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 LiCoO₂ 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 polarization due to activation of electrochemical reaction is much larger than that 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.

Key words: Li ion battery; electrode microstructure; inhomogeneity; polarization

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 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 1 C and 5 C 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 LiCoO₂ 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:

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

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:

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

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, $c_\theta = c_{\text{mx}} - c_3$, and k_0 is a reaction rate constant. The overpotential η is defined as below:

$$\eta = \phi_3 - \phi_2 - U_{\text{OCP}} \quad (3)$$

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

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

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 blade coating technique and rolling press. It includes 94 wt% LiCoO_2 , 3 wt% Polyvinylidene fluoride (PVDF) binder and 3 wt% carbon black. In LIB electrodes, PVDF binder and carbon black usually form porous structure with thin layers for Li ion and electron transport [18]. Due to the low X-ray absorption of the porous binder and carbon black, the PVDF binder phase cannot be distinguished from the pore phase by the nano-CT system. In this study, the pore phase contains both pores and PVDF binder. A synchrotron X-ray nano-CT with a spatial resolution of 58 nm at Beamline 32-ID-C, Advanced Photon Source, Argonne National Laboratory was employed to obtain morphological data of the electrode. The detailed process of preparing the electrode for nano-CT scan can be found in our previous publications [7, 15, 19]. The representative volume of cathode electrode is $24.5 \times 24.5 \times 40.0 \mu\text{m}$, of which the dimension of $40.0 \mu\text{m}$ is the thickness. The thickness of Aluminum current collector and separator are $5 \mu\text{m}$ and $10 \mu\text{m}$ respectively.

The previously developed C++ codes were used to reconstruct the cathode electrode microstructure and generate the mesh for FVM simulation [15, 16]. The mesh in the model included 528384 CVs and 549250 vertices. As shown in Fig. 1, at the inflow boundary, the zero potential as well as fixed Li ion flux was imposed and the fixed Li ion flux was equivalent to the electrical current density imposed at the outflow boundary according to charge conservation. The backward formula was used to discretize the temporary term in the simulation while the Euler method was employed to improve the simulation precision. The

C++ code of simulation was developed on Visual Studio 2010 platform and uses Open Multi-Processing (OpenMP) as parallel means to accelerate the simulation. The current simulations were run on the Dell Optiplex 9020 with Intel (R) Core (TM) i5-4570 CPU @3.20GHz and 16.0 GB memory on the 64-bit Windows 7. Around 70 hours are needed for one simulation of charge or discharge process.

In consideration of the particle size of cathode active material and the meaningful geometric properties of each subdomain, a C++ code was developed to divide the cathode electrode into 8 subdomains equally as the pattern shown in Fig. 1. In the following, for simplicity, subdomains 1 through 4 which are far from the separator were named by the fore group. Subdomains 5 through 8 which are adjacent to separator were then named by the back group. The C++ code can also analyze the geometric properties of each subdomain based on the mesh [15]. In order to compare the 3D model with pseudo 2D model, the radius of spherical cathode active material particles (r) in pseudo 2D model was set as $1.88 \mu\text{m}$ according to the porosity (ε) and average specific interfacial area (A_{ave}) of the 3D representative volume of cathode electrode ($(1 - \varepsilon) \frac{3}{r} = A_{ave}$). In addition, the cathode electrode is divided into two parts equally corresponding to the fore group and back group in Fig. 1. Both the fore group and back group include 4 same subdomains.

2.3 Definition of average variables and polarizations

In order to investigate the correlation between LIB performance and electrode microstructure, the average variables and polarization inside the electrode are introduced. First, the average value of variables is calculated in each subdomain, including Li ion concentration and reaction current density. For each subdomain, the average Li ion concentration is calculated as following:

$$c_{ave-i} = \frac{1}{V_{sub}} \int_{V_{sub}} c_i dv, i = 2, 3 \quad (4)$$

where $i = 2, 3$ stands for electrolyte and cathode active material respectively. c is Li ion concentration and V_{sub} is the corresponding material volume in each subdomain. The average current density of electrochemical reaction in each subdomain is expressed by:

