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Multiscale modeling of lithium-ion battery electrodes based on nano-scale X-ray computed tomography

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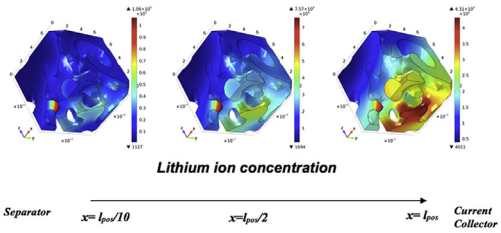
HIGHLIGHTS

- A multiscale model is developed to study lithium ion battery electrodes.
- The electrode microstructure is reconstructed based on X-ray computed tomography.
- The model predicts experimental data more accurately than the homogenous models.
- Inhomogeneity causes wider distribution of properties compared to homogenous models.
- The developed model is applicable to any lithium ion battery electrode material.

GRAPHICAL ABSTRACT



Lithium ion concentration inside electrode microstructure based on Multiscale model simulation

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ABSTRACT

A multiscale platform has been developed to model lithium ion battery (LIB) electrodes based on the real microstructure morphology. This multiscale framework consists of a microscale level where the electrode microstructure architecture is modeled and a macroscale level where discharge/charge is simulated. The coupling between two scales are performed in real time unlike using common surrogate based models for microscale. For microscale geometry 3D microstructure is reconstructed based on the nano-scale X-ray computed tomography data replacing typical computer generated microstructure. It is shown that this model can predict the experimental performance of $LiFePO_4$ (LFP) cathode at different discharge rates more accurate than the conventional homogenous models. The approach employed in this study provides valuable insight into the spatial distribution of lithium -ion inside the real microstructure of LIB electrodes. The inhomogenous microstructure of LFP causes a wider range of physical and electrochemical properties in microscale compared to homogenous models.

1. Introduction

Lithium-ion batteries (LIBs) have attracted a tremendous attention because of their high energy and power density compared to other electrochemical energy storage technologies.

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Recently, automotive industries have put considerable effort to accelerate electrification of vehicles using LIBs [1,2]. For this purpose, among different candidates for cathode material, $LiFePo_4$ (LFP) is believed to be promising choice due to its low price, superb safety, and enhanced rate capability [3–5]. In addition to material selection, the electrode architecture also plays a crucial role in improving the performance of LIBs [6,7]. The microstructure of LIB electrode remarkably influences the performance by providing certain interfacial surface area, lithium ion diffusion path, and active material connectivity [5,8], which particularly critical in automotive applications where the demands of energy and power densities are high [1].

The development of next generation high performance LIBs requires close relation between modeling and experiment. Mathematical models have been used to address physical and electrochemical processes occurring inside the battery and further employed to optimize electrode design. However, traditional models still relies on a simplified picture of homogenous electrode which do not provide sufficient information about the electrode's real microstructure. Newman and co-workers have developed one of the most successful LIB models based on the porous electrode and concentrated solution theory [9,10]. Newman's pseudo-2D (P2D) model assumes that the porous electrode is made of equally sized, isotropic, homogenous spherical particles [9]. This homogenous description of electrode structure results in smooth, uniform intercalation/de-intercalation of lithium inside the host materials and has proven to be successful in characterizing discharge/charge behaviors particularly at low to moderate rates [11,12]. Although P2D model assumptions are not preserved in real LIB porous electrodes, it is widely applied in a variety of LIB research due to its simplicity [13–15]. This includes the rate capability and design investigation [10,16] as well as thermal behavior [17–19] studies. However, it fails to predict the phenomena related to inhomogenous structure of the electrode microstructure such as performance drop at high rates [20,21]. In addition, the well-known method of estimating the specific surface area based on spherical particles and the electrode tortuosity using Bruggeman correction has been controversial [22,23]. Therefore, in order to have more genuine insight in LIBs research, there is a crucial need for an advanced model capable of simulating LIBs behavior based on the real electrode microstructure.

