



Effects of stoichiometric maximum concentration on lithium diffusion and stress within an insertion electrode particle



Yaolong He ^{a,b,c}, Hongjiu Hu ^{a,b,*}, Dawei Huang ^{a,b}

^a Shanghai Institute of Applied Mathematics and Mechanics, Shanghai University, Shanghai 200072, China

^b Shanghai Key Laboratory of Mechanics in Energy Engineering, Shanghai 200072, China

^c College of Sciences, Shanghai University, Shanghai 200072, China

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ABSTRACT

Active materials for either anode or cathode have a stoichiometric upper limit of lithium intercalation. To investigate the effects of stoichiometric maximum concentration (SMC) on the lithium diffusion and diffusion induced stress, we establish an analytical model and compare with existing results. We show that SMC not only facilitates lithium diffusion, but also significantly relieves the maximum stress and its corresponding peak value during lithium insertion, and therefore, declines the probability of fracture in the electrode particle. Moreover, the effect of SMC is found to be more obvious for higher surface current density or lower stress coupling due to the significant concentration gradient of lithium. Finally, by investigating the combined effect of current density and stress, this work provides insights on the presence of SMC, as well as suggestions for the relevant modeling works on whether the SMC should be taken into account for material selection and designing.

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1. Introduction

Today, lithium-ion battery serves as a very important member of rechargeable batteries and has received tremendous popularity in our daily life [1]. Among the intensive studies in the past few years, increasing the battery charge and energy capacity receives a great deal of attention. It has been shown that mechanical stress induced by lithium diffusion is one of the most key factors that obstruct the durability and performance of batteries since it may lead to electrode fracture or fragmentation [2–4], and loss of electric contact with the current collector [5]. It is, therefore, important to describe properly the lithium diffusion and the corresponding diffusion induced stress (DIS) in the electrodes.

Active particles are the crucial components of the active layer in the electrode. DIS in particles may result in fragments inside the particle and thus is essential for material selection and designing [6]. In the literature, many theoretical works have been devoted to determine the particle stress. Some considered the diffusion is driven only by the lithium concentration gradient and described it using Fick's law of diffusion, e.g. the calculations of DIS in cathode particles [7–8] and anode particles like graphite [9]. Some others adopted a stress coupling diffusion model in which diffusion and stress were mutually affected. For example, Christensen and John Newman [10] developed a strongly coupled diffusion model and evaluated the DIS of carbonaceous

particles. Zhang et al. [6] simulated DIS in ellipsoidal LiMn_2O_4 particles with results suggesting that particles with smaller size and larger aspect ratios are desirable to reduce DIS. Chakraborty et al. [11] investigated DIS and deduced the axial growth of a cylindrical silicon particle.

It is well known that active materials for either anode or cathode have an upper limit of lithium intercalation. Although the above results were insightful, neglecting the effect of stoichiometric maximum concentration (SMC) would limit these conclusions only strictly applicable for dilute concentrations and make them disabled in predicting the concentration profiles and DIS within the battery electrode with the higher state of charge or larger influx. Recently, there have been several works addressing SMC effects. Haftbaradaran et al. [12] studied the impacts of SMC on the hydrogen diffusion in nickel in a freestanding plate. Bower et al. [4] proposed a finite strain model with the influence of SMC and compared with the experimental measurements of a silicon thin film deposited on a rigid substrate. Veruska et al. [13] discussed the impacts of concentration-dependent chemical expansion on the diffusion and DIS in a Li_xCoO_2 particle. Purkayastha and McMeeking [14] considered the SMC effect both in lithium chemical potential and flux and identified the impacts of non-dimensional parameters on the maximum DIS. However, it is still not clear that the mechanism how the SMC impacts lithium diffusion and DIS within the active particles. Especially, the effects of material properties and charging operations on the presence of SMC are still unknown. In addition, none of the published reports have distinguished the applicable conditions of the classical diffusion models with/without SMC, and consequently resulting in inappropriate electrode designing for the battery system.

