the logarithmic inelastic strains by $\varepsilon_k^i = \log\lambda_k^i$, Eq. (2) can also be written as $\varepsilon_k = \varepsilon_k^e + \varepsilon_k^i$.

We assume that the Helmholtz-free energy of the host is a function of the elastic strains and the concentration of lithium:

$$W = W(\varepsilon_1^e, \varepsilon_2^e, \varepsilon_3^e, C). \tag{3}$$

According to differential calculus, when the independent variables changes, the free energy changes by $\delta W = (\partial W/\partial\varepsilon_1^e)\delta\varepsilon_1^e + (\partial W/\partial\varepsilon_2^e)\delta\varepsilon_2^e + (\partial W/\partial\varepsilon_3^e)\delta\varepsilon_3^e + (\partial W/\partial C)\delta C$.

Under the rheological assumptions (2) and (3), the thermodynamic inequality (1) becomes

$$\left(J\sigma_1 - \frac{\partial W}{\partial \varepsilon_1^e}\right)\delta\varepsilon_1^e + \left(J\sigma_2 - \frac{\partial W}{\partial \varepsilon_2^e}\right)\delta\varepsilon_2^e + \left(J\sigma_3 - \frac{\partial W}{\partial \varepsilon_3^e}\right)\delta\varepsilon_3^e + J\left(\sigma_1\delta\varepsilon_1^i + \sigma_2\delta\varepsilon_2^i + \sigma_3\delta\varepsilon_3^i\right) + \left(\mu - \frac{\partial W}{\partial C}\right)\delta C \geq 0. \tag{4}$$

This condition holds for arbitrary small changes in the elastic strains, the inelastic strains, and the concentration. In the absence of the change in the inelastic strains and the concentration, $\delta\varepsilon_k^i = 0$ and $\delta C = 0$, the host can still deform elastically by distorting atomic bonds, $\delta\varepsilon_k^e \neq 0$, with no rearrangement of atoms. We assume that the host is in equilibrium with respect to the variation of the elastic strains, so that in (4) the coefficient associated with the variation in every elastic strain vanishes:

$$\sigma_1 = \frac{\partial W(\varepsilon_1^e, \varepsilon_2^e, \varepsilon_3^e, C)}{J\partial\varepsilon_1^e}, \quad \sigma_2 = \frac{\partial W(\varepsilon_1^e, \varepsilon_2^e, \varepsilon_3^e, C)}{J\partial\varepsilon_2^e}, \quad \sigma_3 = \frac{\partial W(\varepsilon_1^e, \varepsilon_2^e, \varepsilon_3^e, C)}{J\partial\varepsilon_3^e}. \tag{5}$$

Under the assumption of partial equilibrium (5), inequality (4) reduces to

$$J(\sigma_1\delta\varepsilon_1^i + \sigma_2\delta\varepsilon_2^i + \sigma_3\delta\varepsilon_3^i) + \left(\mu - \frac{\partial W}{\partial C}\right)\delta C \geq 0. \tag{6}$$

This inequality involves the inelastic strains and the concentration of the lithium.

When the composition of the host is fixed, we assume that the behavior of the host is similar to that of a metal: the host flows without inelastic volumetric change. Denote $J^i = \lambda_1^i\lambda_2^i\lambda_3^i$ and $J^e = \lambda_1^e\lambda_2^e\lambda_3^e$, so that $J = J^eJ^i$. The inelastic expansion of the volume is taken to be entirely due to the absorption of lithium, and is a function of the concentration of lithium:

$$J^i = J^i(C). \tag{7}$$

This assumption places a constraint between the concentration and the inelastic stretches, so that inequality (6) reduces to

$$\left(\sigma_1 + \frac{\mu}{\Omega} - \frac{\partial W}{\Omega\partial C}\right)\delta\varepsilon_1^i + \left(\sigma_2 + \frac{\mu}{\Omega} - \frac{\partial W}{\Omega\partial C}\right)\delta\varepsilon_2^i + \left(\sigma_3 + \frac{\mu}{\Omega} - \frac{\partial W}{\Omega\partial C}\right)\delta\varepsilon_3^i \geq 0, \tag{8}$$

where Ω is the volume per guest atom in the host, defined by $\Omega = J^e dJ^i(C)/dC$. This inequality eliminates the concentration as an independent kinematic variable, and uses the three inelastic stretches as the independent variables.

