Electrochimica Acta 185 (2015) 28–33

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Effects of external mechanical loading on stress generation during lithiation in Li-ion battery electrodes

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A R T I C L E I N F O

Article history:
Received 19 August 2015
Received in revised form 9 October 2015
Accepted 19 October 2015
Available online 30 October 2015

Keywords:
Lithium-ion battery
Diffusion-induced stress
External mechanical loading
Thin plate electrode

A B S T R A C T

Li-ion batteries are ineluctably subjected to external mechanical loading or stress gradient. Such stress can be induced in battery electrode during fabrication and under normal operation. In this paper, we develop a model for stresses generated during lithiation in the thin plate electrode considering the effects of external mechanical loading. It is found that diffusion-induced stresses are asymmetrically distributed through the thickness of plate due to the coupling effects of asymmetrically distributed external mechanical stress. At the very early stage during Li-ions insertion, the effects of the external mechanical loading is quite limited and unobvious. With the diffusion time increasing, the external mechanical loading exerts a significant influence on the evolution of stresses generated in the electrode. External compressed electrode is inclined to increase the value of stresses generated during lithiation, while external tensed electrode tends to decrease the value of stresses, and as the diffusion time increases, the effects of the external mechanical loading on the stresses generated during lithiation become more obvious.

1. Introduction

Li-ion batteries have been widely used in mini-type electric instruments such as cell phones and other small portable electronic devices due to their high specific capacity, light weight, and no memory effects. However, their further applications such as in the fields of electromotive vehicle, large-scale energy storage and aerospace power supply are limited by the poor cycle of life and the capacity loss of themselves. The main reason is due to the deformation and fracture of the electrode caused by the stress generated in electrodes during cycling [1–4], which can result in electrical disconnects that render electrode active materials incapable of storing Li-ions. One of the critical challenges in Li-ion battery studies is the internal stress field distribution produced in the process of charging and discharging.

Much work has been devoted to studying the stresses resulting from cycling of Li-ion batteries due to the intercalation and deintercalation of Li-ions [5–11], however, studies for effects of external mechanical loading on stress generation during lithiation in Li-ion battery electrodes are less. Actually, Li-ion batteries are ineluctably subjected to external mechanical loading or stress gradient during standard usage or storage. Such stress can arise during fabrication of battery materials, which usually involves compression of the electrode to control its porosity [12–14]. Also, such stress can be induced in electrode materials under normal operation, such as batteries operating in high pressure environments, electric/hybrid vehicles or flexible applications [15]. In many cases, the influence of external stresses on the diffusion process and the stress generation during lithiation in Li-ion battery electrodes is so significant that it cannot be neglected. Some researchers have studied the effects of electrode compression on capacity and efficiency of various electrode materials. Novak et al. [16] and Gnanaraj et al. [17] found both the capacity and first cycle efficiency of batteries had a decrease when subjected to high levels of compression. They explained that it was caused by electrode particle fracture for the largest pressures as well as transport limitations within the liquid path. By studying low-loading electrodes prepared with a natural graphite from Superior Graphite and compressed at a range of moderate pressures, Shim et al. found both the reversible capacity and irreversible capacity loss (ICL) had a decrease with increases in pressure [18]. They concluded that the decreased reversible capacity was due to increased stresses generated within the graphite electrode, which also slowed down in Li-ions diffusion process [19]. However, much of these work were conducted using electrochemical characterization. Theoretical studies for the effects of external mechanical loading on stress generation during lithiation in electrodes which are quite necessary for Li-ion batteries have been rare.

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http://dx.doi.org/10.1016/j.electacta.2015.10.097
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In this work, we develop a model for stress generation during lithiation in Li-ion battery electrodes with planar geometries coupled with the effects of external mechanical loading. To begin with, two basic approximations for material properties are introduced as follows [9,10]. Isotropic elasticity analysis of infinitesimal deformation is carried out, and large deformation related to plasticity is out of the scope of this research [20]. Mechanical properties and the diffusion coefficient are independent of Li-ion concentration, which means that Young's modulus, Poisson's ratio and the diffusion coefficient are constants. Yang et al. [21] studied the effects of composition-dependent modulus, finite concentration and boundary constraint on Li-ion diffusion and stresses in a bilayer Cu-coated Si nano-anode. This is an important work to show that mechanical properties of electrode materials will change and have an effect on diffusion-induced stresses during the lithiation/delithiation process. Since we focus on studying the effects of external mechanical loading, changes in material properties during the lithiation/delithiation process still need to be further considered by establishing more sophisticated model.