* Corresponding author at: Shanghai Institute of Applied Mathematics and Mechanics, Shanghai University, Shanghai 200072, China.
E-mail address: huhongjiu@shu.edu.cn (H. Hu).

In this manuscript, we will investigate systematically the role of SMC on lithium diffusion, and the corresponding DIS aiming to provide a simple and accurate basis for theoretical modeling and applications of lithium-ion secondary batteries. An analytical model of mechanochemical diffusion considering SMC in the spherical active material will be established. Evolutions of the lithium concentration, the radial and hoop stresses as well as the maximum stresses will be simulated. Finally, a serviceability map of the current used models will be provided based on the discussions for engineering usage.

2. Methodology

2.1. Continuum modeling of mechanochemical diffusion

In order to consider the SMC effect, we assume that lithium intercalation consumes vacancy sites of the host material. Since vacancies in a material are finite, lithium concentration reaches its maximum when that material is fully intercalated. Considering an element of a host material which subjects to hydrostatic stress σ_h , the mechanochemical potential of lithium per mole is [12]

$$\mu = \mu_s - \mu_v - \Omega \sigma_h \tag{1}$$

Here, $\mu_s = \mu_{s0} + R_g T \ln a_s$ and $\mu_v = \mu_{v0} + R_g T \ln a_v$ are the chemical potentials of the solute atoms and vacancies respectively, where μ_{s0} and μ_{v0} are the invariant reference potentials, a_s and a_v are the activities of the components. R_g and T are the universal gas constant and the temperature respectively. $-\Omega \sigma_h$ is the contribution of mechanical energy, where Ω is the partial molar volume of solute, which represents the change in volume per mole of solute atoms inserted to the element, and σ_h is the hydrostatic stress. Taking c and c_{max} as the concentration and stoichiometric maximum concentration of the solute atoms, lithium and vacancies occupy respectively fixed site fractions of c / c_{max} and $1 - c / c_{max}$. The activities of each component associated with their site fractions are $a_s = \gamma_s \cdot c / c_{max}$ and $a_v = \gamma_v \cdot (1 - c / c_{max})$, where γ_s and γ_v are the corresponding activity coefficients.

Therefore, from Eq. (1), we have

$$\mu = \mu_r + R_g T \ln \left(\frac{c}{c_{max} - c} \right) - \Omega \sigma_h \tag{2}$$

where $\mu_r = \mu_{s0} - \mu_{v0} - R_g T \ln (\gamma_s / \gamma_v)$. In the absence of experimental data, γ_s / γ_v is usually assumed to be homogeneous in the host material. μ_r , therefore, becomes a constant reference chemical potential, which is consistent with the previous works [14,15]. The contribution of the SMC is thus implied in the second term on the right side.

According to conservation condition, lithium diffusion satisfies

$$\frac{\partial c}{\partial t} = \nabla \cdot (-\mathbf{J}) = \nabla \cdot \left(\frac{Dc}{R_g T} \nabla \mu \right) \tag{3}$$

where $\mathbf{J} = -\frac{Dc}{R_g T} \nabla \mu$ is the lithium diffusion flux and D is the lithium diffusivity.

For the lithium diffusion within a spherical particle of radius R , a substitution of Eq. (2) into Eq. (3) results in

$$r \frac{\partial c}{\partial t} = D \frac{c_{max}}{c_{max} - c} \left(2 \frac{\partial c}{\partial r} + r \frac{\partial^2 c}{\partial r^2} \right) + D \frac{c_{max}}{(c_{max} - c)^2} r \left(\frac{\partial c}{\partial r} \right)^2 - \frac{D\Omega}{R_g T} \left(2c \frac{\partial \sigma_h}{\partial r} + r \frac{\partial c}{\partial r} \frac{\partial \sigma_h}{\partial r} + rc \frac{\partial^2 \sigma_h}{\partial r^2} \right) \tag{4}$$

The initial and boundary conditions corresponding to the generally used galvanostatic control are given by:

$$c(r, 0) = 0 \tag{5}$$

$$\begin{aligned} -D \left(\frac{c_{max}}{c_{max} - c} \frac{\partial c}{\partial r} - \frac{\Omega c}{R_g T} \frac{\partial \sigma_h}{\partial r} \right) \Big|_{r=R} &= \frac{i_n}{F} \\ -D \left(\frac{c_{max}}{c_{max} - c} \frac{\partial c}{\partial r} - \frac{\Omega c}{R_g T} \frac{\partial \sigma_h}{\partial r} \right) \Big|_{r=0} &= 0 \end{aligned} \quad \text{for } t > 0 \tag{6}$$

where i_n is the surface current density and F is the Faraday's constant.

