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Smoothed particle hydrodynamics prediction of effective transport coefficients of lithium-ion battery electrodes

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ABSTRACT

We develop a three-dimensional virtual physical property test platform based on the smoothed particle hydrodynamics (SPH) method for the prediction of the effective transport coefficients, including the effective thermal conductivity, effective electronic conductivity, and effective Li^+ species diffusivity of $LiCoO_2$ electrodes of various microstructures. The three-dimensional microstructure of the $LiCoO_2$ electrode is reconstructed by a sphere-based simulated annealing method. SPH simulation results corroborate that the transport processes are strongly affected by the electrode microstructure. The calculated effective thermal conductivity by SPH model agrees well with the theoretical predictions by a semi-empirical effective medium model, while the effective medium model generally gives smaller effective electronic conductivity of the electrode than the SPH model. Comparing the SPH-predicted effective Li^+ species diffusivity with the commonly-used Bruggeman approximation finds that the latter generally overestimates the effective Li^+ species diffusivity of the electrode. Furthermore, we derive the formation factor of electrolyte phase in the reconstructed electrode. It is found that the formation factors calculated from SPH results are in good agreement with former experimental data.

1. Introduction

Lithium-ion batteries have been extensively used as power sources of mobile electronic devices, and are perceived to be promising alternatives to power sources of electric vehicles and other medium- to large-sized power or energy storage devices owing to advantages, e.g. high energy density and near-zero memory effect [1]. Vital performance of lithium-ion batteries, such as safety, cycle life or capacity, is closely related to the effective transport coefficients, including the effective thermal conductivity, effective electronic (Li^+) conductivity, and effective Li^+ (Li) species diffusivity, of electrodes. These effective transport coefficients are mostly determined by the material intrinsic properties and the microstructure of the electrode. The volume fraction of each component, the particle shape and size distribution of solid active material and the geometrical connectivity of individual component etc. all may have profound impact on the effective transport coefficients [2]. Understanding the correlation of the effective transport coefficients and electrode microstructure is the key to the design and optimization of lithium-ion battery electrode microstructure.

The most straightforward theoretical models for the prediction of effective transport coefficients in heterogeneous multi-component materials are generally some combinations of the classic series and parallel models [3–5]. In these theoretical models, the microscopic configurations in porous materials are simplified or idealized and the obtained effective transport coefficients are only dependent on the volume fraction and bulk transport coefficient of each component. To involve the information of the microscopic configurations in porous materials, Kirkpatrick [6] modified the effective medium theory (EMT) model [7] for the calculation of effective thermal conductivity in two-component materials by introducing a "flexible" factor. Based on a simple "step-process" concept, Jiang and Sousa [8] further extended the Carson EMT model [7] for the calculation of effective thermal conductivity in two-dimensional heterogeneous two- and three-component materials. The determination of "flexible" factor with respect to a particular medium usually resorts to physical experiments or numerical modeling.

Due to the rapid development of computer and computational techniques in recent years, numerical methods have been extensively used to predict the effective transport coefficients of multi-component materials. Numerical prediction of effective transport coefficients of lithium-ion battery electrodes consists of two steps [9,10]. The first step is the reconstruction of the microstructure of the electrode. Electrodes comprise multiple components and are of various complicated microstructures. Experimental technique such as focused ion beam/scanning electron microscopy (FIB/SEM) is competent of three-dimensional reconstruction of electrode microstructures [11–14], but it is costly, time-consuming, and can normally generate a limited volume of electrode. Efforts have been expended to develop or utilize numerical methods for the reconstruction of three-dimensional electrode microstructures [15–20]. Compared with other numerical methods such as the Gaussian random field method [15], the multiple point geostatistical method [16], and the process-based stochastic reconstruction method [17,18], the simulated

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annealing method [19–22] is able to accommodate more statistical information extracted from sample electrodes and the reconstructed electrode is thus more approximate to the real one.

The second step is pore- or particle-scale modeling of relevant transport processes, including the heat transport, the charge (electron in the solid active material and additives and Li^+ in the electrolyte) transport, and the species (Li^+ in the electrolyte and Li in the solid active material) transport. The traditional Eulerian-based numerical methods for predicting the effective transport coefficients of multi-component materials such as finite difference method [23] and finite element method [24] generally require expensive or even prohibitive computational cost when the microstructure of the particular material is too complicated. Therefore the micro/mesoscopic simulation methods for transport in porous media have received increasing attention in recent years. Shoshany et al. [25] determined the effective thermal conductivity of porous materials using the Monte Carlo method. Zhang et al. [26] predicted the effective thermal conductivity of moist porous media through a randomly mixed model. Qian et al. [27] and Wang et al. [10] used two-dimensional five-speed (D2Q5) and nine-speed (D2Q9) lattice Boltzmann models, respectively, to predict the effective thermal conductivity of porous materials. Jiang and Sousa [8] developed a two-dimensional virtual physical property test platform based on a relatively novel numerical technique — smoothed particle hydrodynamics (SPH) method. They found that the effective thermal conductivities of two-dimensional heterogeneous two- and three-component materials predicted by the modified EMT model with the "flexible" factor equal to 4.5 agree well with the SPH predictions [8].