Inequality (8) identifies the driving forces for the inelastic stretches. The three driving forces are the principal components of a tensor, which we call the chemo-mechanical driving force. The mean of the principal components is

$$\zeta = \frac{\mu}{\Omega} - \frac{\partial W(\varepsilon_1^e, \varepsilon_2^e, \varepsilon_3^e, C)}{\Omega\partial C} + \sigma_m, \tag{9}$$

where the mean stress is defined by $\sigma_m = (\sigma_1 + \sigma_2 + \sigma_3)/3$. The significance of (9) is interpreted as follows. The chemical potential of lithium in the reservoir is μ, and the chemical potential of lithium in the host is $\partial W/\partial C - \Omega\sigma_m$ [Zhao *et al.*, 2011a; Bower *et al.*, 2011]. When the reservoir and the host are in equilibrium with respect to the exchange of lithium, the chemical potential of lithium in the reservoir equals that in the host, $\mu = \partial W/\partial C - \Omega\sigma_m$. This assumption of the partial equilibrium with respect to reaction is commonly adopted in the literature of lithium-ion batteries, while flow is taken to be a nonequilibrium process [Zhao *et al.*, 2011a; Bower *et al.*, 2011; Cui *et al.*, 2012; Sheldon *et al.*, 2012]. However, it is hard to justify such an assumption of equilibrium with respect to reaction but nonequilibrium with respect to flow, considering that both reaction and flow are mediated by similar atomic processes: breaking and forming atomic bonds. Following our recent paper [Brassart and Suo, 2012], here we do not assume chemical equilibrium; rather, we assume that reaction and flow are *concurrent nonequilibrium processes*. When the reaction is not in equilibrium, the chemical potential of lithium in the host differs from that in the reservoir. The difference defines the driving force for reaction, ζ, given in (9). A positive driving force $\zeta > 0$ promotes lithium to enter the host (lithiation), and a negative driving force $\zeta < 0$ promotes lithium to exude from the host (delithiation).

Define the deviatoric inelastic strains by $e_k^i = \varepsilon_k^i - (\log J^i)/3$. Inequality (8) can be written as

$$(\sigma_1 - \sigma_m)\delta e_1^i + (\sigma_2 - \sigma_m)\delta e_2^i + (\sigma_3 - \sigma_m)\delta e_3^i + \zeta J^{-1}\Omega\delta C \geq 0. \tag{10}$$

The variations of the inelastic stretches δe_k^i measure the progress of flow, and the quantity $J^{-1}\Omega\delta C$ measures the progress of reaction. Inequality (10) confirms that the driving forces for flow are the deviatoric stresses $\sigma_1 - \sigma_m$, $\sigma_2 - \sigma_m$ and $\sigma_3 - \sigma_m$, and the driving force for reaction is ζ. This inequality uses the three deviatoric inelastic strains and the concentration of lithium as kinematic variables. Note that $e_1^i + e_2^i + e_3^i = 0$, only two of the three deviatoric inelastic strains are independent. Consequently, inequality (10) only involves three independent kinematic variables, and is identical to inequality (8). Both inequalities are derived from the basic thermodynamic inequality (1) on the basis of the rheological model.

Inequality (10) places a constraint on the choice of kinetic model. Following Brassart and Suo [2012], we develop a kinetic model by extending the von Mises theory of plasticity. We introduce a scalar measure of the chemomechanical driving force:

$$\tau_{eq} \equiv \sqrt{\frac{1}{2}[(\sigma_1 - \sigma_m)^2 + (\sigma_2 - \sigma_m)^2 + (\sigma_3 - \sigma_m)^2] + q\zeta^2}, \tag{11}$$

where q is a positive constant. When $q = 0$, (11) reduces to the von Mises equivalent shear stress. The form of (11) is motivated by the following considerations. As a generalization of the theory of plasticity of von Mises, we may assume that the yield condition depends on the chemomechanical driving force through a single scalar — a quadratic form of the components of the chemomechanical driving force. For an isotropic host, the most general quadratic form is given by a linear combination of the second invariant of the deviatoric stress and ζ^2. Further study is clearly required to ascertain the range of applicability of this generalization once more quantitative experimental data become available.

