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Softening by electrochemical reaction-induced dislocations in lithium-ion batteries

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ABSTRACT

Electrodes softening during lithium insertion may result in degeneration of their electrochemical performances. In this paper, based on a coupling multiple-slip crystal plasticity formulation with three (i.e., statistically-stored, geometrically-necessary and electrochemical reaction-induced) dislocation densities, a relationship is built up between hardness and the state of charge for electrodes in lithium-ion batteries, which can take into account the indentation size effect during charging and discharging progresses. It is shown that the relationship is helpful in monitoring the state of charge and providing new avenues for applications of high-performance rechargeable batteries.

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There has been a dramatic increase in the demand for high-performance and long-lasting rechargeable batteries, ranging from large-scale grid energy storage to portable electronics and consumer devices [1–3]. Unfortunately, the specific capacity and cycle life of existing lithium-ion batteries (LIBs) remain to be insufficient in their applications for new electrode materials with excellent charge capacities [4]. Although anode materials such as tin (Sn) [5], germanium (Ge) [6], and silicon (Si) [7], have much higher energy storage capacities (993, 992, 1384, and 4200 mA h g^{-1}, respectively) than that of carbon (372 mA h g^{-1}), a major issue is that they experience a large volume change in the first cycle, which may result in cracking, capacity fading and failure of electrodes [8,9]. A fundamental understanding of their structure instability during inserting Li-ions can provide strategies to mitigate mechanical failure.

As is known, diffusion-induced stress by a large volume change plays an important role in electrochemical properties of LIBs, which is believed as the main reason for the rapid capacity loss [10]. Based on the in situ technique and mechanical analysis, the material stability can be partially improved by introducing nanostructures such as nanowires, nanotubes, nanoporous films and nanoparticle [11,12]. Recently, the in situ transmission electron microscopy has been extensively used in exhibiting the lithiation process of electrodes, and furthermore, it has been confirmed that electrochemical reaction-induced dislocations

(EIDs) (see Fig. 1) are produced due to Li-ions diffusion under different states of charge (SOC) [13]. EIDs can be generated by solute diffusion in a material that is dislocation-free, and then relieved by diffusion-induced stress [14]. Hence, whether there is a relationship between EIDs and SOC that can characterize electrochemical performances of LIBs.

Generally, dislocations in crystals are separated into two different categories: geometrically-necessary dislocations (GNDs) that appear in a strain gradient fields due to geometrical constraints of the crystal lattice and statistically-stored dislocations (SSDs) that evolve from random trapping processes during plastic deformation [15]. Based on conventional theories of plasticity [16], indentation hardness is dependent on the density of SSDs. To explain the indentation size effect, Nix and Gao [17] introduced a characteristic length that is related to the indenter shape, shear modulus and intrinsic hardness in terms of the density of GNDs (see Fig. 1c) [18]. In other models that coupled the evolution of dislocation densities of SSDs with GNDs, the effects of texture, geometrical softening and strain hardening were taken into account [19]. However, there is still lack of an integrated approach that can be applied to handle different interrelated dislocation densities in a unified framework and further to accurately predict the large inelastic strain in high-capacity electrodes.

In this paper, such a unified and physically-based model of electrochemical reaction is developed and implemented to investigate the mechanical behaviors of electrode aggregates under inelastic deformation. The model is based on a coupling multiple-slip crystal plasticity formulation, which pertains to three distinct dislocation densities (i.e., SSDs, GNDs and EIDs). As a case study, this model is used for characterizing

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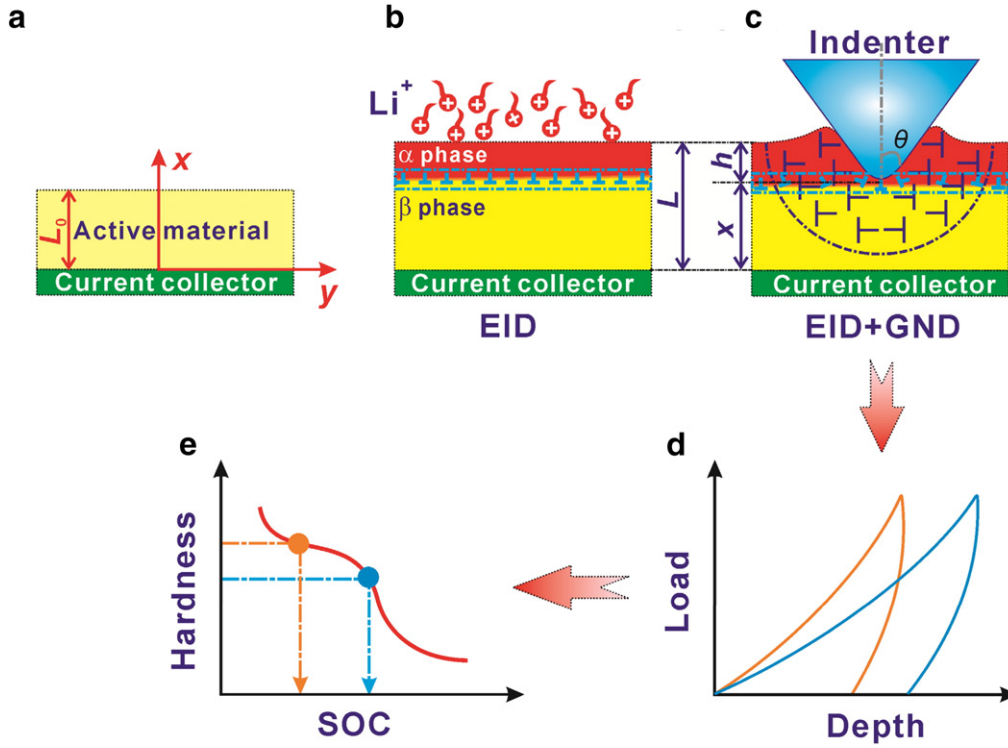E-mail addresses: zsma@xtu.edu.cn (Z. Ma), c.lu@curtin.edu.au (C. Lu).