The SPH method has two defining characteristics, meshfree and Lagrangian-based, which make it more advantageous than the traditional Eulerian-based numerical techniques in what concerns the following aspects: (1) particular suitability to tackle multi-disciplinary transport processes, (2) ease of handling complex free surface and material interface, (3) relatively simple computer codes and ease of machine parallelization, and (4) intrinsic transient essence. Application of the SPH method to predict the effective transport coefficients of lithium-ion battery electrodes can fully benefit from these advantages.

One major objective of the present work is to develop a three-dimensional virtual physical property test platform via pore- or particle-scale SPH numerical model, and innovatively employ it to predict the effective transport coefficients of $LiCoO_2$ electrodes of various microstructures. The electrodes were reconstructed by a previously developed sphere-based simulated annealing method [21,22]. The geometrical connectivity of each component inside the reconstructed electrode is analyzed by the cluster analysis algorithm [28]. We will also derive the formation factor of the electrolyte phase in the reconstructed electrode, and explore the correlation of the effective transport coefficients and electrode microstructure.

2. Methodology

2.1. Reconstruction of electrodes

FIB/SEM images clearly identify that there are three components in $LiCoO_2$ cathodes [21,22]: i) $LiCoO_2$ particles as the solid active material, ii) electrolyte (providing pathways for Li^+ species transport and charge transport) filling the pores, and iii) solid additive particles (say, polyvinylidene fluoride, i.e. PVDF, serving as the binder of $LiCoO_2$ particles, and acetylene black, i.e. AB, which has been added for the enhancement of electronic charge transport). Reconstruction of the three-dimensional microstructure in lithium-ion battery electrodes in terms of the sphere-based simulated annealing algorithm consists of five steps [21,22]:

Step 1: Statistical information extraction. Through experimental analysis and/or from FIB/SEM images of a $LiCoO_2$ cathode, the statistical information including the volume fractions of each component, the size distribution of $LiCoO_2$ particles and the two-point correlation functions for the microstructure of the $LiCoO_2$ cathode, can be obtained.

Step 2: Particle-system initialization. Initially, spherical $LiCoO_2$ particles are randomly positioned in an $L_x \times L_y \times L_z$ box to satisfy the desired volume fraction. With the help of a specially designed random number generator, radii of the spheres are specified to follow the real particle diameter distribution curve obtained from the analysis of $LiCoO_2$ material powder. The overlap of spheres is allowed with a probability given by

$$p(v) = \exp\left(-\frac{v}{\varepsilon_v}\right) \tag{1}$$

where v is the ratio of the overlapping volume to the volume of a sphere and ε_v is a constant.

Step 3: New configuration generation. A new configuration is generated by moving a $LiCoO_2$ particle, which is randomly selected from the old list of particles and moved at a displacement $d\mathbf{r}$ (dx, dy, dz). The moving distance in the x direction dx is determined from the following exponential distribution

$$p(dx) = \begin{cases} \dfrac{1}{a_{dx}\varepsilon_{dx}} \exp\left(-\dfrac{dx}{\varepsilon_{dx}}\right) & dx < L_x \\ 0 & dx \geq L_x \end{cases} \tag{2}$$

where $a_{dx} = 1 - \exp(-L_x/\varepsilon_{dx})$, with ε_{dx} being a parameter controlling the distance of the movement. Likewise, the dy and dz can be determined.

Step 4: Choice of new configuration. After a new configuration is generated, the energy difference $\Delta E = E_{new} - E_{old}$ between the two successive states is evaluated, where the energy or error function is defined by

$$E = \sum_{i=1}^{n} \sum_{u=0}^{u=U_i(\max)} \left(f_i(u) - f_i^0(u)\right)^2 \tag{3}$$

where $i = 1, 2, \ldots, n$ denotes the component identity. $f_i(u)$ represents the ith statistical function of a reconstructed system and $f_i^0(u)$ the corresponding reference statistical function; u is a position vector denoting a distance under the isotropic assumption. Each statistical function $f_i(u)$ can be matched to a maximum distance denoted by $U_i(\max)$. This change of the energy (i.e. the particle movement) is accepted with the probability

$$p(\Delta E) = \begin{cases} \exp\left(-\dfrac{\Delta E}{T}\right) & \Delta E > 0 \\ 1 & \Delta E \leq 0 \end{cases} \tag{4}$$

where T is a parameter representing the role of temperature during the real annealing process, which is reduced by a factor of 0.9 successively during the reconstruction process.

Step 5: Repeat step 2 to step 4 until the $f_i(u)$ of the generated configuration matches the target $f_i^0(u)$ within a tolerance limit.

Step 6: Randomly arrange the additives on the surfaces of $LiCoO_2$ particles to satisfy the desired component volume fraction.

With this microstructure reconstruction method, four $LiCoO_2$ electrodes are reconstructed. The reconstructed electrodes all have dimensions of $13.2 \times 13.2 \times 13.2$ μm. The microstructures of the four reconstructed electrodes are displayed in Fig. 1. Three components, the $LiCoO_2$ particles, the electrolyte (pores) and the additive particles are well distinguished. The electrodes have differing spatial distribution of components and micro-pore configurations, as evident by the section cuts (each of a fixed z position) depicted in Fig. 2. The size distribution of $LiCoO_2$ particles inside all the four electrodes follows the Gaussian distribution of 4.5 μm mean particle size, while volume fractions of