2.2. Diffusion induced stress

Since atomic diffusion is much slower than the elastic deformation, the mechanical equilibrium is treated as a static equilibrium problem. In the absence of any body force, the force balance requires that [16]

$$\frac{d\sigma_r}{dr} + 2 \frac{\sigma_r - \sigma_\theta}{r} = 0 \tag{7}$$

where, σ_r and σ_θ are the radial and hoop stresses, respectively.

Using the analogy between thermal and diffusion induced stress and assuming that the spherical particle is an isotropic linear elastic solid, the radial and hoop stresses induced by the lithium diffusion are given by [17]:

$$\begin{aligned} \sigma_r &= \frac{E}{1 + \nu} \left(\frac{\nu}{1 - 2\nu} \theta + \varepsilon_r \right) - \frac{1}{3} \frac{E\Omega c}{1 - 2\nu} \\ \sigma_\theta &= \frac{E}{1 + \nu} \left(\frac{\nu}{1 - 2\nu} \theta + \varepsilon_\theta \right) - \frac{1}{3} \frac{E\Omega c}{1 - 2\nu} \end{aligned} \tag{8}$$

where E and ν are the elastic modulus and Poisson's ratio of the lithium compounds, respectively. $\theta = \varepsilon_r + 2\varepsilon_\theta$ is the elastic volumetric strain. ε_r and ε_θ are the radial and hoop strains and can be expressed as functions of radial displacement u in the infinitesimal formulation of deformation

$$\varepsilon_r = \frac{du}{dr} \quad \varepsilon_\theta = \frac{u}{r} \tag{9}$$

2.3. Numerical methods

Substituting Eqs. (8) and (9) into Eq. (7) and introducing the traction-free boundary condition at the particle surface, the two-way coupling between stress and lithium diffusion can be decoupled. The obtained radial and hoop stresses are as follows

$$\begin{aligned} \sigma_r &= \frac{2E\Omega}{3(1-\nu)} \left(\frac{1}{R^3} \int_0^R cr^2 dr - \frac{1}{r^3} \int_0^r cr^2 dr \right) \\ \sigma_\theta &= \frac{E\Omega}{3(1-\nu)} \left(\frac{2}{R^3} \int_0^R cr^2 dr + \frac{1}{r^3} \int_0^r cr^2 dr - c \right) \end{aligned} \tag{10}$$

These stresses are exact for any given lithium profile because all mechanical field equations of three-dimensional elasticity, continuity conditions and the boundary conditions have been satisfied. To obtain further the spatial profile of these stresses, the distribution of lithium concentration has to be solved beforehand.

According to Eq. (10) and noting that $\sigma_h = (\sigma_r + 2\sigma_\theta)/3$, the diffusion governing equation as shown in Eq. (4) can be expressed only by the lithium concentration

$$\begin{aligned} rc_{max}(c_{max} - c)^2 \frac{\partial c}{\partial t} &= Dc_{max}^2(c_{max} - c) \left(2 \frac{\partial c}{\partial r} + r \frac{\partial^2 c}{\partial r^2} \right) + Dc_{max}^2 r \left(\frac{\partial c}{\partial r} \right)^2 \\ &\quad - D\lambda(c_{max} - c)^2 \left(2c \frac{\partial c}{\partial r} + r \left(\frac{\partial c}{\partial r} \right)^2 + rc \frac{\partial^2 c}{\partial r^2} \right) \end{aligned} \tag{11}$$

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