We generalize the von Mises flow rule as follows. Let $\gamma^i(t)$ be the inelastic engineering strain under a pure shear stress τ. The rate of the inelastic shear strain is taken to be a function of the pure stress:

$$\frac{d\gamma^i}{dt} = f(\tau). \tag{12}$$

For the host under the multiaxial stresses and in contact with the reservoir of lithium, we postulate that the rates of deviatoric inelastic strains relate to the deviatoric stresses as

$$\frac{de_1^i}{dt} = f(\tau_{eq})\frac{\sigma_1 - \sigma_m}{2\tau_{eq}}, \quad \frac{de_2^i}{dt} = f(\tau_{eq})\frac{\sigma_2 - \sigma_m}{2\tau_{eq}}, \quad \frac{de_3^i}{dt} = f(\tau_{eq})\frac{\sigma_3 - \sigma_m}{2\tau_{eq}}. \tag{13}$$

Furthermore, the rate of concentration of lithium relates to the driving force ζ as

$$\frac{dC}{dt} = f(\tau_{eq})\frac{Jq\zeta}{\Omega\tau_{eq}}. \tag{14}$$

Equations (13) and (14) constitute a flow rule for reactive flow. The flow rule generalizes the viscoplastic model of the von Mises type. So long as $f(\tau_{eq}) \geq 0$, this flow rule satisfies the thermodynamic inequality (10). The deviatoric stresses drive the flow, and the quantity ζ drives the reaction. Flow and reaction couple through the scalar measure of the chemomechanical driving force τ_{eq} defined by (11). If $f(\tau_{eq})$ is an increasing function, the chemical driving force accelerates the flow, and the deviatoric stress accelerates reaction.

4. A Specific Form of the Rheological Model

The rheological model requires the input of three functions: $W(\varepsilon_1^e, \varepsilon_2^e, \varepsilon_3^e, C)$, $J^i(C)$ and $f(\tau_{eq})$, as well as the input of the number q. These inputs are likely obtained by fitting experimental data to some functional forms. Once the external loads σ_1, σ_2, σ_3 and μ are prescribed, the rheological model evolves the kinematic variables λ_1, λ_2, λ_3 and C in time. We now list functions to be used in the numerical examples in the later sections.

We adopt a commonly used viscoplastic model. Let τ_Y be the yield strength measured when the material element is subject to pure shear. When $\tau_{eq} < \tau_Y$, the inelastic strain rate vanishes, $f(\tau_{eq}) = 0$. When $\tau_{eq} \geq \tau_Y$, the inelastic strain rate is given by a power law:

$$f(\tau_{eq}) = \dot{\gamma}_0\left(\frac{\tau_{eq}}{\tau_Y} - 1\right)^m, \tag{15}$$

where $\dot{\gamma}_0$ and m are fitting parameters. In general, τ_Y, $\dot{\gamma}_0$ and m depend on the concentration. In the following numerical examples, for simplicity, we will keep them as constant.

Since elastic deformation is small, we adopt a free energy function quadratic in the elastic strains:

$$W = W_0(C) + J^i G \left[(\varepsilon_1^e)^2 + (\varepsilon_2^e)^2 + (\varepsilon_3^e)^2 + \frac{\nu}{1-2\nu}(\varepsilon_1^e + \varepsilon_2^e + \varepsilon_3^e)^2 \right], \tag{16}$$

where G is the shear modulus, and ν Poisson's ratio; both may depend on the concentration. In the following numerical examples, for simplicity, we will keep them as constant. Substituting (16) into (5), the stresses are found to relate to the elastic strains as

$$\sigma_k = 2G \left[\varepsilon_k^e + \frac{\nu}{1-2\nu}(\varepsilon_1^e + \varepsilon_2^e + \varepsilon_3^e) \right]. \tag{17}$$

Here we retain terms linear in the elastic strains.

We define the chemical part of the free energy function $W_0(C)$ in (16) such that the driving force for reaction (9) is given by [Sethuraman *et al.*, 2010b]:

$$\zeta = \frac{\mu - \mu_0}{\Omega} - \frac{kT}{\Omega} \log\left(\frac{C}{C_{\max} - C} \right) + \sigma_m. \tag{18}$$

We have neglected the terms quadratic in the elastic strains. Here $C^{\max}$ is the maximal concentration of lithium that can be absorbed by the host. The constant μ_0 is chosen such that $\zeta = 0$ when $C = C_{\max}/2$ and $\sigma_m = 0$. By writing (18) we have assumed that the host and the lithium forms a binary ideal solution. Non-ideality can be accounted for by introducing an activity coefficient which depends on the concentration.

Finally, we will assume that the inelastic volume change due to the insertion of lithium, dJ^i/dC, is a constant. We write

$$J^i(C) = 1 + vC, \tag{19}$$

where the volume per lithium atom v is related to Ω by $\Omega = J^e v$. In the following numerical examples, given that $J^e \approx 1$, we will consider that $\Omega \approx v$.

