A Computational Model of the Mechanical Behavior within Reconstructed Li_xCoO_2 Li-ion Battery Cathode Particles

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ABSTRACT

A coupled electrochemical-mechanical model is developed and applied to predict transient three-dimensional stress fields within reconstructed Li_xCoO_2 cathode particles from commercial Li-ion batteries. The reconstructed particle geometries are derived from focused-ion-beam–scanning-electron-microscopy (FIB-SEM) experiments. The study uses three individual particles, representing typical sizes and shapes. The mechanical model incorporates measured anisotropic strain within the Li_xCoO_2 lattice and includes strains due to phase transformations. The stresses are generally found to be compressive in the particle interiors and tensile near the surfaces. Small-scale surface morphology, high Li concentration gradients, and phase transformations are found to have a major influence on the stresses, with particularly high tensile stresses near small protuberances and concave notch-like features on the electrode surfaces. The study considers 1C and 5C discharge rates. The qualitative behaviors are similar at different discharge rates, but the stress magnitudes are higher at higher discharge rates.

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1. Introduction

This paper reports the development of a micro-scale three-dimensional (3D) finite element (FE) linear elastic approach to predict the mechanical behavior within reconstructed Li_xCoO_2 Li-ion battery (LIB) cathode particles during discharge. The mechanical model, which is coupled directly to an electrochemistry model, includes the effects of crystal anisotropy and phase transformations. The study is particularly concerned with predicting the influence of particle size and surface morphology, as well as discharge rates. Results show that tensile stresses, especially on the particle surfaces, can be sufficiently high as to suggest particle fracture.

Representative cathode particles are reconstructed from a commercial battery using focused-ion-beam–scanning-electron-microscopy (FIB-SEM) [1]. The FIB-SEM experiments typically produce reconstructions for an assembly of particles within a 3D rectangular domain measuring a few tens of microns on a side [2]. Individual particles can be extracted from the assembly of particles, and the present study uses three individual reconstructed particles with different sizes and shapes.

The particle mechanical behavior is closely coupled with the transient Li-concentration field within the cathode particles.

Thus, the approach depends upon coupling an electrochemical simulation with the mechanical simulation. The electrochemical simulation is accomplished in a finite-volume (FV) setting using extensions of the ANSYS Fluent software [2]. The mechanical simulation is accomplished in an FE setting using extensions of the ANSYS Mechanical software.[1] At each time step during a transient discharge simulation, the Li-concentration field within the particles must be communicated from the electrochemical simulation to the mechanical simulation.

The mechanical simulations depend upon constitutive relationships between the stress and strain tensors. The present study uses data published by Reimers, et al. [3], considering the effects of both isotropic and anisotropic stress-strain relationships. The Li_xCoO_2 lattice experiences significant volume changes and phase transformations during the lithiation (discharge) process [3]. The diffusion-induced stresses (DIS) can be very high, potentially exceeding the material strength and leading to electrode degradation and particle fracture. The present results show that stresses can be particularly high in the vicinity of notch-like features on the particle surfaces. Results also show that high discharge rates and phase transformation occurring during the Li intercalation also contribute to high stresses.

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The study focuses on isolated particles that are not constrained by neighboring particles (i.e., under free-expansion conditions). The present study also considers isothermal behavior. Thus the results reveal behaviors that are solely attributed to internal diffusion-induced stresses.

The electrode particles from actual batteries can vary significantly and randomly in size, shape, and surface morphology. The physical connections between particles within the electrode assembly and the electrical contacts vary randomly within the porous electrode assembly. Moreover, the crystallographic orientations within particles are random. Thus, although the simulations presented here are quantitative using actual reconstructed particles, the results must be understood in a qualitative context. The broad objective is to glean observations and trends that are generally applicable.

2. Prior literature

There is significant foregoing research concerning the mechanical behavior of Li-ion battery cathodes. Reconstructed LIB electrode particles have been extracted from electrodes using a variety of microscopic techniques [4–6,2,7]. Lim et al. [5] developed computational simulations to show that lithiation-induced stresses depend on geometric characteristics, with the stresses being much higher in reconstructed Li_yC_6 and Li_xCoO_2 particles than in idealized, spherical particles. Likewise, Seo et al. [4] and Chung et al. [6] used reconstructed particles of $LiMn_2O_4$ compounds in an FE solid mechanics simulation. Chung et al. [6] reported that the DIS are much greater in actual particles that in spherical particles. These investigations [4–6] were based on elastic, isotropic, single-phase individual particles and made use of the thermal analogy to compute diffusion strains [8,9]. The present investigation develops an analogous approach, but additionally considers phase transformation and crystal anisotropy as well as particle surface morphology.