$$J_{ave}^{Li} = \frac{1}{A_{sub}} \int_{A_{sub}} J^{Li} ds \quad (5)$$

where J^{Li} is the current density of Li ion intercalation / deintercalation reaction and A_{sub} is the interface area between cathode active material and electrolyte in each subdomain. Second, the polarization is considered mainly due to activation of electrochemical reaction and charge transport of species. For each subdomain, the average value of polarization due to activation of electrochemical reaction (PAER) and polarization due to charge transport (PCT) in electrolyte or active materials is extended to 3D model from the polarization definitions in Ref [17], which are expressed by:

$$\eta_{p1} = \frac{1}{A \cdot J_{total}} \int_{A_{sub}} J^{Li} \eta ds \quad (6)$$

$$\eta_{p2-i} = -\frac{1}{A \cdot J_{total}} \int_{V_{sub}} J_{i,j} \phi_{,j} dv, i = 2, 3, j = 1, 2, 3 \quad (7)$$

where subscript “,” is derivative. $j = 1, 2, 3$ is the Cartesian coordinate component, and ϕ is the corresponding material potential. A is the cross section area of separator, which is also the area of inflow boundary or outflow boundary. J_{total} is the current density at the outflow boundary.

3. Results and discussion

The porosity, tortuosity in x axial direction and specific interfacial area of each subdomain inside the cathode electrode are shown in Fig. 2. The largest porosity is 0.51 in subdomain 5 and the smallest porosity is 0.14 in subdomain 4. The average porosity of total cathode electrode is 0.33. The largest specific interfacial area is 1258 mm^{-1} in subdomain 6 and the smallest specific interfacial area is 740 mm^{-1} in subdomain 4. The average specific interfacial area is 1066 mm^{-1} in the total cathode electrode. The largest tortuosity is 27.04 in subdomain 3 and the smallest tortuosity is 3.08 in subdomain 2. The average tortuosity is 6.05 in the total cathode electrode. The results exhibit that the cathode electrode has an inhomogeneous microstructure.

(a) porosity

(b) tortuosity in x axial direction

(c) specific interfacial area

Fig. 2 Geometric properties of subdomains in the cathode electrode microstructure

(a) OCP curve[20]

(b) discharge curves

(c) charge curves

Fig. 3 LiCoO_2 OCP curve and the discharge and charge curves from 3D model and corresponding pseudo 2D model at 1 C and 5 C rates.

(a) Li ion concentration in LiCoO_2 (mol/mm^3)

(b) Li ion concentration in electrolyte (mol/mm^3)

(c) reaction current density at the interface (A/mm^2)

Fig. 4 Distributions of concentration and reaction current density at 1600 s and 3200 s respectively at 1 C discharge rate, the left one is at 1600 s and the right one is at 3200 s.

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2 With the half cell model shown in Fig. 1, the galvanostatic discharge and charge
3 processes were simulated. The simulated charge and discharge profiles at 1 C rate and 5 C
4 rates at the temperature 298.15 K are shown in Fig. 3. The two red points on the OCP curve
5 indicate the starting OCP for the discharge and charge processes respectively. The current
6 density corresponding to 1 C rate is 1.88×10^{-5} A/mm². In battery modeling field, it has been
7 accepted that pseudo 2D model can give relatively correct results at low discharge or charge
8 rate. As shown in Fig. 3, the results from the 3D model and pseudo 2D model are similar. In
9 this study, the results of pseudo 2D model at 1 C rate can serve as a validation for the 3D
10 model.
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19 **3.1 1 C discharge and charge**

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21 Due to microstructural inhomogeneity, the physical and electrochemical processes in the
22 electrode are inhomogeneous. Fig. 4 shows the inhomogeneous distribution of Li ion
23 concentration and reaction current density in the cathode electrode at 1600 sec and 3200 sec at
24 1 C discharge rate. Fig. 4(c) shows that the electrochemical reaction is concentrated in the
25 fore group with small porosity at the end of discharge. Due to Li ion consumption by this
26 concentrated reaction, Li ion concentration in electrolyte is much lower in the fore group at
27 3200 sec. Based on the simulation results, average Li ion concentration and reaction current
28 density in each subdomain were calculated, which are shown in Fig. 5.
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(a) 3D model

