Journal of Power Sources 336 (2016) 8–18

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Three-dimensional finite element study on stress generation in synchrotron X-ray tomography reconstructed nickel-manganese-cobalt based half cell

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HIGHLIGHTS

- 3D realistic NMC microstructures generated using synchrotron X-ray tomography.
- Coupled lithium intercalation and phase transitions effect on stress generation.
- Stresses inside particles increase dramatically when considering phase transitions.
- Cracks form on the surface of isolated particles in the conductive channel.
- High stress is more likely to occur at concave regions rather than convex regions.

ARTICLE INFO

Article history:
Received 8 August 2016
Received in revised form
14 October 2016
Accepted 17 October 2016

Keywords:
Synchrotron X-ray tomography
NMC
Phase transitions
Finite element
Stress
Diffusion

ABSTRACT

In this study, the stress generation caused by phase transitions and lithium intercalation of nickel-manganese-cobalt (NMC) based half cell with realistic 3D microstructures has been studied using finite element method. The electrochemical properties and discharged curves under various C rates are studied. The potential drops significantly with the increase of C rates. During the discharge process, for particles isolated from the conductive channels, several particles with no lithium ion intercalation are observed. For particles in the electrochemical network, the lithium ion concentration increases during the discharge process. The stress generation inside NMC particles is calculated coupled with lithium diffusion and phase transitions. The results show the stresses near the concave and convex regions are the highest. The neck regions of the connected particles can break and form several isolated particles. If the isolated particles are not connected with the electrically conductive materials such as carbon and binder, the capacity loses in battery. For isolated particles in the conductive channel, cracks are more likely to form on the surface. Moreover, stresses inside the particles increase dramatically when considering phase transitions. The phase transitions introduce an abrupt volume change and generate the strain mismatch, causing the stresses increase.

1. Introduction

Lithium ion rechargeable batteries (LIBs) are one of the most promising candidates for portable electronics and electric vehicles applications due to their high energy density [1]. Many technological improvements have been made to increase the energy density and cycle life of LIBs, including suppressing dendrites formation [2,3], reducing side reactions [4,5], and preventing thermal runaway [6,7]. One of the critical challenges of LIBs is to enhance the mechanical stability of electrode materials. Diffusion induced stresses [8,9] and phase transition [10,11] during the operations of LIBs can cause fracture and mechanical failure. Hence, it is important to understand the stress generation in battery materials.

Many studies have been done to study the stress generation to prevent the mechanical failures of LIBs [9,12–16]. Zhang et al. [14,15] studied the diffusion induced stresses in $LiMn_2O_4$ under

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http://dx.doi.org/10.1016/j.jpowsour.2016.10.052
0378-7753/

galvanostatic and potentiodynamic conditions using ellipsoid shaped particle model. Cheng and Verbrugge [13] investigated the strain energy of a spherically-shaped electrode particle under a periodic voltage excitation source. They evaluated the crack nucleation using strain energy density method. However, many of these studies employed single sphere particle model, and diffusion kinetics and electrochemical processes were simplified greatly. There are some attempts to simulate the stress generation of realistic microstructures in LIBs. Lim et al. [8] studied the diffusion induced stresses of realistic microstructures of Li_XCoO_2 and Li_XC_6 particles reconstructed by synchrotron X-Ray tomography. Wu et al. [17] investigated the mechanical behavior of $LiMn_2O_4$ cathode reconstructed by 2D SEM images under discharge conditions. The phase transition was not considered in the study.

Stresses caused by phase transition inside the electrode materials are detrimental to electrode particles. Phase transition can introduce abrupt volume changes to the structure, leading to structure instability. However, the studies of stress generation including diffusion induced stress and phase transitions are rare. Park et al. [10] calculated the stresses with phase transition and intercalation in $LiMn_2O_4$ particles, but the geometry used in the model was simple shaped particles. Renganathan et al. [11] simulated the stress inside the porous electrode by taking advantage of the P2D model. They evaluated the stresses at the phase interface. Although the stresses caused by phase transition and Li intercalation have been considered in above works, some important features cannot be captured using homogeneous microstructures, such as the diffusion kinetics at high C rates and the geometry effect on stresses. Thus, a realistic microstructure based stress generation study with phase transition and intercalation is necessary.

