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Effects of concentration-dependent elastic modulus on the diffusion of lithium ions and diffusion induced stress in layered battery electrodes

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HIGHLIGHTS

- Modulus stiffening enhances the Li-ion diffusion & increases the stress in anode.
- Modulus softening hinders the Li-ion diffusion & decreases the stress in anode.
- The mechanism for effect of varying modulus on diffusion & stress is elucidated.
- Analytic solution of the peak stress considering concentration dependent modulus is given.
- The conditions of neglecting modulus variation during lithiation are obtained.

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ABSTRACT

A stress assisted diffusion model considering concentration-dependent elastic modulus of active material has been established for the multi-layered electrodes of lithium batteries. The physical mechanism for the effect of modulus variation on the Li-ion diffusion and corresponding biaxial stress is well elucidated. Moreover, the analytic solutions of maximum stress in both active layer and collector are respectively derived. It has been found that the modulus stiffening gives rise to the additional stress gradient and enhances Li-ion diffusion, therefore to increase the biaxial stress in the plate electrode. In contrast, modulus softening makes the stress assisted diffusion less significant and the corresponding stresses are reduced. These coupled effects are more significant during potentiostatic charging and galvanostatic charging with high charging rates. Moreover, the maximum stress in the active layer is independent of charging process, but depends upon the elastic modulus variation due to Li-ion insertion. Finally, with increasing thickness ratio between collector and active material, the impacts of concentration dependent modulus on the Li-ion diffusion in active layer decreases, whereas this effect on maximum stress in the current collector increases.

1. Introduction

Diffusion of lithium ions in electrode is one of the most important processes in the charging and discharging of Li-ion batteries. Stress induced by the diffusion may lead to mechanical degradation such as fracture or fragmentation of the electrode material, and therefore limit the durability and performance of batteries. It is important to describe the Li-ion diffusion and diffusion induced stresses (DISs) accurately.

Diffusion of lithium ions is very complicated because it is affected by many factors, such as concentration gradient [1–4], saturation effects [5], and even the stress induced by the diffusion itself [6–8]. Among the factors stress was found to play important roles. For example, Zhang et al. found that stress gradient significantly enhanced Li-ion diffusion in electrode particles [6]. Gao and Zhou further indicated that stress gradient played much more significant role in the Li-ion diffusions than other factors seen in cathode lattice [7]. Song et al. proposed that the in-plane stress in a bilayer electrode could either facilitate Li-ion diffusion or retard the diffusion depending on the electrode curvatures and bending stresses [8].

The above conclusions are drawn under the assumption that the elastic modulus of active material does not vary during lithiation.

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However, it has been reported that the elastic modulus of graphite tripled in lithiation with the final product of LiC_6 [9], and the modulus of Si decreased from 170 GPa of crystalline Si to 35.4 GPa of $Li_{22}Si_5$ [10–13]. Taking such a considerable variation of elastic modulus into account, it is wondered how the stress and stress assisted Li-ion diffusion would be impacted.

Until recently, very few publications have addressed this problem. Deshpande et al. [14] investigated the effect of concentration-dependent elastic modulus on the DISs in a cylindrical electrode particle and reported that moderate modulus softening by lithiation can reduce the fracture tendency at the center of the electrode. However, it was assumed that the Li-ion diffusion is unaffected by stress, and the influence of varying modulus on Li-ion diffusion were not identified. Yang et al. [13] took into account the concentration-dependent elastic modulus for a Cu–Si bilayer electrode and concluded the concentration-dependent modulus is important for stress field but not so important for the Li-ion diffusion process. However, it is still not clear that the mechanism how concentration-dependent modulus impacts the Li-ion diffusion and corresponding DISs.

This work aims to study the impacts of concentration-dependent elastic modulus on the Li-ion diffusion and corresponding DISs in a symmetric layered electrode. An analytic model is established. With the active materials chosen as graphite and Si which are the representative lithiation hardening and softening material, respectively, evolutions of Li-ion concentration and biaxial stresses along plate thickness are examined, with which the physical mechanism for the coupled effect of stress assisted diffusion and concentration-dependent elastic modulus is well elucidated. Moreover, the intensity effect of concentration-dependent elastic modulus was studied systematically under different charging conditions and thickness ratios between current collector and active layer.