(d) pseudo 2D model

Li ion concentration in LiCoO_2

(b) 3D model

(e) pseudo 2D model

Li ion concentration in electrolyte

(c) 3D model

(f) pseudo 2D model

reaction current density at the interface

Fig. 5 Average variables in each subdomain inside cathode electrode at 1 C discharge rate (The solid lines stand for the fore group while the dashed lines stand for the back group)

Fig. 5(a) reveals that the porosity, specific interfacial area, and state of discharge (SOD) have important effects on the average Li ion concentration distribution in active materials. In general, the specific interfacial area determines the average Li ion concentration in cathode active material if the intercalation reaction rate is uniform. During the discharge process, the Li ion concentration in active material increases. Fig. 5(a) shows that the fore group with smaller specific interfacial area has smaller concentration in cathode active material than the back group with larger specific interfacial area. The largest concentration difference is $4.91 \times 10^{-6} \text{ mol / mm}^3$ at SOD 0.67 between subdomain 4 and subdomain 6. However, the intercalation reaction rate is not uniform in an inhomogeneous electrode microstructure. Among the fore group, although subdomains 1 and 2 have the similar specific interfacial area, subdomain 2 has the largest concentration due to its local largest porosity. Among the back group, subdomains 5 and 7 have the similar specific interfacial area, but subdomain 5 has higher concentration due to its local larger porosity. SOD also has effect on Li ion concentration. At the beginning of discharge process, all subdomains have similar intercalation reaction rate. The subdomains with higher specific interfacial area will have larger Li ion concentration on the cathode active material surface. As shown in Fig. 3, from SOD 0 to about 0.4, OCP changes rapidly with Li ion concentration. Higher Li ion concentration will cause OCP to decrease more. According to equation 1, the overpotential will also decrease and it will cause intercalation reaction rate to decrease. This is the negative feedback mechanism that we have discussed in our previous publication [15]. Because the Li ion concentration at the surface of cathode active material enters the plateau period earlier than that of the interior, the SOD about from 0.4 to 0.8 becomes the actual plateau period. Because the OCP keeps almost constant during the period, the negative feedback mechanism disappears and the concentration difference will increase. After SOD 0.8, the OCP changes with Li ion concentration rapidly again, the negative feedback mechanism will make Li ion concentration in each subdomain converge to almost the same value at the end of discharge process. The structural effect on Li ion concentration in active material will be intensified during the plateau period and will be weakened during the other periods.

Fig. 5(b) exhibits that Li ion concentration in electrolyte deviates from the initial value of $1.0 \times 10^{-6} \text{ mol / mm}^3$. The concentration of the back group in electrolyte exceeds the initial value while fore group's concentration declines due to the position in the direction of Li ion transport and the Li ion consumptions of electrochemical reaction. However, the concentration of the fore group deviates from the initial value much more than that of the back group. It is because of the smaller porosity and larger tortuosity of the fore group and the Li ion concentration gradient generated as the motivation of Li ion diffusion during discharge

process. Generally, small tortuosity means low resistance for Li ion transport and more Li ions tend to flow through that path. The porosity determines the total electrochemical reaction current in each subdomain and also has an effect on the concentration distribution in electrolyte. Fig. 2 and Fig. 5(b) also show that the tortuosity determines the concentration in electrolyte at the same distance away from the separator. For example, among the fore group, subdomain 2 has the largest porosity so that its concentration changes least away from the initial value. At the same time, subdomain 4 has the smallest porosity among the fore group but its concentration is larger than those of subdomains 1 and 3 because of its smaller tortuosity. Therefore, the porosity and tortuosity tend to act on the ionic transport in electrolyte together rather than only the porosity or the tortuosity.