Recent advances in the X-ray computed tomography (XCT) have made nano-scale 3D microstructures capturing a reality. Nano-XCT offers the capability to non-destructively resolve the 3D structure of porous electrode as it provides high spatial resolution 2D stack to computationally reconstruct a 3D image of the electrode microstructure. The obtained 3D geometry could be an alternative to commonly used computer-generated geometries [20,24] in LIB 3D models. LIBs research involving XCT can be categorized into two general groups: the morphological studies and multiphysics modeling. The first group is dedicated to characterizing the 3D microstructure, particle distribution, pore scale morphological and transport properties analysis [22,25,26]. The second group, on the other hand, utilizes reconstructed 3D microstructure to simulate multiphysics phenomena occurring inside the cell such as discharge/charge performance [27], thermal behavior [28] and stress analysis [26]. Yan et al. [27] simulated the discharge behavior of $LiCoO_2$ (LCO) based on nano-XCT data. Their results show that the distributions of electrolyte concentration, current density, over potential and intercalation reaction rate are significantly different from the results obtained from the P2D model. Furthermore, the microstructure inhomogeneity is found to be responsible for the performance loss particularly at high discharge rates. Lim et al. [26] modeled diffusion-induced stress inside LCO particles which were reconstructed using XCT. Their results demonstrated that the highest von Mises and Tresca stresses in a reconstructed particles are several times greater than those obtained from the simple spherical or ellipsoid particle with the same volume. Yan et al. [28] simulated the heat generation during galvanostatic discharge in LCO microstructure. Their results show that the simulation based on reconstructed microstructure predicts more heat generation than the P2D model at high discharge rates. The simulation based on the reconstructed microstructure commonly results in the wider distribution of physical and electrochemical properties. The authors attributed the higher predicted heat generation to this wider electrochemical properties distribution. Chung et al. [29] studied the electrochemical and chemo-mechanical response of $LiMn_2O_4$ (LMO) cathodes based on the XCT method. Their simulations show that particle size polydispersity of microstructures impacts the local chemical and electrical behavior of a porous electrode.

In the present work, we aim to develop a model based on the real microstructure of the electrode. Among different candidates, LFP was chosen as the focused technology due to the aforementioned reasons. Applying the above mentioned method on the electrode with nano-particles, e.g. LFP, to study multiphysics phenomena, poses the inherent multiscale difficulty involved in the LIB research [30]. Models involve microstructure study LIBs behavior in two different length scales simultaneously; the first scale is in the range of the particle size which is couple of micrometers in case of LCO and LMO and tenth of nanometers for LFP. In this work, this scale is called “microscale” wherein electrode architecture is incorporated in the model. The second scale is in the range of the electrode thickness, typically 100 μm, where discharge/charge is characterized and here is called “macroscale”. For a micro-particle electrode, the model length scale is from 10^{-6} to 10^{-2} m considering both microscale and macroscale. However, the scale is from 10^{-8} to 10^{-2} m for a nano-size particles. Thus, comparing electrodes made of nano-particles and micro-particles, the difference between model length scale ranges is two orders of magnitudes bigger in case of electrode with nano-particles. This requires around 10^6 times more mesh elements in 3D that would burden a huge extra amount of computational cost on the model simulation. To avoid this, the concept of multiscale modeling has been employed to investigate LFP electrode behavior [30–33]. First, the electrode microstructure was reconstructed based on the nano-XCT data and the intercalation flux were obtained based on the simulation results on microscale. Then, the intercalation flux was exported to the macroscale to update the state variables such as electric potentials and specious concentrations in macroscale. Finally, the intercalation flux is updated based on the recent updated variables and sent back to microscale domain [34]. In this study, linking between microscale and macroscale is accomplished through coupling of equations at two sub-scales simultaneously [34], meaning that all the governing equations are solved concurrently in two scales and state variables are transferred between them in real time. To couple sub-scale models, another approach reported in the literature is serial coupling [35]. In the serial coupling, a surrogate-based model is determined from the pre-processed simulation data carried out on the microscale. The surrogate model is obtained based on the numerical experiment performed on microscale. For this, a quasi-steady state simulation of the governing equation is performed based on an experiment design for the initial values of state variables. Then, to couple the two scales, database and look up table [36,37] approach is used to couple microscale with macroscale. Although using serial method diminishes computational time, it includes error due to uncertainty in fitting the empirical model to microstructural data. In addition, the assumption of quasi steady state in microscale is highly questionable in a mainly time dependent model.

The purpose of this study is to establish an advanced imaged-