2. Methodology

Consider a layered electrode in which two active layers with equal thickness h are symmetrically bonded to a current collector with thickness h_c as shown in Fig. 1. Let the thickness direction be aligned with the z-axis and the in-plane of electrode with x- and y-axes. Li-ions are inserted through the two side surfaces and blocked by the current collector. The electrode does not bend during charging due to symmetry. Following the analogy between thermal stresses and diffusion induced stresses [5,6,8,13–18], the two non-zero in-plane biaxial stresses in the active layer are given by

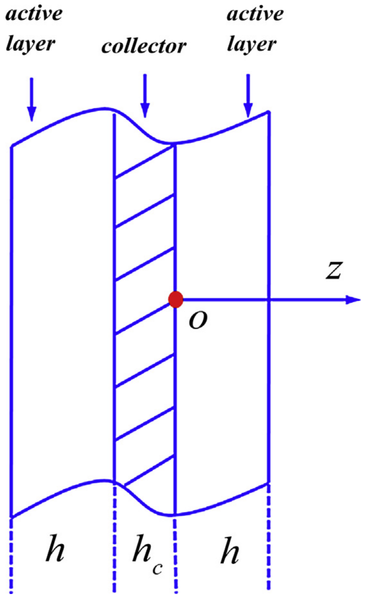

Fig. 1. Configuration of a symmetric multilayer electrode.

$$\sigma_x = \sigma_y = \frac{E}{1-\nu}(\varepsilon_0 - \Omega c/3) \tag{1a}$$

where ε_0 is the in-plane strain, Ω is the partial molar volume of solute, c is the molar Li-ion concentration, E is the biaxial modulus, and ν is the Poisson's ratio.

As Cu is inactive to Li-ion alloying, the in-plane biaxial stresses in current collector can be expressed by simplifying Eq. (1a) as follows,

$$\sigma_x = \sigma_y = \frac{E_c}{1-\nu}\varepsilon_0 \tag{1b}$$

where E_c is the biaxial modulus of current collector.

Here, we focus on a free-standing electrode. The in-plane strain ε_0 can be obtained from the mechanically free boundary condition

$$\int_{-(h+h_c)}^{h} \sigma_x \mathrm{d}z = 0 \tag{2}$$

Substituting Eq. (1) into Eq. (2), we have

$$\varepsilon_0 = \frac{2}{3}\frac{\Omega \int_0^h Ec\mathrm{d}z}{E_c h_c + 2\int_0^h E\mathrm{d}z} \tag{3}$$

Substituting Eq. (3) back to Eqs. (1a) and (1b), the biaxial stresses in active layer and current collector can be obtained respectively, when the distribution of Li-ion concentration along layer thickness is determined. It can be found that the stress in the active layer changes with Li-ion concentration, while the stress in the current collector would not vary along the thickness direction as the in-plane strain of the plate electrode is coordinate independent. It is noticed that if the modulus of active layer is constant, the stress in the current collector would be no difference for the Li-ion diffusion, whether it is described by Fick's law or stress assisted diffusion theory. This is because the in-plane strain expressed by Eq. (3) is function of the charge process only if the active layer modulus is invariant. The biaxial stress in the current collector is thus irrelevant with the Li-ion concentration distribution.

In the presence of internal stresses and concentration-dependent elastic modulus, the chemo-mechanical potential takes the following form [13,19]:

$$\mu = \mu_0 + RT\ln c - \Omega\sigma_h - \sigma_h^2 \frac{\partial}{\partial c}\left(\frac{1-\nu}{E}\right) \tag{4}$$

where μ_0 is an invariant reference potential, $R = 8.314472$ J K^{-1} mol^{-1} is the universal gas constant, T is the temperature and $\sigma_h = 2\sigma_x/3$ is the hydrostatic stress. The second term on the right side of Eq. (4) represents the contribution of configurational entropy. Haftbaradaran et al. [5] believed that this term is also impacted by the saturation effect at relatively high Li-ion concentration, and Yang et al. [13] further assumed the saturation affected the Li-ion diffusion flux in the same way. However, more experimental data are required to affirm the mechanism of the saturation effect. Since we focus on the effects of concentration-