The average electrochemical reaction current density in each subdomain is not uniform as shown in Fig. 5(c). In our mathematical model, the values of overpotential and reaction current density are negative during the discharge process. The absolute value determines the magnitude of overpotential and intercalation reaction current density. At the beginning of discharge process, the cathode active material is imposed a uniform concentration. The electrolyte potential descends along the Li ion transport direction. Therefore, the fore group has a smaller overpotential than the back group according to equation 3. It leads to smaller reaction current density of the fore group according to equation 1. Because the fore group's porosity and specific interfacial area are smaller, the Li ion concentration of fore group in cathode active material increases slower, which makes the fore group's OCP descend less. Soon after, the OCP difference between the two groups exceeds the electrolyte potential difference. Therefore, the overpotential of the fore group becomes larger than that of the back group. So does the reaction current density. The higher reaction current density in subdomains with low porosity can help to maintain Li ion concentration uniformity. When the subdomains enter the OCP plateau period, the OCP difference between two groups becomes less and then the differences of overpotential and reaction current density incline to reduce. Due to the difference of porosity, the difference of Li ion concentration in the two groups will increase, as shown in Fig. 5(a). After the subdomains leave the OCP plateau, the back group with high porosity will have smaller reaction current density and the fore group with low porosity will have higher reaction current density, so that they will have converged Li ion concentration in cathode active material at the end of discharge process. Because the Li ion concentration at the surface of cathode active material in the back group is approaching the stoichiometric maximum concentration at the end of discharge process, the exchange current density becomes very small according to equation 2. In addition, the intercalation reaction mainly takes place in the subdomains of fore group due to its smaller porosity and corresponding low

Li ion concentration. In order to maintain the total summation of reaction current density of equation 1, the fore group's reaction current density increases steeply. The reaction current density difference between two groups increases significantly at the end of discharge process. Fig. 2 and Fig. 5(c) show that the reaction current density is related to the combination of porosity, SOD and position. When the reaction current density rises, the Li ion concentration in electrolyte descends, and vice versa, as shown in Fig. 5. At the end of discharge process, the fast rise of fore group's reaction current density results in the fast descend of fore group's Li ion concentration in electrolyte as shown in Fig. 5(b). Altogether, it is obvious that the porosity, SOD and position play an important role in the distribution of Li ion concentration and reaction current density.

As shown in Fig. 5, the simulation results of the 3D model with realistic cathode electrode are different from those of pseudo 2D model. It is because pseudo 2D model doesn't take the microstructural inhomogeneity into account. Fig. 5(d) shows that the Li ion concentration in cathode active material of the fore and back groups is almost the same due to the homogeneous structure assumption in pseudo 2D model. Fig. 5(e) shows that the Li ion concentration in electrolyte of the two groups has much smaller difference compared to the 3D model and the difference does not change after its quick establishment at the beginning of discharge. Fig. 5(e) also shows that the Li ion concentration in electrolyte of both groups is below the initial value due to the consumption of Li ion in the electrode. However, Fig. 5(b) shows that the Li ion concentration in the back group of electrolyte is slightly larger than the initial value. It is because the back group has larger porosity and smaller tortuosity than the fore group as shown in Fig. 2. Fig. 5(f) shows that the electrochemical reaction current density of the two groups has some variations over the whole discharge process. It is mainly due to the variation of OCP during the discharge process, which is the same as we discussed for the 3D model result shown in Fig. 5(c). However, the magnitude of the variation is less than 5% of the variation in 3D model. This comparison demonstrates that the microstructural inhomogeneity has significant impact on the electrochemical processes in LIB electrodes.

(a) 3D model

(d) pseudo 2D model

PIT

(b) 3D model

(e) pseudo 2D model

PAER

(c) 3D model

(f) pseudo 2D model

PIT + PEAR over the cathode electrode

Fig. 6 Polarization due to ionic transport and electrochemical reaction in each subdomain inside cathode electrode at 1 C discharge rate and the total polarization in the electrode