Although a few recent studies have considered anisotropic Li diffusion in polycrystalline Li_xCoO_2 particles [10–12], the effects of anisotropy on the stress response in geometrically complex electrode particles has not been reported. Additionally, most analytical and numerical investigations of DIS in LIBs have not incorporated the effects of volumetric and/or lattice strains that result from phase transformations. However, Park et al. [13] have incorporated phase-transformation-induced stresses in a 3D numerical model of spherical $LiMn_2O_4$ particles. Their results showed that stresses associated with phase transformations were greater than those developed when considering the intercalation process alone. Analytical methods, such as moving boundary and porous electrode theory, have been developed to investigate the effects of phase transition and/or phase coexistence during Li intercalation [14–17]. These approaches, however, were limited by the following assumptions: a) isotropic elastic behavior in smooth, idealistic particles, b) two phases concentrically coexisting, c) Li transport is decoupled from intercalation-induced stress phenomena, and d) phase coexistence modeled as Li-poor or Li-rich phases. Regarding the latter, no published literature suggests that either of the two hexagonal phases in the phase coexistence region of Li_xCoO_2 is richer in Li than the other. In addition, smooth and spherical particles are unable to capture stress concentrations that can develop in local concave regions of actual cathode particles. Understanding and predicting the mechanical behavior of electrodes is practically important. For example, capacity fade can be associated with diffusion-induced stress [4]. Even under normal operating conditions, particles can fracture and thus degrade battery performance. Particle fracture can originate from locally high stresses leading to the formation and growth of microcracks [18]. Such processes are known to be intensified at high discharge rates [19]. If a fractured particle looses

electrical contact with neighboring particles or current collection foils, it can no longer participate electrochemically and the battery resistance increases and capacity fades [13,20]. Additionally, fragmentation exposes fresh electrode surfaces to the electrolyte solvent, thus promoting the growth of new surface solid electrolyte interface (SEI) films [20,4].

Hydrostatic stress gradients are known to influence Li diffusion with electrode particles [21]. Thus, in addition to mechanical degradation associated with diffusion-induced stress, the stress state couples back into the electrochemistry problem. This effect is neglected in the present study, but is the subject of active model development.

3. Particle reconstruction and computational discretization

Fig. 1 illustrates the process used to define the single particles used in the present study. A commercial cell (here, Lishen[2] LR18650AH) is disassembled and a small portion of a cathode is prepared for FIB-SEM imaging [1]. The raw data from the FIB-SEM consists of approximately 200 two-dimensional SEM slices, with each slice being separated by approximately 60 nm. In Fig. 1 the white areas in the FIB-SEM slices represent the cathode particles and the black space represents the pore space that would be filled by electrolyte solvent. As discussed by Wiedemann et al. [2], the 3D cube is reconstructed using the Mimics software.[3] The 3D geometry is represented in STL (STereoLithography) format, which is a computational definition of the particle surfaces. For the purposes of the present study, individual particles are extracted from the rectangular assembly of many particles. The individual particle geometry is also represented in STL format, which is used as the basis for computational discretization.

Fig. 2 illustrates the three reconstructed cathode particles used in the present study. The particles, labeled P_1, P_2, and P_3, are rendered at the same scale to show the relative particle sizes. In addition to the reconstructed particles, a perfectly smooth spherical particle (labeled P_s) is also modeled. Cathode particles may be polycrystalline with a few grains or be composed of a single grain [22]. The present model assumes that each particle is composed of a single crystal for the anisotropic studies.

To be electrochemically active, the particles must be connected to other particles and ultimately to current-collection foils in the battery. The yellow patches on particles (Fig. 2) indicate the surface positions through which electrical current enters the particle during discharge. Lithium enters the particles via charge-transfer reactions on the surfaces that are in contact with the electrolyte solution. The anisotropic Li_xCoO_2 crystal grain orientation is illustrated by the *xyz* axes which correspond to the *abc* crystallographic axes. In the present study, the electrical contact areas (yellow patches) and crystal orientation are assigned somewhat arbitrarily. However, in all cases the electrical contacts are essentially aligned with the *c*-axis of the Li_xCoO_2 lattice.

The electrochemical model, which has been described previously [2], uses an FV mesh that is generated using the TGRID algorithm. The structural model uses the five degree-of-freedom (DOF) element SOLID 227 that is implemented in ANSYS Mechanical v14.5. This element consists of a 3D 10-node tetrahedron. The tetrahedral elements were selected for a variety of reasons. First, coupled-field elements are required in order to couple the mechanical response to the chemical diffusions. These particular elements in ANSYS Mechanical are tetrahedral or hexahedral elements. However, the tetrahedral elements provide a lower error when numerical solutions are compared to analytic