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Analysis of Polarization in Realistic Li Ion Battery Electrode Microstructure Using Numerical Simulation

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ABSTRACT

In order to explore the local effects of electrode microstructural inhomogeneity, a half cell Li ion battery was built with reconstructed realistic $LiCoO_2$ cathode electrode which was divided equally into eight subdomains. A previously developed C++ code was used to simulate the discharge and charge processes using finite volume method. The geometric properties of each subdomain were characterized by porosity, tortuosity and specific interfacial area. The average variables, such as Li ion concentration and reaction current density, and polarization due to different sub-processes, such as activation of electrochemical reactions (PAER) and charge transport of species were calculated in each subdomain. The inhomogeneous geometric properties result in non-uniform polarization distribution. The polarization due to ionic transport depends on the position, tortuosity and porosity. The porosity, specific interfacial area, state of discharge/charge and position play an important role in the distribution of PAER. The PAER difference between subdomains tends to enlarge at the end of discharge process but to reduce at the end of charge process although the main electrochemical reaction always takes place in the subdomains with smaller porosity. In addition, the PAER is much larger than the polarization due to ionic transport. By comparing with the results from pseudo 2D model, we found that microstructural inhomogeneity in the 3D model has significant impact on global polarization and polarization distribution in the electrode. The presented method provides a possibility to study local effect of inhomogeneous geometric properties.

1. Introduction

Rechargeable Li ion batteries (LIBs) have been considered a promising power source for electric vehicles [1–6]. Despite the great progress in research on advanced LIB technologies, challenges still exist to increase the energy and power densities, reduce the cost, improve the safety and life of the batteries for electric vehicles to be cost competitive with gasoline automobile. One of the reasons is that there is still no mechanistic relationship between the microstructure of LIB electrodes and corresponding desirable performance and safety characteristics. The structure of the electrodes at the micro- and nano-scales plays a critical role in determining the performance of a LIB because the electrode's composite matrix must be designed to provide both electron and Li ion transportation, which eventually affects the LIB's voltage, specific capacity, and discharge/charge rate [7]. In addition, the electrode microstructure controls the interfacial reactions in LIBs, such as Li ion intercalation/deintercalation reaction, solid electrolyte interface growth, and other side reactions, which affect the performance, safety, and life of LIBs.

Numerical simulation based on comprehensive mathematical models and reconstructed realistic electrode microstructure is an effective method to study the relationship between the microstructure of LIB electrodes and corresponding performance. To this end, several numerical approaches with realistic electrode microstructure have been employed to investigate the local effects and global performance of LIB electrodes. For instance, Stephenson et al. explored the dynamic particle packing model and the stochastic grid model to predict the three dimensional (3D) electrode microstructure with a set of fundamental interdomains and bulk interaction parameters obtained from a limited set of two dimensional (2D) images [8]. They also studied the relationship between 3D microstructure and ion transport performance. Hutzenlaub et al. reconstructed $LiCoO_2$ cathode electrode with three phases based on focused ion beam scanning electron microscope (FIB-SEM) images, assuming that the carbon-binder

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phase is not ionic conductive [9]. Afterward, Hutzenlaub et al. studied the effect of nanoporosity in carbon-binder domain on the porosity, tortuosity, contact area, and ionic conductivity [10]. Wiedemann et al. reconstructed the realistic 3D microstructure of LIB cathodes from FIB-SEM and predicted the temporal and spatial distribution of Li ion concentrations and potentials within the cathode active material using finite volume method (FVM) without considering the variation of potential and Li ion concentration in electrolyte [11]. Wu et al. simulated the deformations and stresses due to the Li ion intercalation via a multi-physics microstructure resolved model of realistic electrode geometries [12]. Roberts et al. reconstructed 3D electrode microstructure from experimental imaging or particle size distributions and presented a framework for coupled simulations of electrode mechanics driven by Li ion intercalation [13]. Aiming at high power density applications, Chung et al. studied the impact of particle size polydispersity on energy density and stress of the reconstructed 3D microstructure of commercial $LiMn_2O_4$ electrode and computer generated electrode [14]. They concluded that the high surface roughness of realistic microstructure favored high instantaneous power performance but accelerated side reactions which have a negative impact on power performance. Based on X-ray nano-computed tomography (nano-CT) images, Yan et al. reconstructed the electrode microstructure and developed a FVM framework to conduct 3D simulation of a half cell with $LiCoO_2$ cathode [15,16]. They found that the physical and electrochemical variables were distributed in a wider range than that from the pseudo 2D model due to the microstructural inhomogeneity.

