



A model for crack initiation in the Li-ion battery electrodes



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ABSTRACT

The development of high energy density Lithium-ion batteries is of intense interest due to their application in the electric car and consumer electronics industry. The primary limiter in using high energy density battery electrodes is the cracking of the electrode material due to the severe strain caused by the charging–discharging cycles. In this paper, a linear perturbation model is used to describe the evolution of the electrode surface under stress. The driving force for the surface undulation formation is the reduction in the electrode strain energy. The kinetics of mass transport is described by the surface and volume diffusion. The model predicts that the Si electrode will develop surface undulations of the order of sub-1 μm length scale on the electrode surface, showing a reasonable agreement with experimental results reported in literature. Such surface undulations roughen the anode surface and can form notches that can act as crack initiation sites. It is also shown that this model is applicable when the temperature of the system is not constant and the system is not isolated. The limitations of the model are also discussed.

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1. Introduction

The desire to achieve the highest possible time-between-charging for the electronic devices as well as the desire to reduce the fossil fuel usage is driving the development of high energy density Li-ion batteries [1]. A great deal of current research on the Li-ion batteries has concentrated on identifying novel electrode and electrolyte materials. Amongst the various material candidates for the Li-ion batteries, silicon (Si) is of particular interest as an anode due to its very high theoretical charge capacity (4200 mAh/g) [2] along with its abundance in earth's crust. Although the capacity of Si electrode is about 10 times higher than the commercially used material graphite, Si undergoes large (~350 to 400%) volume expansion during charging cycle resulting in electrode pulverization and early capacity fade [3]. Several nano-geometries have been explored to overcome this problem in the form of nano-rods on a plane [4,5]; Si–C core shell nanostructures [6,7], Si nanotubes [8], Si nano films with [9] or without [10–15] soft substrates, hollow nanospheres [16], and coated nano-rods [17,18]. Although the nano-structured electrodes help accommodate the strain and prevent the build-up of stresses, the total electrode volume available in these cases, however, is limited primarily due to the low total volume of the nanostructures.

The major obstacle in using high energy density electrode materials (Si or otherwise) is the cracking and the resulting pulverization of the electrode due to high deformation during lithiation. This process

involves crack initiation at the electrode surface or interior and its growth under the mechanical forces [3,19–21]. Several studies have been carried out to find a critical crack size and its growth in lithiated Si. Suo and co-workers [22–25] studied combined diffusion and the resulting stress accumulation at high and low charging rates. They also modeled the inelastic deformation in Si considering diffusion, elastic–plastic deformation, and fracture. Chiang and co-workers [26,27] have created an electrochemical shock map that shows the regime of failure depending upon the charging rate, particle size, and the inherent fracture toughness of the material. They also showed that minimizing the principal shear strain, rather than minimizing net volume change as previously suggested, is an important new design criterion for crystal chemical engineering of electrode materials for mechanical reliability. Medium range order in disordered Si is an important consideration for crack propagation in the electrodes [28–30]. Fluctuation electron microscopy experiments along with simulations have established a medium range orientational order in amorphous silicon [28,29]. This medium range order, as described by paracrystalline models, consists of topologically crystalline grains which are strongly strained and a disordered matrix between them [28]. Verbrugge and co-workers [31–33] have proposed a tensile stress-based criteria for the growth of cracks within a spherical insertion electrode. They considered both interfacial (electrochemical) kinetics and intercalate diffusion. Gao and co-workers [34,35] developed a cohesive model of crack nucleation in an initially crack-free strip electrode under galvanostatic intercalation and de-intercalation processes. They applied a cohesive zone model of crack nucleation in a cylindrical electrode under axisymmetric diffusion induced stresses. The cracks were assumed to exist at a certain

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periodicity. The above models provide an excellent picture of the *crack growth* in a battery electrode under lithiation stresses. The exact mechanisms of how the surface cracks evolve from surface features, however, have not been fully investigated.

Li et al. [3] have observed that a flat bulk Si anode surface develops a characteristic surface roughness at a length scale of $<1 \mu\text{m}$ upon lithiation. They observed that some surface cracks grow to form a fractal pattern at a higher length scale of tens of micrometers. Note that they observed that the Si surface roughness/undulations grow with time upon lithiation, although the amplitude and the dominant wavelengths were not quantitatively characterized. Such sub-micron surface features can potentially act as crack initiation sites. Similar to the bulk silicon, the nanostructured Si anodes are also shown to form surface undulations upon lithiation. Direct TEM observations of Si nano-rod anodes undergoing lithiation [36] show clear Si surface undulations at a wavelength of about 100–200 nm and an amplitude of about tens of nm (Fig. 3d in Ref. [36]).

In this communication, we develop a linear perturbation model to describe the formation and evolution of surface undulations in Li-ion battery electrode films under stress caused by Li intercalation. The formulation takes into account the fact that the Li-ion battery electrode is not an isolated system and that the temperature can change during lithiation. Additionally, no assumptions are made regarding pre-existing flaws on the surface. It is shown that the formulation follows the description of the rumpling problem in metallic thin films previously addressed by the author [37]. A competition between surface energy and strain energy is shown to be the driver for the mass transport. The kinetics of mass transport is described by surface and volume diffusion. The model predicts that the surface undulations with 0.2 to $1 \mu\text{m}$ wavelength grow at the highest rate and dominate the surface in a reasonable agreement with experimental results from literature [3,36]. These undulations can give rise to notches that can act as crack initiation sites. Implications of the model in terms of the microstructural evolution at or near the surface of the battery electrode are discussed. Finally, the limitations of the model are discussed in detail.