5. Lithiation and Delithiation of a Host under Vanishingly Small Current and Stress

As a first illustration of the theory, we consider a host subject to cyclic lithiation and delithiation under vanishingly small current and stress. In the initial state, the host is stress-free and lithium-free. Subsequently, the host is connected to a reference electrode of lithium metal by a conducting wire, while lithium ions can migrate from the reference electrode to the host through an electrolyte. A voltage source imposes a constant electric current during both lithiation and delithiation. The rate of lithiation is characterized by the time t_0 needed to reach full capacity, so that the constant rate of lithiation and delithiation is given by $dC/dt = \pm C^{\max}/t_0$. This time needed for lithiation and delithiation is taken to be long compared to the time needed for diffusion, $t_0 \gg h^2/D$, where D is the diffusivity of lithium in silicon, and

h is the characteristic length of the host. Consequently, the distribution of lithium in the host is homogeneous.

In the absence of stress, the scalar measure of the chemomechanical stress (11) reduces to $\tau_{eq} = \sqrt{q}|\zeta|$. According to the rheological model of Sec. 4, lithiation proceeds when $\zeta > \tau_Y/\sqrt{q}$, delithiation proceeds when $\zeta < -\tau_Y/\sqrt{q}$, and the concentration remains constant when $|\zeta| \leq \tau_Y/\sqrt{q}$. Inserting the expression (18) for ζ into the flow rule (14), we obtain the chemical potential needed to insert and extract lithium at a constant rate:

$$\frac{\mu - \mu_0}{\Omega} = \pm\frac{\tau_Y}{\sqrt{q}}\left[\left(\frac{\Omega C_{\max}}{\sqrt{q}\dot{\gamma}_0 t_0(1+\Omega C)}\right)^{1/m} + 1\right] + \frac{kT}{\Omega}\log\left(\frac{C}{C_{\max} - C}\right). \qquad (20)$$

The positive sign holds during lithiation, and the negative sign during delithiation. Equation (20) identifies a dimensionless rate of insertion, $\Omega C_{\max}/\dot{\gamma}_0 t_0$. For amorphous silicon, representative numerical values are: $\Omega = 1.5 \times 10^{-29}\,\mathrm{m}^3$ and $\tau_Y = 1\,\mathrm{GPa}$. The maximum concentration is obtained from the observation that the volume change of fully lithiated silicon is about 300%: $\Omega C_{\max} = 3$. In the absence of experimental reference values, the viscoplastic parameters are set to $\dot{\gamma}_0 = 1 \times 10^{-6}\,\mathrm{s}^{-1}$ and $m = 4$. A typical curve is represented in Fig. 3 for $T = 300\,\mathrm{K}$ and $t_0 = 1000\,\mathrm{h}$. The curve gives the chemical potential as a function of the concentration during stress-free swelling, and exhibits pronounced hysteresis, even for the present low rate of lithiation and delithiation.

The voltage against the reference electrode is obtained by the relation $\Phi = -\mu/e$, where e is the elementary charge (a positive constant). In the quasi-static limit

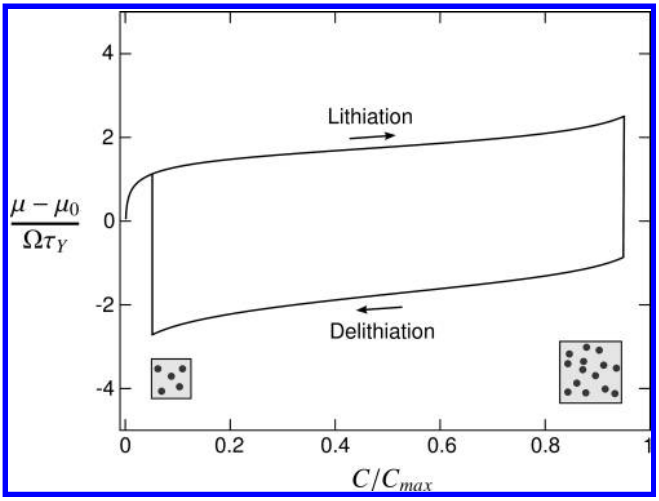


Fig. 3. Lithiation and delithiation under a stress-free condition, represented on the plane of concentration and chemical potential.

