Cooperative surface effect and dislocation effect in lithium ion battery electrode

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ABSTRACT

This paper is concerned with the coupled effect of surface and dislocation mechanisms on diffusion induced stress in spherical nanoparticle electrode for improving lithium ion battery life undergoing potentiostatic solute insertion and extraction. The coupled effect and the size effect on radial and tangential stresses and strain energy in spherical electrode are evaluated. The results show that the coupled effect weakens tensile stress and even makes tensile stress to become compressive stress, which differs from the classical solutions. In addition, lithium ion battery materials with higher Poisson's ratio and larger positive surface modulus as well as more dislocation density enhance compressive stress. This coupled effect induced stress suppressing crack nucleation and propagation offers a useful way of mitigating internal damage during battery cycling. The difference in strain energy reveals that dominant resistance to crack propagation is due to dislocation mechanism rather than due to surface mechanism. These results also show that it is possible to control and tune surface modulus and dislocation density in conjunction with the methods of nanotechnology to obtain a longer service life of battery.

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1. Introduction

Energy is the fundamental challenge to sustain the future energy needs of humans [1–3]. Due to the rapid development and dissemination of modern technologies on a global scale, various problems have arisen, for instance global warming and energy shortages of fossil fuel and environmental pollution. In order to solve a series of problems, there is an urgent appeal for using renewable energy sources (solar and wind) and providing highly effective storage as well as supplying of mobile energy for meeting the application of a wide variety of electronics and vehicles. In the high energy storage area, electrochemical energy storage based on migration of electrons to achieve the transformation of energy between chemical energy and electrical energy has flourished more than two centuries. Despite being capable electrochemical devices by electrochemical capacitors and fuel cells, lithium ion batteries (LIBs) have far outmatched them in the light of superior rate capability, high energy density, well cycle performance and wide commercial application [1–5]. Thus, LIBs shoulder to meet the energy demand of human society.

LIBs show the subject of rapidly growing research efforts due to their outstanding physical properties [1–3], and now have developed leaps and bounds on the verge of the large scale usage in automotive and mobile electronic devices such as electric vehicles (EV/HEV/PHEVs), notebooks and smart phones [6–8]. During LIB charging, lithium ion (Li-ion) by intercalation reaction is firstly extracted from a negative electrode, and then diffuses through the electrolyte towards a positive electrode. While during LIB discharging, the electrochemical process of the respective electrodes by extraction and intercalation goes by contraries [9–12]. In recent years, many factors such as plastic deformation and concentration gradient during charging and discharging process can strongly affect the distribution of diffusion induced stress (DIS) [13–15]. For example, three dimensional (3D) simulations of ellipsoidal particles under galvanostatic Li-ion intercalation was studied by Zhang et al. [16], who show smaller sizes and larger aspect ratios reducing DIS. Cheng and Verbrugge [17] indicated the surface mechanism with surface modulus and surface tension relieving DIS in nanoparticles. Ye et al. [18] observed that Li-ion concentration gradient fluctuates dynamically due to temperature. They found that Li-ion concentration gradient decreases with the increasing temperature using electrothermal modeling and experiment. Deshpande et al. [19] developed the effects of concentration and the dependent elastic modulus on DIS in nanowire electrode structures, and showed DIS causing the nucleation and growth of cracks in detail. Han et al. [20] demonstrated the grain boundary effect on Li-ion effective diffusivity, and also considered this effect on DIS during LIB charging. He et al. [21] reported the impacts of concentration dependent elastic modulus and corresponding DIS in a symmetric layered electrode, and reported the impacts of concentration dependent modulus on the Li-ion diffusion as active layer decreases,

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Nomenclature

r, θ, ψ	spherical coordinates
ρ	dislocation density (m^{-2})
b	Burgers vector (m)
β	solute lattice contraction coefficient
Ω	partial molar volume of the solute (mol m^{-3})
σ_θ^s	surface stress (N m^{-1})
ε_θ^s	surface strain
λ^s, μ^s	surface Lamé constants (N m^{-1})
τ^s	deformation-independent surface tension (J m^{-2})
k^s	surface modulus (N m^{-1})
$\triangle P$	Laplace pressure and surface energy (N m^{-2})
Γ	surface energy per unit area (J m^{-2})
Ω	partial molar volume of the solute (mol m^{-3})
R	radius of the spherical electrode (m)
v	Poisson's ratio
E	Young's modulus (N m^{-2})
M	Taylor orientation factor
α	empirical constant
μ	shear modulus
u	radial displacement (m)
σ_r	radial stress (N m^{-2})
σ_θ	tangential stress (N m^{-2})
σ_τ	dislocation induced stress (N m^{-2})
ε_r	radial strain
ε_θ	tangential strain
$C(r,t)$	solute concentration at radius r at time t (mol m^{-3})
C_0	initial solute concentration (mol m^{-3})
C_R	solute concentration in the radius R (mol m^{-3})
D	diffusion coefficient of the solute ($m^2 s^{-1}$)
t	time (s)
ϕ	dimensionless radius
φ	dimensionless time
ξ_r	dimensionless radial stress
ξ_θ	dimensionless tangential stress
ξ_τ	dimensionless dislocation induced stress
e	strain energy density (J m^{-3})
W^*	dimensionless strain energy
E_{total}	total elastic energy (J)
E_{bulk}	strain energy due to bulk deformation (J)
$E_{surface}$	strain energy due to surface deformation (J)
$E_{dislocation}$	strain energy due to dislocation (J)