2. Basic Theory

2.1. Diffusion equation

We model the insertion and extraction of Li-ions as a diffusion process. The species flux can be defined as [22]

$$J = -Mc\nabla\mu \tag{1}$$

where M is the mobility of Li-ions, c is the Li-ion concentration and μ is the chemical potential, which is given by

$$\mu = \mu_0 + RT\ln c - \Omega\sigma_h \tag{2}$$

where $\mu_0$is the initial chemical potential and is assumed to be a constant. R is a gas constant, T is absolute temperature, Ω is the partial molar volume of the Li-ion, σ_h is the hydrostatic stress. Since atomic diffusion in solids is much slower than elastic deformation, mechanical equilibrium is established much faster than that of diffusion. Mechanical equilibrium is, therefore, treated as a static equilibrium problem, thus the linear elasticity theory is applicable for the coupling of diffusion-induced stresses and external stresses. The hydrostatic stress σ_h can be expressed as

$$\sigma_h = \frac{1}{3}\sum_{i=x,y,z}(\sigma_{di} + \sigma_{ei}) \tag{3}$$

where σ_{di} is the diffusion-induced stress due to the concentration gradient and σ_{ei} denotes the external mechanical loading induced stress, respectively.

Substituting Eq. (2) into Eq. (1), the species flux can be expressed as

$$J = -MRT(1 - \frac{\Omega c\partial\sigma_h}{RT\ \partial c})\nabla c = -D_{eff}\nabla c \tag{4}$$

where D_{eff} is the effective diffusion coefficient in a stressed isotropic solid. Substituting Eq. (3) into Eq. (4),D_{eff} can be given by

$$D_{eff} = D(1 - \frac{\Omega c\partial\sigma_h}{RT\ \partial c}) = D\left\{1 - \frac{\Omega c}{3RT}\frac{\partial\left[\sum\limits_{i=x,y,z}(\sigma_{di} + \sigma_{ei})\right]}{\partial c}\right\} \tag{5}$$

where $D = MRT$is the diffusion coefficient in a stress-free isotropic solid. Combining Eq. (4) with the mass conservation equation $\frac{\partial c}{\partial t} + \nabla\cdot J = 0$, we obtain the diffusion equation as follows

$$\frac{\partial c}{\partial t} = D\left\{\nabla^2 c - \frac{\Omega c}{3RT}\nabla^2\left[\sum_{i=x,y,z}(\sigma_{di} + \sigma_{ei})\right] - \frac{\Omega\nabla c}{3RT}\nabla\left[\sum_{i=x,y,z}(\sigma_{di} + \sigma_{ei})\right]\right\} \tag{6}$$

2.2. Diffusion-induced stresses

Consider an electrode plate of thickness l subjected to a constant uniform charging current density on both of its side faces [2,23], as shown in Fig. 1. The electrode plate is considered to be an isotropic linear elastic solid and is mainly composed of the active particles. The effect of the electrolyte is neglected though it can be included using a more sophisticated model such as the work conducted by Zhang et al. [24] and Renganathan et al. [25], and the aim of our work is to study the effects of external mechanical loading. Analogous to thermal stresses [26], for a given concentration profile, the nonzero diffusion-induced stress components due to the insertion of solute atoms into host are only $\sigma_{dy}$and σ_{dz}, which are two equal transverse stresses and can be given by

$$\begin{aligned}\sigma_{dy} &= \sigma_{dz} \\ &= \frac{E\Omega}{3(1-\nu)}(\frac{1}{l}\int_0^l cdx - c) + \frac{2(2x-l)}{l^3(1-\nu)}\int_0^l E\Omega c(x - \frac{l}{2})dx\end{aligned} \tag{7}$$

where E and ν are Young's modulus and Poisson's ratio, respectively.

In general, the thin electrode plate is subjected to a unidirectional gradient stress field due to the mechanical loading combination of bending M_z and tension F_y. As illustrated in Fig. 1, the unidirectional gradient stress field can be expressed as

$$\sigma_{ex} = \sigma_{ez} = 0, \sigma_{ey} = p_0 x + a_0 \tag{8}$$

where p_0 denotes the stress gradient due to mechanical bending and a_0 is the tensile stress. It should be noted that Fig. 1 only shows the case of$p_0 > 0$, in fact, $p_0$can be negative and zero and are also studied.

Substituting the diffusion-induced stress Eq. (7) and external loading induced stress Eq. (8) into Eq. (6) yields

$$\frac{\partial c}{\partial t} = D\left\{(1 + \theta c)\nabla^2 c + \theta(\nabla c)^2 - \frac{12\theta}{l^3}\nabla c\int_0^l (x - \frac{l}{2})cdx - \frac{\Omega p_0}{3RT}\nabla c\right\} \tag{9}$$

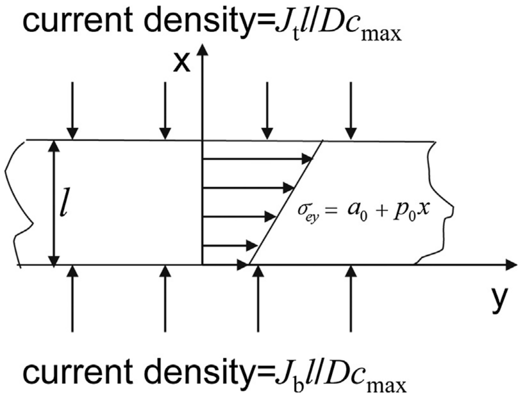

Fig. 1. Sketch of a plate electrode under galvanostatic charging, namely a uniform current density on surfaces.