The polarization due to ionic transport in electrolyte (PIT) and PAER are shown in Fig. 6. Because the polarization due to electron transport in the cathode active material is much smaller than that in electrolyte, the corresponding polarization is not presented here. Due to the consumption of electrochemical reaction, Li ion concentration in electrolyte decreases in the current density direction. There are two primary factors that affect the polarization due to ionic transport in electrolyte. First, Li ion flows in electrolyte from the back group to the fore group. Second, Li ion flows along the easiest path to participate in electrochemical reaction. That means PIT depends on the position and tortuosity. Basically the ionic current of the back group is larger than that of the fore group. However, because the back group has larger porosity and less tortuosity in the current study, the PIT of the back group is not necessarily larger than that of the fore group. The porosity and tortuosity in Fig. 2 determine that Li ion can easily flow in electrolyte along the straight path from the subdomain 6 to subdomain 2 because of the smallest tortuosity and the largest porosity among their groups. Consequently the PIT of subdomain 6 has the largest value during most of the discharge period. On the contrary, Li ion flows hardly in electrolyte along the straight path from the subdomain 5 to subdomain 1 because subdomain 5 has the largest tortuosity among the back group. Li ion may transport partially from subdomain 2 to other subdomains among the fore group. It should be noticed that Fig. 2(b) doesn't present tortuosity in all orientations but only in the x direction and it is hard to use the tortuosity data in Fig. 2(b) to interpret all the phenomena in Fig. 6(a). At the end of discharge process, Fig. 5(c) shows that the electrochemical reaction is concentrated in the fore group, leading to fast rise of the PIT in subdomains 3 and 4. Similar to the reaction current density mentioned above, the PAER is also primarily determined by the porosity, SOD and position. At the beginning, the PAER of the fore group is lower than that of the back group due to the electrolyte potential. Soon after, the PAER of the fore group exceeds that of the back group because of its smaller porosity. During the plateau period, the PAER of the two groups is close to each other and even the PAER of the back group is slightly larger than that of the fore group at about 2400 sec. At the end of discharge process, the electrochemical reaction mainly takes place in the fore group because of its smaller porosity and specific interfacial area. In addition, the Li ion concentration at the surface of cathode active material is approaching the stoichiometric maximum concentration and the exchange current density in equation 2 becomes very small simultaneously. In order to preserve the total electrochemical reaction rate, the overpotential needs to increase according to equation 1. Both the two factors lead to a steep increase of PAER especially in subdomains 3 and 4 as shown in Fig. 6(b). The inhomogeneous microstructure tends to increase the polarization significantly at the end of discharge process for LiCoO₂ cathode electrode. In addition, at 1 C discharge rate, PAER is much larger than PIT.

Fig. 6(d) shows that the PIT in pseudo 2D model is much smaller than that in 3D model. The PIT of the fore group is much smaller than that of the back group in the pseudo 2D model and the PIT does not change much during the discharge process, which are different from the 3D model results. It is because that the PIT depends on the porosity, tortuosity and position in 3D model but it only depends on position in pseudo 2D model. Fig. 6(e) exhibits that the PAER in pseudo 2D model is also smaller than that in 3D model due to the homogeneity assumption, especially at the end of discharge. Figs. 6(c and f) show the total polarization in the electrode due to PIT and PAER in 3D model and pseudo 2D model, respectively. The microstructural inhomogeneity in the 3D model leads to the larger polarization than pseudo 2D model, especially for PIT. The result demonstrates that the microstructural inhomogeneity has more impact on Li ion transport. Another interesting feature shown in Figs. 6(c and f) is the variation of PIT and PAER during the discharge process. The PIT in 3D model is not monotonic, but it is monotonically increasing in pseudo 2D model. We believe that the microstructural inhomogeneity causes inhomogeneous Li ion transport and electrochemical reaction, which could result in the nonmonotonicity of PIT during the discharge process.

(a) 3D model

(d) pseudo 2D model

Li ion concentration in LiCoO_2

(b) 3D model

(e) pseudo 2D model

Li ion concentration in electrolyte

(c) 3D model

(f) pseudo 2D model

reaction current density at the interface

Fig. 7 Average variables in each subdomain inside cathode electrode at 1 C charge rate (The solid lines stand for the fore group while the dashed lines stand for the back group)

During the charge and discharge processes, Li ion concentration in Fig. 7(a) and Fig. 5(a) are basically symmetric. However, during the charge process, Li ion concentration of the fore group in cathode active material is larger than that of the back group because of its lower porosity. Li ion concentration deviation from its initial value in electrolyte is primarily determined by the position of each subdomain and the tortuosity during the charge process. For instance, subdomain 2 has the lowest tortuosity and the largest porosity among the fore group so that its concentration exceeds its initial value least.