In this paper, the electrochemical performance and the stress generation inside the cathode microstructure including phase transition and Li intercalation will be calculated using synchrotron X-ray reconstructed NMC half cell. The paper is organized as follows: In Section 2, the details of imaging processing and reconstruction of NMC half cell are given. In Section 3, a set of mathematical formulations describing the electrochemistry and the stresses in LIBs are listed. In Section 4, the electrochemical performance of NMC half cell under various C rates are studied. The geometry effect on stress is discussed. The stress distributions in the particles are also analyzed. Conclusions are given in Section 5.

2. Microstructure reconstruction and finite element mesh

The microstructure used for the model was obtained by synchrotron X-ray tomography at beamline 2-BM at the Advanced Photon Source, Argonne National Laboratory. The NMC cathode ($LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$) used in the experiment was from a commercial LG HE4 18650 cell. The NMC 18650 cell was disassembled in argon filled glove box, and the cathode materials were carefully scratched off. A set of gray-scale images ware obtained with a voxel size of 0.65 μm after synchrotron X-ray tomography. The carbon and binder phase was neglected in this study, because it is hard to distinguish it from the background. It is noted that the lack of carbon and binder phase may cause isolated NMC particles. In order to reduce the computational cost, an edge preserving smoothing filter and small islands removal filters were applied followed by greyscale threshold segmentation. The resulting reconstruction was a cuboid with a dimension of 45 μm × 45 μm × 33 μm. The cross section images before and after image processing are shown in Fig. 1 (a) and (b). Overall, the images after processing preserve the major microstructural features of the unprocessed images.

In order to simulate the electrochemical performance, a three-dimensional finite element model of the NMC half cell was created. The NMC half cell was made up of cathode, electrolyte and separator domains. A separator with 10 μm thickness was added to the cathode domain (Fig. 1 (c)). The pore space in the cathode domain was filled with electrolyte. The porous structure in the separator was neglected. Two domains were meshed and imported into Comsol Multiphysics for further simulation.

3. Model description

The mathematical model consists of electrochemistry sub-model and mechanics sub-model. The electrochemistry model describes the species and charge transports in the NMC half cell. The mechanics model computes the mechanical stresses and diffusion induced stresses in active particles.

3.1. Electrochemistry

The electrochemistry model describing battery kinetics, mass and charge transports is based on the work of Doyle et al. [18] and Fuller et al. [19]. In order to distinguish different domains, subscript of $i = 1$ and 2 denotes the active cathode particles and the electrolyte. Here, we assume the lithium diffusivity and the electrical conductivity remain the same after the phase transition.

3.1.1. Active cathode particles

The charge balance in the active cathode particles follows the Ohm's law:

$$\nabla\cdot(-k_1\nabla\phi_1) = \nabla\cdot J_1 = 0 \quad (1)$$

where k_1 is the electrical conductivity of the active cathode particles; ϕ_1 is the electrical potential and J_1 is the current density in NMC particles.

The transport of Lithium ions in active particles is described by the modified Fick's law [15,20], which includes the effect of stresses on diffusion:

$$\frac{\partial c_1}{\partial t} + \nabla\cdot\left(-D_1\nabla c_1 + \frac{D_1\Omega c_1}{RT}\nabla\sigma_h\right) = 0 \quad (2)$$

where c_1 is the lithium ion concentration in solid particles; D_1 is the diffusivity of lithium ions in NMC electrode; R is the universal gas constant; T is temperature, which is set 273 K in this study; Ω is the partial molar volume of active particles; $\sigma_h = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$ is the hydrostatic stress (σ_{ij} is stress component in the stress tensor).

3.1.2. Electrolyte

The charge transport equation of the electrolyte phase couples the concentration of lithium ions and the electrical potential, and has the following form:

$$\nabla\cdot\left(-k_2\nabla\phi_2 + \frac{2k_2RT}{Fc_2}\left(1+\frac{\partial lnf_2}{\partial lnc_2}\right)(1-t_+)\nabla c_2\right) = \nabla\cdot J_2 = 0 \quad (3)$$

where k_2 is the electrical conductivity of the electrolyte, ϕ_2 is the electrical potential; F is the Faraday constant; c_2 is the lithium ion concentration in the electrolyte; t_+ is the transference number of positive ions, which is set 0.363 in this study; f_2 is the mean molar activity coefficient of the electrolyte.

The mass transport of lithium ions in the electrolyte is expressed as:

$$\frac{\partial c_2}{\partial t} + \nabla\cdot\left[-D_2\left(1-\frac{dlnc_0}{dlnc_2}\right)\nabla c_2 + \frac{J_2t_+}{F}\right] = 0 \quad (4)$$