Effects of electrode particle morphology on stress generation in silicon during lithium insertion

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ABSTRACT

We study the effects of particle morphology and size on stress generation during Li insertion into Si particles using a fully coupled diffusion-elasticity model implemented in a finite element formulation. The model includes electrochemical reaction kinetics through a Butler–Volmer equation, concentration-dependent material properties, and surface elasticity. Focusing on two idealized geometries (hollow spheres and cylinders), we simulate stresses during Li insertion in Si. These systems describe a wide variety of morphologies that have been fabricated and studied experimentally, including particles, nanowires, nanotubes, and porous solids. We find that stresses generated in solid particles during Li insertion decrease as particle radii decrease from μm-scale, but reach a minimum at about 150 nm. Surface stresses then begin to dominate the stress states as the particle size continues to decrease. The minimum occurs at larger radii for hollow particles. We also find that hollow particles experience lower stresses than solid ones, but our results suggest that there is not a significant difference in maximum stress magnitudes for spherical and cylindrical particles. Studying the influence of concentration-dependent elastic moduli we find that while they can significantly influence stress generation for potentiostatic insertion, their role is minimal when surface reaction kinetics are considered.

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1. Introduction

There is an increasing awareness that mechanical effects play significant roles in the performance and lifetime of rechargeable lithium ion batteries. Mechanical effects primarily arise from the deformation that occurs when Li ions are inserted into and extracted from active hosts in battery electrodes. Battery electrodes are typically heterogeneous materials consisting of an active material (∼80% by mass) held together by a binder (∼10% by mass) doped with a conductive additive (∼10% by mass). In addition to these composite electrodes that essentially consist of a random aggregate of active particles, micro and nanofabrication technologies are being widely used to fabricate ordered arrays of active materials for electrodes [1–4]. In the cathode, metal oxides are the active material of choice and in the anode carbonaceous materials are most commonly used. Electrochemical surface reactions generate a flux of Li ions that diffuse into the active particles, resulting in deformation of the particle. The associated volume changes can range from a few to a few hundred percent depending on the materials used. Volume changes can lead to cracking of the electrode and the

particles themselves, as well as debonding of the particles from the binder. This can result in electrical disconnects that render portions of the active material incapable of participating in Li storage which is manifested as capacity fade during cycling.

Today, at least three areas of research are actively pursued that are related to mechanical effects: (i) the development and use of new active materials, (ii) making particles in the nanometer scale, and (iii) making particles with different morphologies. These all impact the amount and type of deformation that can occur during Li insertion as well as the resulting stresses that can drive mechanical degradation. Although these research areas are not necessarily being pursued just to address mechanical phenomena, they all play an interesting role.

An especially exciting pursuit is the use of silicon as an active material for anodes because it exhibits the highest known capacity (>4000 mAh g^{-1} compared to ∼372 mAh g^{-1} for carbon) [5,6]. This high capacity comes with the challenge that Si expands about 300–400% [1,7] during Li insertion; at full saturation each Si atom accommodates 4.4 Li atoms [8,9]. The strain associated with Li insertion is typically non-uniform through a particle and as such results in stresses that can crack and degrade Si anodes [6]. Details of this stress development are not well understood, although recently it was shown that particle size can play a significant role on stresses during elastic deformation

[10], and that inelastic deformation can occur [11,12] which influences the resulting stresses and thus probably fracture.

Numerous recent studies have shown that Si anodes with nm-scale morphologies are more resistant to mechanical degradation during Li insertion and cycling, and that this resistance depends significantly on the particle morphology. Li et al. [2] showed that anodes with Si particles ranging from 50 to 100 nm have better cycling performance than those with particles in the μm range. Chan et al. [1] showed that Si nanowires show better cycling performance than Si films or powders consisting of micrometer sized particles. Anodes made of structured arrays of Si nanotubes where electrochemical insertion reactions occur on the outer surface of the tube, but not on the inner surface, showed better cycling performance than anodes with either particle or nanowire architectures [3]. Kim et al. [4] fabricated nano-porous Si anodes with pore width and wall feature sizes in the range of 40–100 nm, and demonstrated that this architecture also exhibits better cycling performance than anodes with particle or nanowire architectures. These porous materials can be idealized as parts of thin spherical shells. The improvement from nanoscale architectures is related to the stresses developed during Li insertion, however a complete understanding of why particle size and morphology play such an important role is lacking. The goal of this paper is to contribute to a better understanding of the interaction between particle geometry and stresses by simulating the coupled diffusion and mechanics of Li insertion in Si as driven by electrochemical surface reactions.