During the charge process, both the overpotential and reaction current density are positive values because of the deintercalation of Li ion from LiCoO_2 . The distribution of reaction current density is different from that during the discharge process. However, the reaction current density is still primarily determined by the porosity, state of charge (SOC), and position of subdomains, which is similar to the discharge process. At the beginning of charge process, the overpotential and reaction current density of the fore group is smaller than that of the back group, which is caused by the electrolyte potential. After that, the overpotential and reaction current density of the fore group becomes larger than that of the back group because of its smaller porosity via the relation of concentration and OCP. However, at the end of charge process, the reaction current density doesn't change steeply because the exchange current density has a comparatively large value according to equation 2. Subdomains in the fore group with smaller porosity will have smaller exchange current density and the subdomains in the back group with larger porosity will have larger exchange current density. Thus the difference of reaction current density between two groups becomes smaller at the end of charge process than that at the end of discharge process.

Figs. 7(d, e and f) exhibit similar phenomena as the 1 C discharge process. The Li ion concentration in cathode active materials and electrolyte and the electrochemical reaction current density of the fore and back groups are almost the same. As we discussed for 1 C discharge, the difference between the results of 3D model and those of pseudo 2D model is due to the microstructural inhomogeneity in 3D model.

(a) 3D model

(d) pseudo 2D model

PIT

(b) 3D model

(e) pseudo 2D model

PAER

(c) 3D model

(f) pseudo 2D model

PIT + PAER over the cathode electrode

Fig. 8 Polarization due to ionic transport and electrochemical reaction in each subdomain inside cathode electrode at 1 C charge rate and the total polarization in the electrode

As shown in Fig. 8, the PAER is also much larger than the PIT at 1 C charge rate. But

there is no steep rise of the polarization of the fore group at the end of charge process because the electrochemical reaction current doesn't increase fast. Instead, there are much larger polarization differences between the subdomains at the beginning of charge process compared to that at the beginning of discharge process. It is because the exchange current density is very small when the initial Li ion concentration in active material particles approaches the stoichiometric maximum concentration according to equation 2. In order to satisfy the specified electrochemical reaction rate, the overpotential must be large. Thus the PAER difference is large as shown in Fig. 8(b), but the reaction current density difference is not large as shown in Fig. 7(c). At the beginning of charge process, the PAER of the back group is larger than that of the fore group because of the electrolyte potential descending along the Li ion transport direction. Hence the Li ion concentration at the surface of cathode active material as well as the exchange current density increases. Therefore the overpotential and PAER descends. After the SOC exceeds the plateau period about from 0 to 0.2 in Fig. 7(c) due to faster increase of Li ion concentration at the cathode active material surface than inside, the PAER of the fore group becomes larger than that of the back group via the relation of concentration and OCP. Since the fore group has larger reaction current density than the back group after the plateau period, the PAER of the fore group rises but the PAER of the back group descends, i.e. at 1600 sec and 2000 sec. And at the end of charge process, the exchange current density approaches the maximum value, the overpotential descends and leads to the decrease of PAER of both the fore group and back group. The negative feedback mechanism between concentration and reaction current density causes PAER to converge like the reaction current density shown in Fig. 7(c). Thus the PAER difference between the fore group and back group tends to decrease at the 3200 sec. Similar to the discharge process, the electrochemical reaction mainly takes place in the fore group especially in subdomain 4 because of its smaller porosity and specific interfacial area. But the PAER difference doesn't become very large due to the relatively large exchange current density. The inhomogeneous microstructure doesn't tend to enlarge the PAER difference between the subdomains at the end of charge process for LiCoO₂ cathode electrode.

Fig. 8(d) shows that the PIT in pseudo 2D model is much smaller than that in 3D model and the PIT of the fore group is much smaller than that of the back group in the pseudo 2D model. Fig. 8(e) exhibits that the PAER in pseudo 2D model is slightly smaller than that in 3D model. As shown in Figs. 8(c and f), the total PIT in 3D model is much higher than that in pseudo 2D model in the 3D model. The PIT in 3D model is not monotonic, but it is monotonically increasing in pseudo 2D model. Same as the 1 C discharge, these phenomena are mainly due to the microstructural inhomogeneity in 3D model.

