



Examining the validity of Stoney-equation for *in-situ* stress measurements in thin film electrodes using a large-deformation finite-element procedure

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HIGHLIGHTS

- Critical examination on the validity of Stoney equation in film electrodes.
- Effects of concentration dependent elasticity to *in-situ* stress measurements.
- Effects of finite deformation to *in-situ* stress measurements.
- A robust electrochemical-mechanical coupling FE procedure.

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ABSTRACT

During the lithiation and delithiation of a thin film electrode, stress in the electrode is deduced from the curvature change of the film using the Stoney equation. The accuracy of such a measurement is conditioned on the assumptions that (a) the mechanical properties of the electrode remain unchanged during lithiation and (b) small deformation holds. Here, we demonstrate that the change in elastic properties can influence the measurement of the stress in thin film electrodes. We consider the coupling between diffusion and deformation during lithiation and delithiation of thin film electrodes and implement the constitutive behavior in a finite-deformation finite element procedure. We demonstrate that both the variation in elastic properties in thin film electrodes and finite-deformation during lithiation and delithiation would challenge the applicability of the Stoney-equation for *in-situ* stress measurements of thin film electrodes.

1. Introduction

Battery performance is largely compromised by the stress in active cathode and anode particles because of large volume change associated with the diffusion of lithium-ions during battery charge/discharge cycles [1–3]. Understanding battery degradation has stimulated a growing interest in studying the electrochemical-mechanical coupled fields and the subsequent stress variation during lithiation and delithiation. Many researchers are focusing on Si-based and Sn-based anodes because of their high charge capacities and relatively low density. However, high capacities usually are associated with huge volume expansion and high stress, causing poor cycle life. A robust numerical implementation of diffusion-finite deformation in strongly coupled phenomena is, therefore, necessary for simulating large strain (~300%) in silicon- or tin-based electrodes for lithium ion battery applications.

It is generally agreed that the lithiation and delithiation in batteries involve electrochemical-mechanical coupling. Taking Si as an example, the electrochemical lithiation of crystalline Si exhibits complicated structural changes [4], such as phase transition and volume changes [5]. As a result, significant stress change occurs, which has been related to the performance of the battery. Given the experimental difficulties in quantifying the coupling effects, intensive endeavors have been made in developing numerical methods in the past decade to capture the electrochemical-mechanical processes in batteries [6–12]. Anand et al. (2012) [13] has used a Cahn–Hilliard-type theory for species diffusion coupled with large elastic–plastic deformations.

When applying the Stoney equation for stress measurements [14,15], the accuracy is contingent upon the assumption that the elastic and plastic properties of the electrode remain unchanged during lithiation. However, there are obvious changes in the mechanical properties in the process of lithiation and delithiation of electrodes [16–18].

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In this paper, we demonstrate via finite element method based computations how the variation of elastic properties could influence the stress measurement and the stress-capacity relationship in thin film battery electrodes. We first present in Sec. 2 the numerical implementation of diffusion-finite deformation strongly coupled problems. We report the curvature response as a function of lithium concentration-dependent elastic modulus and discuss the limitation of the Stoney equation for stress measurements in thin film electrodes in Sec. 3. We conclude in Sec. 4 with final remarks.

2. The finite element formula

Here we introduce the diffusion-induced finite deformation coupled equations for modeling the electrode's finite deformation in the process of charge or discharge. Previously, many researchers have demonstrated that there exists a stress–capacity hysteresis in electrode materials, and the irreversible deformation is greater than the elastic deformation [17–20]. We introduce, therefore, a large inelastic deformation theory to our diffusion-finite deformation fully coupled theory, which, we believe, can be applied to many electrode materials. We discuss, in the following, diffusion process and finite deformation process separately.

2.1. Diffusion process for the finite deformation

At any given time t , the lithium ion concentration $\phi(\mathbf{x}, t)$ at a material point \mathbf{x} in the electrode structure (v) is governed by the diffusion equation [21].

$$\frac{\partial \phi}{\partial t} + \nabla \cdot \mathbf{J} = 0 \text{ (in } v), \quad (1a)$$

where $\nabla = \frac{\partial}{\partial x_i}$ is the gradient relative to current position x_i [22]. Hence the initial configuration \mathbf{X} coincides with the current one \mathbf{x} at $t = 0$, i.e., $X_i = x_i(t = 0)$, and the subscript i runs from x to z in the Cartesian coordinate system. The boundary condition is given as

$$\phi = \tilde{\phi}, \text{ (on } \Gamma_1) \text{ and } \mathbf{J} \cdot \mathbf{n} = J_i n_i = -J^s \text{ (on } \Gamma_2) \quad (1b)$$

Here J^s is the component of surface flux, \mathbf{n} is the surface normal, and Γ_1 and Γ_2 represent the surface of the volume v . Here, the galvanostatic current boundary condition J^s is related to the current density i^s via $J^s = \frac{i^s}{F}$ [23], and F is the Faraday constant.