While coupled species diffusion and mechanics has been studied for decades in many different contexts, only recently have analyses appeared for electrochemical insertion electrodes. Christensen and Neuman developed a fully-coupled diffusion-mechanics model to describe the behavior of spherical particles during insertion [13]. They then used this model to simulate stress generation and predict fracture in spherical $Li_yMn_2O_4$ particles [14]. Zhang et al. later developed a fully-coupled diffusion-mechanics model by treating diffusion induced strains analogously to thermal eigenstrains [15] and showed that their model provides more conservative estimates of stresses generated during insertion than the model proposed by Christensen and Neuman [13]. Zhang et al. studied Li insertion into Mn_2O_4 with the Li influx described by a constant current and through Butler–Volmer surface reaction kinetics [15,16]. In a series of recent papers Cheng and Verbrugge [17–19] provided valuable analytical solutions for the one-way-coupled diffusion induced stresses in particles for galvanostatic and potentiostatic driven insertion. They have also considered simplified surface reaction kinetics, modeling them as a convective boundary condition and introducing an electrochemical Biot number to classify the regimes where bulk diffusion or surface reactions dominate the process [19]. The latter is particularly valuable in understanding the roles of various parameters in the design of strain-resistant electrodes. Deshpande et al. studied the effects of surface stress [20] and concentration-dependent elastic constants [21] and showed that they can make a significant impact on stress development during potentiostatic or galvanostatic insertion. The latter study is especially timely as the dependence of elastic constants has recently been computed for Li–graphite and LiSi compounds using density functional theory [9,22]. Golmon et al. [10] used a fully-coupled diffusion-mechanics model with Li insertion driven by Butler–Volmer electrochemical reaction kinetics to study the effect of particle size on stress generation in Si particles. They developed a map that communicates the roles of particle size and Li insertion rate (related to charging rate in an actual battery) on the maximum stresses developed.

The studies outlined above have focused on stress generation during insertion/extraction with the understanding that stresses drive mechanical failure and damage. A few efforts have pursued more accurate failure criterion based on linear elastic fracture mechanics, which is appropriate given the brittleness of many of the insertion materials [23–31]. These studies have revealed the important roles of elastic anisotropy [31] and the nonuniform stress states that result during insertion [29].

In this paper we build on these previous modeling efforts and present a fully-coupled stress-diffusion model with electrochemical surface reactions at the electrode/electrolyte interface that incorporates surface stress [10,32–35] and concentration-dependent material properties. The model is presented in a general form amenable to a finite element formulation which can then be used to simulate arbitrary geometries. We use the model to simulate stresses during Li insertion in Si, focusing on two basic geometries: hollow spherical and cylindrical shells. These geometries are selected as they describe a wide variety of morphologies that have been fabricated and studied experimentally, including particles, nanowires, nanotubes, and porous solids. After studying the evolution of Li concentration and stresses during electrochemical insertion, we study the roles of surface stress and concentration-dependent elastic moduli for various particle sizes and morphologies. We then form parameter maps of the maximum stress components as functions of various parameters of relevance in the design of strain-tolerant electrodes.

2. Coupled stress-diffusion model

In general, during insertion (or extraction) ion transport occurs in both the active material and the surrounding electrolyte, coupled through electrochemical reactions at the particle surface. Here we idealize the situation and only consider transport and mechanics in the active host. The interaction with the electrolyte is modeled through a boundary condition on the particle surface that describes the Li ion flux into the particle in terms of the kinetics of the electrochemical charge-transfer reaction at the interface. In our model the electrolyte has a constant prescribed concentration of Li ions c_l and electric potential ϕ_l. The particle is assumed to be at a spatially constant potential, ϕ_s, and the potential difference, $\eta = \phi_l - \phi_s$, drives the electrochemical reaction kinetics, as discussed later. Fig. 1 illustrates the problem domain and the degrees of freedom of interest within each region.

Following Zhang et al. [15], we model the electrode particle as a linear elastic solid with diffusion-induced eigenstrains and extend that formulation to incorporate the effects of surface stress [33–35], which play an increasingly important role as feature sizes decrease to the nm scale. Assuming that the mechanical response is much faster than diffusion and neglecting body forces and inertia effects, deformation in the electrolyte is described by a linear
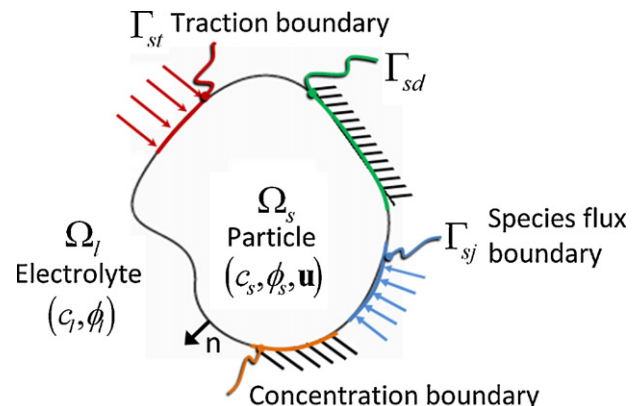

Fig. 1. Electrode particle.