Fig. 1. Extracting SOC from indentation hardness based on the dislocation theory. a, an active material with a thickness of L_0 on a rigid current collector before lithiation. b, EIDs appear with insertion of Li-ions because of concentration gradient. Then, the thickness of an active material becomes L due to Li-ion diffusion-induced deformation. c, indentation is conducted to consider EIDs and GNDs. d, the load-depth curves obtained from indentations under different SOCs. e, SOC can be extracted from indentation hardness.

SOC of electrodes in LIBs via indentation experiments, as illustrated in Figs. 1d and 1e.

Let us consider a film electrode with thickness L_0, where electrochemical reaction is suffering a flux of Li-ions into an active material, as illustrated in Fig. 1a. To study the microstructural evolution in such a multiphase material, it is necessary to consider both diffusion in each phase and migration of phase boundaries [20]. Here, our attention is mainly on the dislocation generation in a film electrode, and thus for simplicity, a series of one-dimensional step-like profiles of Li-ion distribution with a flexible sigmoid (or generalized logistic) function are assumed to mimic the movement of a sharp boundary between unlithiation and lithiation phases [21], that is

$$\frac{c(x,t)}{c_0} = \frac{1}{1 + exp\left[-\chi\left[\frac{x}{L} - \left(1 - \frac{kt}{L}\right)\right]\right]} \tag{1}$$

where $c(x,t)$ is the Li-ion concentration at position x and time t, c_0 is the concentration at a steady stage, and $L = L_0(1 + \eta SOC)$ is thickness of the active material under a given SOC with an expansion coefficient η ($\eta = 2.7$ and 2.0 for Si [22] and Sn [23]). Here, two dimensionless parameters can be defined as

$$\chi = \frac{D}{kL} \tag{2}$$

where χ is the relative rate of diffusion and reaction and indicates the sharpness of Li concentration jumping from 0 to 1. If χ is large, the Li diffusion is fast and lithiation is limited by reaction [24]. Let D denote the diffusion coefficient of Li-ions in electrodes and k is the velocity of reaction front.

Fig. 2a shows the Li-ion distribution in a film electrode at various diffusion times with $\chi = 100$. As expected, Li-ions gradually diffuse into

the active material under the driving force of concentration gradient. The bottom has the lowest concentration and finally reaches a maximum concentration c_0. Generally, lithiation involves two consequent processes: Li diffusion through the lithiated phase and chemical reaction at the two-phase boundary. Thus, Eq. (1) can represent either the lithiation that is rate-limited by reaction at the phase boundary or the Li diffusion in a steady state [8,25]. In terms of Li concentration, SOC is employed to evaluate the charging process of film electrodes, which is defined as

$$SOC = \frac{\int_0^L c(x,t)dx}{Lc_0} \tag{3}$$

Introducing the density (ρ_e) of EIDs into the dislocation theory, the shear strength τ can be calculated by

$$\tau = \alpha\mu b\sqrt{\rho_t} = \alpha\mu b\sqrt{\rho_s + \rho_g + \rho_e} \tag{4}$$

where ρ_t is the total dislocation density, ρ_s is the density of SSDs, ρ_g is the density of GNDs, μ is the shear modulus, α is an empirical constant, and b is the Burgers vector. The storage of SSDs is mainly from a random trapping process of mobile dislocations, which can be characterized by a vanishing net Burgers vector. In contrast, the storage of GNDs leads to a polarized dislocation density, resulting from the curvature of a crystal lattice under incompatible plastic strain. By exerting the solute concentration gradient, the density ρ_e^x of EIDs at position x due to Li-ions diffusion can be written as

$$\rho_e^x = \frac{\phi}{b}\frac{\partial c(x,t)}{\partial x} \tag{5}$$

where ϕ is a solute lattice contraction coefficient that is related to the partial molar volume of solute [14]. As seen in Fig. 2b, EIDs only exist at the electrochemical reaction interface between unlithiated and