There are several models for the effect of stress on lithium ion flow. The commonly used one expresses the flux, \mathbf{J} , a function of the gradient of a stress-dependent chemical potential μ (e.g. [13,22,24–27])

$$\mathbf{J} = -\frac{D(\phi, \mathbf{x})}{RT} \nabla \mu(\phi, \sigma_h, \mathbf{x}, t) \quad (1c)$$

where $D(\phi, \mathbf{x})$ is the diffusivity depending on concentrations and current positions, R is the gas constant and T is the absolute temperature. Note that different groups may use slightly different formula of μ although the same factors were taken into account (e.g. [13,22,27]). Eqn. (1c) reflects the influence of stress on concentration and *vice versa*. As the exact dependence of μ on σ remains debatable, we adopt a simple form (e.g. [24–27])

$$\mu(\phi, \sigma_h, \mathbf{x}, t) = \mu_0 + RT \ln \frac{\phi}{\phi_{max}} - \Omega \sigma_h \quad (1d)$$

where μ_0 is the referential potential, ϕ_{max} is the maximum lithium concentration, Ω is the lithium ions partial molar volume and σ_h is the hydrostatic stress, i.e., $(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$. The second term represents an entropic contribution to the free-energy, while the third term is the work done by the applied stress. Combining Eqns. (1c) and (1d), the flux equation can be rewritten as

$$\mathbf{J} = -\frac{D(\phi, \mathbf{x})}{\phi} \nabla \phi(\mathbf{x}, t) + \frac{D(\phi, \mathbf{x})\Omega}{RT} \nabla \sigma_h \quad (2)$$

We consider a linear dependence of diffusivity on concentration and consider isotropic diffusion $D(\phi, \mathbf{x}) = D_0 \phi$.

In general, the concentration ϕ is associated with compound phase $A_\psi B$ in the electrode where A and B indicate the lithium and the anode electrode material respectively, and the subscript ψ indicates the lithium fraction ranging from 0 to ψ_{max} . Its connection with ϕ is defined by

$$\phi = \frac{\psi}{V_\psi N_a}, \quad (3)$$

where V_ψ is the volume of the compound $A_\psi B$ and is a function of ψ , and N_a is Avogadro's number. Taking lithium-silicon battery system as an example, the volume of the compound $Li_\psi Si$ is [28,29].

$$V_\psi = \left(1 + 3.2 \frac{\psi}{\psi_{max}} \right) \times 10^{-28} \text{ m}^3, \quad (4)$$

and the maximum lithium fraction is $\psi_{max} = 4.4$ ($Li_{4.4}Si$ [30]). For numerical convenience, we consider ψ as a continuous variable. We write the diffusion equation in terms of ψ , and Eqn. (1a) is given as

$$\frac{V_\psi - \psi V'_\psi}{V_\psi^2 N_a} \frac{\partial \psi}{\partial t} + \nabla \cdot \mathbf{J} = 0 \text{ (in } v) \quad (5a)$$

where $V'_\psi = \frac{\partial V_\psi}{\partial \psi}$, and the boundary conditions are

$$\psi = \tilde{\psi}, \text{ (on } \Gamma_1) \text{ and } J_i n_i = -J^s \text{ (on } \Gamma_2) \quad (5b)$$

for prescribed concentration and ion flux, respectively. The flux equation (Eqn. (2)) is then written as

$$\mathbf{J} = -D_0 \nabla \left(\frac{\psi}{V_\psi N_a} \right) + \frac{D_0 \Omega}{RT} \left(\frac{\psi}{V_\psi N_a} \right) \nabla \sigma_h \quad (5c)$$

According to eqn. (5a) and eqn. (5b), the variational form δW_d of the above diffusion equation is given as

$$\delta W_d = \int_v \delta \psi \frac{V_\psi - \psi V'_\psi}{V_\psi^2 N_a} \frac{\partial \psi}{\partial t} dv - \int_v \delta \psi_i J_i dv - \int_s J^s \delta \psi ds = 0 \quad (6)$$

where v and s are the volume and the surface of the deformed body, respectively. The differentiation of δW_d is

$$\begin{aligned} d\delta W_d = & \int_v \delta \psi H(\psi) \frac{\partial d\psi}{\partial t} dv + \int_v \delta \psi_i D_0 H(\psi) d\psi_i dv \\ & - \int_v \delta \psi_i \frac{D_0 \Omega}{RT} \sigma_{h,i} H(\psi) d\psi dv \\ & - \int_v [\delta \psi_i G_{,m}(\psi) du_{m,i} + \delta \psi_m G_{,i}(\psi) du_{m,i}] dv \end{aligned} \quad (7)$$

where $H(\psi) = \frac{\partial \phi}{\partial \psi} = \frac{V_\psi - \psi V'_\psi}{V_\psi^2 N_a}$, $G_{,i}(\psi) = D_0 H(\psi) \psi_i - \frac{D_0 \Omega}{RT} \frac{\psi}{V_\psi N_a} \sigma_{h,i}$. The first three terms on the RHS of eqn. (7) are associated with diffusion, and the last one is the finite deformation-induced stiffness matrixes.

2.2. The finite deformation problems for electrodes

Since large volume changes occur in the negative electrode in high capacity batteries, and the Cauchy stress is affected by rigid-body rotation (not frame invariant), an objective stress rate with respect to the logarithm strain rate is desired. The objective stress rate can be acquired by the Jaumann rate [31] as

$$\dot{\sigma}_{ij}^J = \dot{\sigma}_{ij} + \sigma_{ik} W_{kj} - W_{ik} \sigma_{kj} \quad (8)$$

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