



Diffusion-induced stress and strain energy affected by dislocation mechanisms in a cylindrical nanoanode



Xiangdong Li^{a,b}, Qihong Fang^{a,b}, Jia Li^{a,b}, Hong Wu^c, Youwen Liu^{a,b,*}, Pihua Wen^d

^a State Key Laboratory of Advanced Design and Manufacturing for Vehicle Body, Hunan University, Changsha, Hunan Province 410082, PR China

^b College of Mechanical and Vehicle Engineering, Hunan University, Changsha, Hunan Province 410082, PR China

^c State Key Laboratory for Powder Metallurgy, Central South University, Changsha, Hunan Province 410083, PR China

^d School of Engineering and Material Sciences, Queen Mary, University of London, London E14NS, UK

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ABSTRACT

Based on diffusion kinetics and dislocation theory, this paper describes an analytical model to analyze the effects of mixed dislocation mechanisms on diffusion-induced stress (DIS) and total strain energy when Li-ions insert a cylindrical nanoanode. Electrochemical Biot number (EBN) coupled into diffusion kinetics is analogous to the Biot number in heat-transfer systems and can govern the whole progress of Li-ion diffusion. The results show that diffusion-induced tensile radial stress can be reduced by dislocation work hardening stress and converted to compressive stress near the electrode surface. The presence of dislocations in the diffused electrode reveals that dislocations can be generated by DIS and in turn partially relieve the radial stress. Under small EBN charging, the degree of dislocation work hardening stress relieving the radial stress is obvious and meanwhile the influence of dislocation strain energy upon total strain energy is more significant. To predict the nucleation and propagation of cracks, it is more necessary to consider dislocation strain energy under small EBN control. These quantitative results also indicate that both EBN and dislocation density can be possibly controlled and coordinated based on nanotechnology so as to prolong the cycle life of batteries.

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1. Introduction

Ever since 1991, when Sony Company launched lithium ion batteries (LIBs) for the first time, the related industries have been developing rapidly. As a significant secondary battery system, LIBs possess much higher energy density, comparatively smaller cubage, quicker charging or discharging, longer span for repetitive use and lower production costs [1–5]. Furthermore, LIBs enjoy tremendous popularity due to their successful applications in automotive and portable electronic devices such as electric vehicles, medical instruments, smart phones, laptops and digital cameras [6–9]. In addition, LIBs are also applied to wind power and solar energy sources gradually [10]. To meet the demands of the various types of electric vehicles and the associated performance requirements, electrode materials with high theoretical storage capacity and safety, such as Si, Sn, Ge, Mn and Al, have been reported widely [11]. The electrodes with the structure of nanoparticle, nanowire and nanoporous material also have been taken into account as promising materials due to their shorter transport pathways, higher specific surface area and larger spaces to accommodate DIS [12–15]. However,

the huge volume change percent by up to about 400% can be caused by the transport of Li-ions into Si active material and this may result in irreversible capacity loss [9]. It is obvious that the evolution of DIS is the major problem for such a volume expansion in electrode. Conceivably, the mechanical degradation induced by fracture and decrepitation in electrode becomes one of the key factors in limiting the stability and durability for the next-generation LIBs [16]. For the sake of preventing electrode degradation, the method of reducing the electrode size is an effective existing strategy.

During insertion/extraction of Li-ions into/from electrode, multi-scale mechanical damages such as microstructure damage in active particles and adhesive damage at the interface of active layer and current collector in porous particles come into being due to the influences of various factors induced by electrochemical reactions, phase change and DIS [17,18]. In recent years, a variety of electrodes with some factors affecting the distribution of DIS such as spherical nanoparticles, nanowires, nanofilms and porous materials have been studied. Prussin [19] developed a mathematical model about DIS by analogy to thermal stress in a thin silicon wafer. The analytical solutions to DIS for spherical, cylindrical and thin plate electrodes were derived by Li [20]. Gao et al. [21] showed that stress can contribute to the Li-ion diffusion based on the research of nanowire and tends to make Li-ions flow from the high elastic energy zone to the low zone. Cheng et al. [22] studied the effect of surface mechanisms on DIS in spherical nanoparticles, with the suggestion

* Corresponding author at: College of Mechanical and Vehicle Engineering, Hunan University, Changsha 410082, PR China. Tel.: +86 731 86892189; fax: +86 731 88822330.

E-mail address: liuyouwen8294@sina.com (Y. Liu).

that the surface stress can relieve DIS. Cheng et al. [23] put forward the criteria for avoiding crack initiation in spherical particles by using a combination of interfacial electrochemical reactions and diffusion kinetics. Cui et al. [24] investigated the process of phase change for Si electrode during lithiation and showed that the movement of phase interface is determined by the ratio of boundary electrochemical reaction rate and solid phase diffusion rate. According to the density functional theory, Qi et al. [25] suggested that the elastic modulus of graphite increases from 10 GPa (pure graphite) to 108 GPa (LiC₆) during lithiation. This huge change of the elastic modulus is bound to affect the distribution of DIS and Li-ion diffusion. The effects of concentration-dependent elastic modulus on Li-ion diffusion and DIS in layered electrodes were studied by He et al. [26]. They concluded that the modulus stiffening leads to additional stress gradient and enhances Li-ion diffusion while the less significant the stress-assisted diffusion in a lithiation softening material. Song et al. [27] pointed out that stress-assisted diffusion is only determined by the properties of the active material in a symmetric plate electrode.