($\Omega C_{\max}/\dot{\gamma}_0 t_0 \to 0$), the hysteresis gap in the chemical potential, $\Delta\mu$, reduces to:

$$\frac{\Delta\mu}{\Omega} = -\frac{e\Delta\Phi}{\Omega} = \frac{2\tau_Y}{\sqrt{q}}. \tag{21}$$

Relation (21) allows us to determine the constant q from experimental voltage-concentration curves by measuring the jump in voltage between lithiation and delithiation for a given state of charge. Experimental results at low charging rate and under presumably stress-free conditions [Beaulieu *et al.*, 2001] demonstrated gap in voltage of about 0.2 V, which corresponds to $q \approx 1$.

6. Lithiation and Delithiation of a Thin-Film Electrode Bonded to a Substrate

As a second illustration of the theory, we consider a thin film of a host attached to a rigid substrate. The host is stress-free and lithium-free in the initial state, and is subject to cyclic lithiation and delithiation afterwards. Again, the concentration of lithium is supposed to be homogeneous in the host. The surface of the host in contact with the electrolyte is taken to be traction-free, $\sigma_3 = 0$. The in-plane stresses are equal-biaxial, $\sigma \equiv \sigma_1 = \sigma_2$. The mean stress is $\sigma_m = 2\sigma/3$. The scalar measure of the chemomechanical stress (11) reduces to

$$\tau_{eq} = \sqrt{\frac{\sigma^2}{3} + q\zeta^2}. \tag{22}$$

Upon lithiation, the host undergoes an inelastic volume expansion (19) which must be accommodated by elastic and inelastic deviatoric stretches. The in-plane elastic strain relates to the stress as

$$\varepsilon_1^e = \frac{1-\nu}{2G(1+\nu)}\sigma. \tag{23}$$

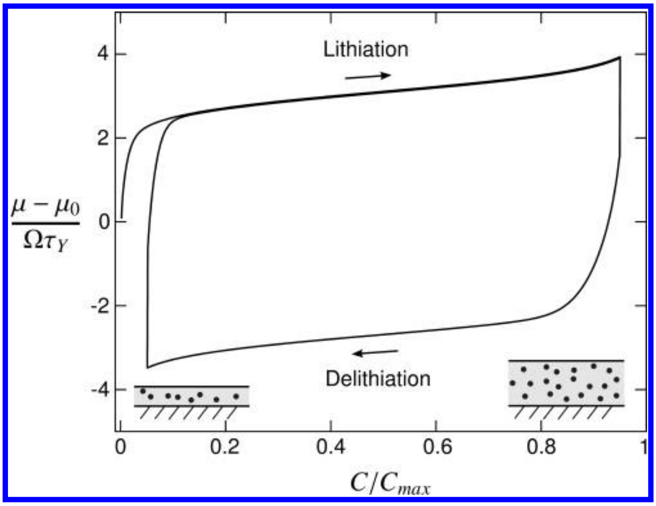
The constraint of the substrate prevents in-plane expansion: $\varepsilon_1 = \varepsilon_2 = 0$. Consequently, the inelastic strain is $\varepsilon_1^i = -\varepsilon_1^e$, and the deviatoric inelastic strain is $e_1^i = \varepsilon_1^i - (\log J^i)/3 = -\varepsilon_1^e - (\log J^i)/3$. The flow rule (13) specializes to

$$-\frac{1-\nu}{2G(1+\nu)}\frac{d\sigma}{dt} - \frac{\Omega}{3(1+\Omega C)}\frac{dC}{dt} = f(\tau_{eq})\frac{\sigma}{6\tau_{eq}}. \tag{24}$$

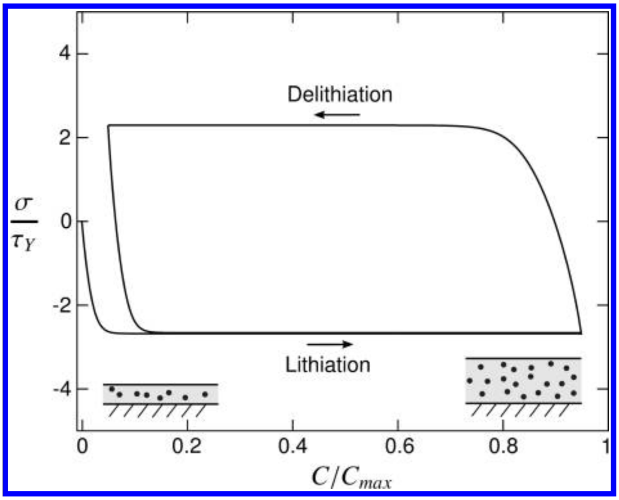
The flow rule (14) specializes to

$$\frac{dC}{dt} = \frac{Jqf(\tau_{eq})}{\Omega\tau_{eq}}\left[\frac{\mu-\mu_0}{\Omega} - \frac{kT}{\Omega}\log\left(\frac{C}{C_{\max}-C}\right) + \frac{2\sigma}{3}\right]. \tag{25}$$