whereas this effect on the maximum stress increases with increasing thickness ratio the collection to active material. Recently, Wei et al. [22] took into account the dislocation mechanics on DIS in a spherical particle electrode. They showed that the edge dislocations by solute diffusion can relieve the DIS. More recently, Li et al. [23] pointed out that the solute diffusion induced dislocation can suppress the crack nucleation and propagation under potentiostatic and galvanostatic solute insertion and extraction in a cylindrical electrode.

In the above mentioned works, researchers have separately studied the effect of DIS affected by various influence factors based on experimental research, computer simulations and theoretical models of physical properties of LIBs. However, few works have specifically considered the coupled effect undergoing Li-ion diffusion. Hence, understanding the stability of LIB in the cycling process is of great scientific and technological interest and significant economic impact. The main aim of this study is to build a theoretical model to study the combined effects of Li-ion DIS and dislocation induced stress as well as surface stress.

In the paper, we analyze a spherical electrolyte model to consider the coupled effect under LIB charging at potentiostatic operation, and calculate the stress fields and strain energy for LIB stability. In addition,

surface stress and dislocation induced stress as well as strain energy (SE) are predicted to affect the magnitude and distribution of SE and DIS when size of spherical electrode is at the nanoscale. We provide a theoretical method for prolonging LIB life in spherical nanoparticle electrode by taking into account the coupled effect.

2. Analytical model

Consider a spherical negative electrode with diameters $2R$ in Fig. 1a, a simple structure of operating principle, in which cathode and anode are connected to a current collector from Fig. 1b. Graphite and silicon commonly form the negative electrode, on the other hand, a lithium compound ($LiFePO_4$, $LiMnO_2$, or $LiCoO_2$) is commonly constitutive of the positive electrode. All kinds of morphologies (thin films, nanoparticles and powder structured electrode), which increase higher electrical conductivity and mechanical bond using conductive additive and inactive binder, can be achieved based on their machining method. The positive and negative electrodes, spaced through liquid and solid electrolytes, react electrochemically to make Li-ion transport from cathode to anode during charging and backwards upon LIB discharging process in Fig. 1b.

Research and development of new electrode materials with improved electrochemical performance have always been a focus, and methods have been widely applied. With progress of knowledge of electrode materials it has been found that their surface structures are of great importance to help to improve the electrochemical performance of electrode materials [24]. According to the results of the recent research, a high density of mobile dislocation nucleation by solute diffusion can effectively reduce DIS [22,23]. Based on these theories, we design a spherical electrode structure by surface modification method as shown in Fig. 2, which in sit heat treatment can be used to produce a predefined dislocation density and keep the relation between dislocation density and solute concentration. According to the work of Prussin [25], the arbitrary radial infinitesimal spherical element with the surface layer thickness dr is shown in Fig. 2. The solute concentration of bulk is assumed $C(r, t)$ on the lower surface r of the diffusion layer, following the concentration on the upper surface $r + \Delta r$ then becomes $C(r, t) + (\partial C/\partial r)dr$. The diffusion induced dislocation density can be expressed as $\rho(r, t)$. Using the solute concentration gradient, the dislocation density $\rho(r, t)$ can be obtained [22,23,25]

$$\rho(r, t) = \frac{\beta}{b} \frac{\partial C(r, t)}{\partial r} \tag{1}$$

where b is Burgers vector, and β solute lattice contraction coefficient with partial molar volume $\Omega/3$. Thus, a structure of spherical electrode can suppress DIS, reduce the crack nucleation tendency, and improve the stability of electrode material.

The task now is to determine the stress field in the nanoscale spherical electrode for analyzing the structural stability under LIB charging at potentiostatic operation. Due to the large ratio of surface region to volume for nanoscale LIB electrode, the surface effect should be considered in studying the mechanical response of materials containing nanoparticles and nanoinclusions [26], which may introduce a considerable traction on the surface and interface. This is due to differences in the nature of the bonding between surface and interior atoms in a solid, and this difference results acting on a solid surface in equilibrium spacing referred to as the surface stress. Regardless of body force and based on the previous work [27–29], the surface constitutive relation on a nanospherical electrode can be described as follows

$$\sigma_\theta^s = \tau^s + 2(\mu^s + \lambda^s)\varepsilon_\theta^s = \tau^s + k^s \varepsilon_\theta^s \tag{2}$$

where σ_θ^s and ε_θ^s denote surface stress and strain component, λ^s and μ^s are surface Lamé constants, and τ^s is deformation-independent surface tension.