2. Model

Consider a battery electrode film of Si as shown in Fig. 1. Consider for the time being that the Si is polycrystalline (i.e. diffusion is isotropic) and that the usual chemical potentials are driving the Li inside the electrode during charging cycle. As the charging goes on, the Si film will go under compressive stress during lithiation. The high diffusivity of the Li material inside and on the surface of Si, however, can give rise to some surface rearrangements driven by the desire to lower the free energy. To describe the roughness formation, the surface of the electrode can be decomposed into infinitely many sinusoidal undulations. The assumption is that we analyze each wave independently and the resultant surface is linear superposition of the waves. A single surface perturbation of wavelength is $h(x, t) = a(t) \cos(\omega x)$, with $\omega = 2/\lambda$ (Fig. 1b). The actual surface profile can be described as, $\sum_k^\infty a_k \cos(\omega_k x)$.

For a semi-infinite body of unit depth under a remote stress (Fig. 1b), the strain energy density in the body per unit volume is $U(\epsilon_{ij})$. The internal energy of the system is comprised of the strain energy and surface energy, i.e.,

$$\epsilon = \int_V U(\epsilon_{ij}) dV + \int_S \gamma dS. \quad (1)$$

The system free energy is,

$$F = \epsilon - \int_V Ts(V) dV, \quad (2)$$

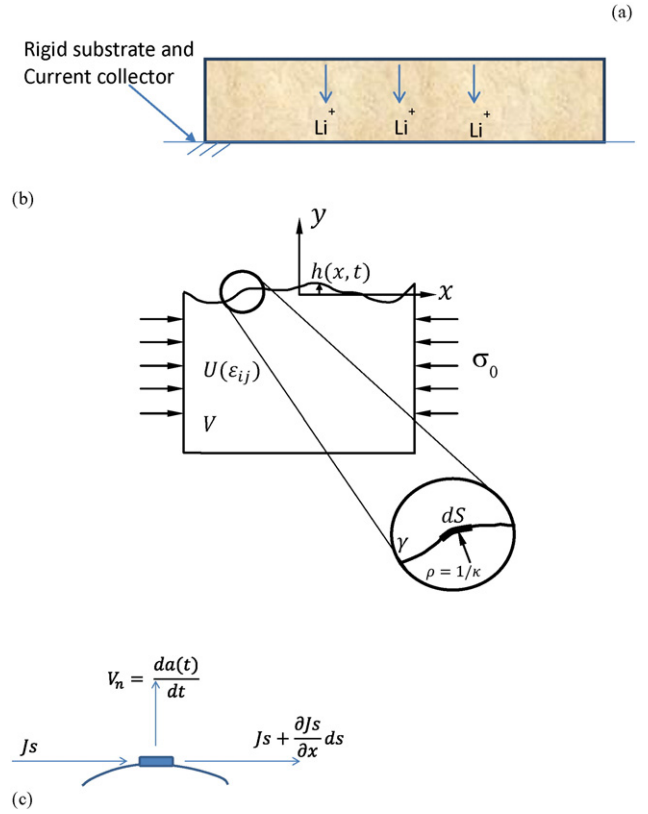


Fig. 1. (a) Li diffusion normal to the electrode surface driven by battery chemical potential, (b) surface of a battery film under compressive residual stresses, and (c) conservation of volume at the surface.

where ‘ $s(V)$ ’ is the local entropy and T is the total absolute temperature of the solid. From Eqs. (1) and (2),

$$F = \int_V U(\epsilon_{ij}) dV + \int_S \gamma dS - \int_V Ts(V) dV. \quad (3)$$

The time rate change of the free energy is,

$$\begin{aligned} \dot{F} = & \int_V \frac{\partial U(\epsilon_{ij})}{\partial t} dV + \int_V U(\epsilon_{ij}) \frac{\partial (dV)}{\partial t} + \int_S \frac{\partial \gamma}{\partial t} dS + \int_S \gamma \frac{\partial (dS)}{\partial t} \\ & - \int_V \frac{\partial T}{\partial t} s(V) dV - \int_V T \frac{\partial s(V)}{\partial t} dV - \int_V Ts(V) \frac{\partial (dV)}{\partial t}. \end{aligned} \quad (4)$$

In writing Eq. (4), it is assumed that the spatial gradients of U and T are negligible compared with their time variations. The spatial gradient of U can be ignored if the surface stress is uniform, while for a thin layer such as a battery electrode, the spatial gradient of T can be ignored if the heat conduction is fast enough to make the gradients insignificant. A simple derivation [38,39] shows that,

$$\int_S \gamma \frac{\partial (dS)}{\partial t} = - \int_S \kappa \gamma V_n dS. \quad (5)$$

Furthermore, for small perturbations of the surface, the strain energy change in the bulk is negligible compared to that on the surface. Hence,

$$\int_V U(\epsilon_{ij}) \frac{\partial (dV)}{\partial t} = \int_S U(\epsilon_{ij}) V_n dS. \quad (6)$$

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