For a given rate of lithiation and delithiation, $dC/dt = \pm C^{\max}/t_0$, a combination of (24), (25), (22), (18) and (15) leads to an ordinary differential equation for $\sigma(t)$. Once the function $\sigma(t)$ is determined, the function $\mu(t)$ can be determined from (25). Typical curves for the chemical potential and the stress are shown in Fig. 4, taking $G = 38.5$ GPa, $\nu = 0.3$ and $q = 1$. Other numerical values of the material and loading parameters are identical to those of the previous example.



(a)



(b)

Fig. 4. Lithiation and delithiation of a thin-film electrode constrained on a substrate, represented (a) on the plane of concentration and chemical potential, and (b) on the plane of concentration and stress.

Comparing Figs. 3 and 4(a), we note that the effects of stress on the evolution of the chemical potential are twofold. First, the levels of chemical load required to insert and extract lithium at constant rate are higher (in absolute values) in the thin-film host, which implies larger hysteresis. This effect can be attributed to the contribution of the mean stress to the driving force for reaction, Eq. (9). Indeed, the mean stress is (mostly) compressive during lithiation and tensile during delithiation, so that the mean stress hinders reaction. Second, a pre-existing stress lowers the threshold value of the chemical load for insertion or extraction after load reversal. This can be seen from the magnitude of the jumps in chemical potential (the vertical portions of the curve) in Fig. 4(a), as compared to Fig. 3. This follows from the contribution of the stress in the yield condition $\tau_{eq} = \tau_Y$, according to which a deviatoric stress always reduces the magnitude of the driving force ζ needed for reaction, as compared to an unconstrained situation. In addition, the sign of the pre-existing mean stress in expression (9) of ζ favors reaction at load reversal.

The evolution of stress with concentration shows steep sign changes during load reversal, followed by steady state regimes [Fig. 4(b)]. During transient portions of the curves, the inelastic volume expansion is accommodated by both elastic and inelastic deviatoric deformations. The first ones instantaneously cause stresses, which in turn cause the host to flow according to the flow rules (13). As the stress increases in magnitude, so does the flow rate. At some point, the flow rate is sufficient to fully accommodate the inelastic volume expansion with prescribed rate, so that the rates of elastic deformation and stress vanish; see also (24). In the steady state, we find that $d \log J^i/dt = d\varepsilon_3^i/dt = d\varepsilon_3/dt$. That is, the inelastic volume change is entirely accommodated by out-of-plane expansion.

In the steady state regime, a combination of (24) and (25) shows that the in-plane stress and the driving force for reaction are related by $\zeta = -\sigma/2q$. The equivalent chemomechanical stress (22) is then given by $\tau_{eq} = |\sigma|\sqrt{(1/3) + (1/4q)}$. In the quasi-static limit where $\Omega C_{\max}/\dot{\gamma}_0 t_0 \to 0$, we have $\tau_{eq} \to \tau_Y$. In the present case with $q = 1$, we find that $|\sigma| \to 1.31\tau_Y$. As the results presented in Fig. 4 correspond to a dimensionless rate of insertion of the order of unity, the absolute value of the stress in the steady state regime in Fig. 4(b) is significantly higher than its quasi-static limit.

Contrary to the chemical potential concentration curves, the stress-concentration curves do not present any jump in the stress value at load reversal. However, the steep slope regions cannot be attributed to elastic loading and unloading, which is not allowed in a concentration-driven simulation. Indeed, the flow rules (13) indicate that insertion and extraction are necessarily accompanied by plastic flow for non-vanishing deviatoric stress, thus preventing (purely) elastic unloading. Therefore, the steep slope regions should be regarded as elasto-viscoplastic unloading.

7. Concluding Remarks

We have presented a theory of reactive flow in large-deformation electrodes. The model is able to predict hysteresis in voltage-concentration curve at vanishingly small rate of lithiation and delithiation and in the absence of stress. For a host under combined chemical and mechanical load, we construct a chemomechanical yield surface and flow rules which predict lithiation-assisted plastic flow. Additional experimental results are needed to validate and refine the theory.

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