3.2 5 C discharge and charge

(a) 3D model

(d) pseudo 2D model

Li ion concentration in LiCoO_2

(b) 3D model

(e) pseudo 2D model

Li ion concentration in electrolyte

(c) 3D model

(f) pseudo 2D model

reaction current density at the interface

Fig. 9 Average variables in each subdomain inside cathode electrode at 1 C discharge rate (The solid lines stand for the fore group while the dashed lines stand for the back group)

(a) 3D model

(d) pseudo 2D model

PIT

(b) 3D model

(e) pseudo 2D model

PAER

(c) 3D model

(f) pseudo 2D model

PIT + PAER over the cathode electrode

Fig. 10 Polarization due to ionic transport and electrochemical reaction in each subdomain inside cathode electrode at 5 C discharge rate and the total polarization in the electrode

(a) 3D model

(d) pseudo 2D model

Li ion concentration in LiCoO_2

(b) 3D model

(e) pseudo 2D model

Li ion concentration in electrolyte

(c) 3D model

(f) pseudo 2D model

reaction current density at the interface

Fig. 11 Average variables in each subdomain inside cathode electrode at 5 C charge rate (The solid lines stand for the fore group while the dashed lines stand for the back group)

(a) 3D model

(d) pseudo 2D model

PIT

(b) 3D model

(e) pseudo 2D model

(b) PAER

(c) 3D model

(f) pseudo 2D model

PIT + PAER over the cathode electrode

Fig. 12 Polarization due to ionic transport and electrochemical reaction in each subdomain inside cathode electrode at 5 C charge rate and the total polarization in the electrode

Figs. 9, 10, 11 and 12 exhibit the average variables, PIT and PAER in each subdomain inside cathode electrode for 5 C discharge and charge processes, respectively. In general, the phenomena and mechanisms that cause the phenomena are the same as we discussed for the 1 C discharge and charge results in section 3.1. Here, we want to highlight several important differences between 1 C and 5 C processes. (1) The average variables in the subdomains of 3D model span in a much wider range for 5 C processes, especially for the Li ion concentration in electrolyte and the electrochemical reaction current density. (2) The PIT and PAER in the subdomains of 3D model span in a much wider range for 5 C processes. (3) PIT counts more weight in the total polarization for both 3D model and pseudo 2D model for 5 C processes compared to 1 C processes. (4) At 5 C discharge and charge, PIT starts to count for a significant weight of total polarization in 3D model, but it still not significant in pseudo 2D model. For instance, the PIT counts more than 29% of the polarization at the end of charge in 3D model, but less than 4% in pseudo 2D model.

4. Conclusion

A C++ code was developed to build a half cell LIB model with the reconstructed realistic microstructure of LiCoO_2 cathode electrode. Discharge and charge processes of the half cell LIB was simulated at 1 C and 5 C rates using 3D FVM framework. In order to relate local effects to geometric properties, the cathode electrode is equally divided into 8 subdomains and the geometric properties as well as the average variables and polarization were calculated in each subdomain. The results show that inhomogeneous geometric properties lead to non-uniform distribution of physical and electrochemical variables and polarization. The porosity, specific interfacial area, tortuosity, position and SOD / SOC have significant influence on the average variables and polarization. The PIT could be related to the tortuosity not only in the thickness direction but also in other directions. The PAER is much larger than PIT at 1 C discharge/charge rate. 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. At 5 C processes, the average variables and polarizations in the subdomains of 3D model span in a much wider range and PIT starts to count for a significant weight of total polarization in 3D model. Compared with the results from pseudo 2D model, the results from 3D model show that microstructural inhomogeneity has significant impact on global polarization and results in more inhomogeneous distributions of Li ion concentration, electrochemical reaction, and polarization in the electrode.