Although the above numerical studies were conducted based on the realistic microstructure of electrode, the local effect of geometric properties such as porosity, tortuosity and specific interfacial area, on local physical and electrochemical processes was not discussed except the active material particle size. The purpose of this paper is to present a method to analyze the local polarization due to different sub-processes, i.e. charge transport of species and activation of electrochemical reaction, inside an inhomogeneous LIB electrode using numerical simulation method with realistic microstructure. This method provides a possibility to evaluate the impact of local geometric properties on the polarization and could help to identify the problems for polarization and improve electrode designs. Nyman et al. split the polarizations in a LIB into parts associated with the activation of electrochemical reactions, mass transport and inadequate contact and then provided a valuable tool to quantify the polarization of sub-processes [17]. Their analysis was based on the simulation results of pseudo 2D model of COMSOL software without consideration of the realistic electrode microstructure. In the current study, the previously developed 3D FVM framework using C++ language [15,16] was extended to investigate the local effects of the microstructural inhomogeneity. First, a half cell model was built with the reconstructed realistic microstructure of a $LiCoO_2$ cathode electrode via nano-CT technology. Then the cathode electrode microstructure was equally divided into 8 subdomains and the average variables and polarization were calculated through integrating variables over each subdomain. With the previously developed FVM framework [15], the discharge and charge processes of a half cell were simulated at 1C and 5C rates. Based on the simulation results, the average variables and polarization were calculated in each subdomain. In order to compare the 3D model with pseudo 2D model, the same simulations and data analysis were conducted using pseudo 2D model. Finally, the local effects of inhomogeneous geometric properties on detailed distribution of average variables and polarization inside the $LiCoO_2$ cathode electrode were discussed.

2. Models and definition

2.1. Mathematical model

The battery charge/discharge model includes the conservation of charge and mass in electrodes and electrolyte and the Butler–Volmer equation. The boundary conditions, assumptions, mesh generation and FVM simulation of the half cell were used in our previous publication [15]. In consideration of the Bulter–Volumer equation discussed below especially, it is given by:

$$i^{\mathrm{Li}} = i_0\left\{\exp\left(\frac{\alpha F}{RT}\eta\right) - \exp\left[-\frac{(1-\alpha)F}{RT}\eta\right]\right\} \tag{1}$$

where i^{Li} is the reaction current density, i_0 is the exchange current density, η is the surface overpotential, and α is a symmetry factor that represents the fraction of the applied potential promoting the cathodic reaction. The exchange current density i_0 is given by:

$$i_0 = Fk_0(c_2)^{\alpha}(c_\theta)^{\alpha}(c_3)^{1-\alpha} \tag{2}$$

where c_2 and c_3 are the Li ion concentration in the electrolyte and the cathode active material at their interface respectively, c_θ is the difference between stoichiometric maximum concentration (solubility limit) and current concentration on the surface of the active material particles, $c_\theta = c_{\max} - c_3$, and k_0 is a reaction rate constant. The overpotential η is defined as below:

$$\eta = \phi_3 - \phi_2 - U_{\mathrm{OCP}} \tag{3}$$

where ϕ_3 and ϕ_2 are the potential of the cathode active material and the electrolyte at the interface respectively, and U_{OCP} is the open circuit potential (OCP) at the interface.

2.2. 3D LIB model

A half cell LIB model is shown in Fig. 1 built with reconstructed realistic microstructure of $LiCoO_2$ cathode electrode directly from nano-CT images. The $LiCoO_2$ cathode was fabricated using doctor

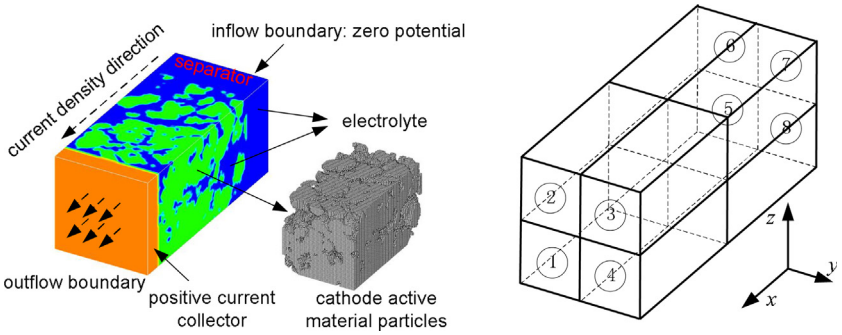

Fig. 1. Illustration of a representative half cell LIB with cathode electrode and subdomains of the cathode electrode.