The above mentioned literatures concerned with DIS are generally based on the operation of galvanostatic and potentiostatic charging or discharging, while little literatures lay emphasis on the evolution of DIS under charging or discharging with various solute diffusion capacities. A variety of factors affecting DIS are considered in many reports, however few reports consider the effects of the mixed dislocation mechanisms on DIS and strain energy. Recently, Huang et al. [28] observed a high density of mobile dislocations in a single SnO₂ nanowire electrode during the electrochemical lithiation. The lithiation front, the phase boundary between the unlithiated phase and the lithiated phase, propagates along the radial direction of the cylindrical nanoparticle. A high density of dislocation zone, which is called “Medusa zone”, appears in an electrode during lithiation. Dislocations nucleate at the lithiation front and move into the interior of the electrode. Under the conditions of galvanostatic and potentiostatic charging, Wei et al. [29] and Li et al. [30] studied the effects of edge dislocation mechanisms on DIS within a spherical nanoparticle electrode and a cylindrical nanoparticle electrode, respectively. They suggested that dislocation-induced stress can reduce DIS. Chen et al. [31] analyzed DIS and the distribution of edge dislocations in a nanostructured thin film electrode under galvanostatic and potentiostatic charging.

Electrochemical reactions on the interface between electrolyte and electrode were studied by researchers mentioned above according to the sophisticated methods that consist of galvanostatic and potentiostatic operations. In fact, the electrode charging or discharging is an extremely complex electrochemical reaction process. However, galvanostatic or potentiostatic operation may not accurately reflect the multi-scale coupled problem that comprises elements of transport phenomena, electrochemical reaction characteristics and solid mechanics. This paper aims to establish a multi-scale coupled model to study the influences of mixed dislocation mechanisms upon DIS and total strain energy in a cylindrical nanoelectrode under a dynamic charging process approximately from galvanostatic to potentiostatic charging. By combining the characteristics of electrochemical reaction and DIS in a charging system wherein no interaction forces among intercalate species are significant, this paper focuses on controlling and tuning the appropriate EBN and dislocation density for improving battery life and avoiding fracture. It is expected that these theoretical results for the modified radial stress and total strain energy can provide a strategy to obtain a longer cycle life of LIBs.

2. Analysis model

2.1. Theoretic analysis for the mechanics

The stress expressions were derived by Timoshenko and Goodier in a thin plate affected by temperature [32]. Amounts of literatures reported the efforts on developing mathematical models about DIS similar to

thermal stress [33–36]. On the interface between electrode and electrolyte, electrochemical reactions are of the essence and thus result in stress field during Li-ion intercalation. DIS may give rise to mechanical degradation such as fracture and consequently limit the durability and performance of LIBs. Therefore, it is quite necessary to describe the evolution of DIS accurately.

A cylindrical nanoelectrode with radius R is schematically depicted in Fig. 1. The electrode is considered as an isotropic homogeneous linear elastic solid with small deformation, and the mechanical properties are independent of solute concentration. Due to the symmetry of the cylindrical electrode and solute diffusion process, only the radial stress component, the tangential stress component and the axial stress component exist in electrode. In the cylindrical coordinate system, the constitutive equations associated with solute concentration are described as follows

$$\varepsilon_r = \frac{1}{E} [\sigma_r - \nu(\sigma_\theta + \sigma_z)] + \frac{1}{3} \Omega C(r, t) \quad (1)$$

$$\varepsilon_\theta = \frac{1}{E} [\sigma_\theta - \nu(\sigma_r + \sigma_z)] + \frac{1}{3} \Omega C(r, t) \quad (2)$$

$$\varepsilon_z = \frac{1}{E} [\sigma_z - \nu(\sigma_r + \sigma_\theta)] + \frac{1}{3} \Omega C(r, t) \quad (3)$$

where ε_r , ε_θ , ε_z and σ_r , σ_θ , σ_z are the strain and stress components along the radial, tangential and axial directions, respectively. E is the Young's modulus, ν is the Poisson's ratio, Ω is the partial molar volume of Li-ions. $C(r, t)$ is the molar concentration of Li-ions.

Since elastic deformation is a much faster process when compared with atomic diffusion in solids, the mechanical equilibrium can be regarded as a quasi-static problem [37]. Therefore, the equation of quasi-static mechanical equilibrium regardless of the body force is given as

$$\frac{\partial \sigma_r}{\partial r} + \frac{\sigma_r - \sigma_\theta}{r} = 0 \quad (4)$$

For the analysis of infinitesimal deformation, the strain components correlated with the radial displacement u in the cylindrical coordinate system are written as [38]

$$\begin{cases} \varepsilon_r = \frac{du}{dr}, \\ \varepsilon_\theta = \frac{u}{r}. \end{cases} \quad (5)$$

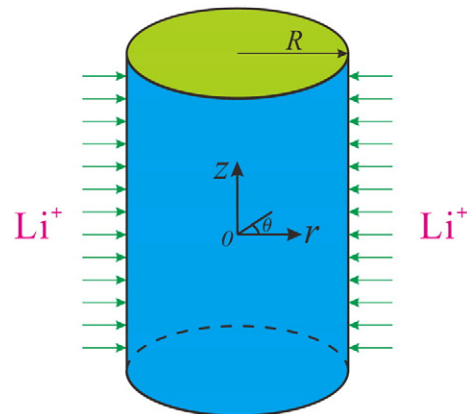


Fig. 1. Schematic illustration of Li-ion diffusion into a cylindrical electrode modeled as diffusion uniformly at the electrode surface.

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