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References

- [1] T.M. Bandhauer, S. Garimella, T.F. Fuller, A critical review of thermal issues in lithium-ion batteries, *Journal of The Electrochemical Society*, 158 (2011) R1-R25.
- [2] Y. Chen, J.W. Evans, Heat Transfer Phenomena in Lithium/Polymer-Electrolyte Batteries for Electric Vehicle Application, *Journal of the Electrochemical Society*, 140 (1993) 1833-1838.
- [3] U.S. Kim, J. Yi, C.B. Shin, T. Han, S. Park, Modelling the thermal behaviour of a lithium-ion battery during charge, *Journal of Power Sources*, 196 (2011) 5115-5121.
- [4] V. Srinivasan, C.Y. Wang, Analysis of Electrochemical and Thermal Behavior of Li-Ion Cells, *Journal of The Electrochemical Society*, 150 (2003) A98-A106.
- [5] G.-H. Kim, A. Pesaran, R. Spotnitz, A three-dimensional thermal abuse model for lithium-ion cells, *Journal of Power Sources*, 170 (2007) 476-489.
- [6] V. Ramadesigan, P.W.C. Northrop, S. De, S. Santhanagopalan, R.D. Braatz, V.R. Subramanian, Modeling and Simulation of Lithium-Ion Batteries from a Systems Engineering Perspective, *Journal of The Electrochemical Society*, 159 (2012) R31-R45.
- [7] C. Lim, B. Yan, L. Yin, L. Zhu, Geometric Characteristics of Three Dimensional Reconstructed Anode Electrodes of Lithium Ion Batteries, *Energies*, 7 (2014) 2558-2572.
- [8] D.E. Stephenson, B.C. Walker, C.B. Skelton, E.P. Gorzkowski, D.J. Rowenhorst, D.R. Wheeler, Modeling 3D Microstructure and Ion Transport in Porous Li-Ion Battery Electrodes, *Journal of The Electrochemical Society*, 158 (2011) A781-A789.
- [9] T. Hutzenlaub, S. Thiele, N. Paust, R. Spotnitz, R. Zengerle, C. Walchshofer, Three-dimensional electrochemical Li-ion battery modelling featuring a focused ion-beam/scanning electron microscopy based three-phase reconstruction of a LiCoO₂ cathode, *Electrochimica Acta*, 115 (2014) 131-139.
- [10] L. Zielke, T. Hutzenlaub, D.R. Wheeler, C.-W. Chao, I. Manke, A. Hilger, N. Paust, R. Zengerle, S. Thiele, Three-Phase Multiscale Modeling of a LiCoO₂ Cathode: Combining the Advantages of FIB-SEM Imaging and X-Ray Tomography, *Advanced Energy Materials*, (2014) 1401612.
- [11] G.M.G. Andreas H. Wiedemann, Scott A. Barnett, Huayang Zhu, Robert J. Kee, Effects of three-dimensional cathode microstructure on the performance of lithium-ion battery cathodes, *Electrochimica Acta*, 88 (2013) 580-588.

- [12] W. Wu, X.R. Xiao, M. Wang, X.S. Huang, A Microstructural Resolved Model for the Stress Analysis of Lithium-Ion Batteries, *Journal of the Electrochemical Society*, 161 (2014) A803-A813.
- [13] S.A. Roberts, V.E. Brunini, K.N. Long, A.M. Grillet, A Framework for Three-Dimensional Mesoscale Modeling of Anisotropic Swelling and Mechanical Deformation in Lithium-Ion Electrodes, *Journal of the Electrochemical Society*, 161 (2014) F3052-F3059.
- [14] D.-W. Chung, P.R. Shearing, N.P. Brandon, S.J. Harris, R.E. Garcia, Particle Size Polydispersity in Li-Ion Batteries, *Journal of The Electrochemical Society*, 161 (2014) A422-A430.
- [15] B. Yan, C. Lim, L. Yin, L. Zhu, Three Dimensional Simulation of Galvanostatic Discharge of LiCoO_2 Cathode Based on X-ray Nano-CT Images, *Journal of The Electrochemical Society*, 159 (2012) A1604-A1614.
- [16] B. Yan, C. Lim, L. Yin, L. Zhu, Simulation of heat generation in a reconstructed LiCoO_2 cathode during galvanostatic discharge, *Electrochimica Acta*, 100 (2013) 171-179.
- [17] A. Nyman, T.G. Zavalis, R. Elger, M. Behm, G. Lindbergh, Analysis of the Polarization in a Li-Ion Battery Cell by Numerical Simulations, *Journal of The Electrochemical Society*, 157 (2010) A1236-A1246.
- [18] M. Yoshio, R.J. Brodd, A. Kozawa, *Lithium-ion batteries : science and technologies*, Springer, New York :, 2009.
- [19] C. Lim, B. Yan, L. Yin, L. Zhu, Simulation of diffusion-induced stress using reconstructed electrodes particle structures generated by micro/nano-CT, *Electrochimica Acta*, 75 (2012) 279-287.
- [20] K. Kumaresan, G. Sikha, R.E. White, Thermal Model for a Li-Ion Cell, *Journal of The Electrochemical Society*, 155 (2008) A164-A171.