Study on Microstructures of Electrodes in Lithium-ion Batteries Using Variational Multi-Scale Enrichment

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Abstract

Performance and degradation of a Li-ion battery reflect the transport and kinetics of related species within the battery's electrode microstructures. The variational multi-scale principle is adapted to a Li-ion battery system in order to improve the predictions of battery performance by including multi-scale and multiphysics phenomena among the particle aggregates in the electrode; this physics cannot be addressed by conventional homogenized approaches. The developed model is verified through the direct numerical solutions and compared with the conventional pseudo-2D (P2D) model method. The developed model has revealed more dynamic battery behaviors related to the variation of the microstructure—such as particle shape, tortuosity, and material composition—while the corresponding result from P2D shows a monotonous change within different structures.

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1. Introduction

One key solution for the challenges related to pollution and transportation energy costs is to replace conventional fuels with cost-competitive and domestically-produced alternatives, such as advanced batteries. The development of an advanced battery, with a corresponding reduction in its cost, requires optimal battery design and battery health management. The optimal battery design allows for minimizing unnecessary components that increase both weight and cost. Also, battery performance and life expectancy are quite dependent on how a battery is used, which means that optimal battery health management can significantly increase the life of a battery and reduce its cost. In particular, current battery systems are substantially oversized for meeting power and energy performance requirements at the end-of-life, which indicates the importance of adequate battery health management.

Optimal battery design and health management via modeling is the most effective way in terms of processing time and cost, compared to experiments. However, modeling tools for these purposes must include appropriate design elements and must be accurate in prediction. In this light, current battery models are not sufficient because they suffer from an important drawback, a lack of detailed morphology of the internal structures of electrodes. Modern battery electrodes involve micro-/nano-composites of ionic storage materials and ionic/electronic conductors. Consequently, battery performance is determined by the local transport of ions and electrons through inhomogeneous internal structures and kinetic reactions at the interfaces among them. These spatial inhomogeneities generate localized fluxes and irregular gradients of species concentration, and eventually different cell voltage responses. Consequently, in order to achieve the best battery performance, a battery designer must control and optimize the species transport path, interface surface area, and kinetic reaction rate. Therefore, a microstructural battery modeling tool is necessary.

Further, the degradation of battery performance is closely related to the composition and structure of the constituent particles in the electrode. Interfacial side reactions and kinetics, interfacial surface areas, mechanical particle networks, and transport phenomena are microphysical processes and therefore are affected by the characteristics of the involved microstructures in the electrodes. As a result, most of the proposed degradation mechanisms in Li-ion batteries—such as active materials dissolution, SEI (solid-electrolyte interphase) layer formation, and mechanical failure—are directly connected to the microstructure of the electrodes [1,2,3,4]. Consequently, it is essential to elucidate the microstructural effects on battery performance and to optimize the microscopic feature in the electrode materials of Li-ion batteries to fully understand the physics inside the cells, and eventually to resolve the given problems.

A Li-ion battery cell can be decomposed into scales of three different lengths: meso-, micro-, and nano-scale. The kinetics and transport phenomena at the micro- and nano-scales must be linked to the meso-scale perspective, including electrode geometry, porosity, and thermal behavior. Generally, the shape of particles in the electrode materials is assumed to be ideal—such as is the case with spheres and ellipsoids [8, 9]. However, the real microstructure of the electrodes involves irregularly shaped particles as reported in [5, 6, 7]; as a result, the transport and kinetics are non-uniform throughout the entire electrode domain. Consequently, the simulation results using such a homogenized model cannot account for the uncertainty of the battery response coming from geometric irregularity at the particle scale.

Several experimental studies have been conducted to investigate the effects of microstructure on battery performance. It has been reported that smaller particles showing larger areas of interface between the solid particle and the electrolyte can enhance capacity [10]. Volume fraction effects on capacity have been conducted by changing the temperature and pressure on the cell [11, 12].

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5 However, all of these studies were limited to reporting *only* the observation—without quantifying the
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7 microstructural features of battery performance. Moreover, those results are limited to specific
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9 materials, which is impractical for an application to battery systems with different materials and
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11 structures.
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16 In the modeling and simulation work, the pseudo 2D (P2D) model [8] has been widely used in
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18 predicting battery performance. This model relies on the continuum-based porous electrode theory,
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20 in which active particles are modeled via a homogenized pseudo 2D approach. This model was
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22 extended to investigate different active material composition effects on power and energy
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24 performance [13], mechanical stress in the particles when the cell is subjected to a mechanical load
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26 [14], and gas evolution influence on battery cell degradation [13]. However, this method is limited to
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28 the study of the homogenized system, and therefore it cannot account for the effects of microscopic
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30 particle percolation and the geometry of the particle on battery cell performance. At the particle
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32 scale, the Li-ion diffusion process coupled with mechanical stress loading was simulated using
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34 thermal analogy volume expansion [9]. The developed electrochemical-mechanical model
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36 predicted that ellipsoidal particles with a smaller volume and a larger aspect ratio are desirable in
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38 terms of the stress level inside the particles. The intercalation-induced stress at the particle scale
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40 was further coupled to crack propagation problems with the following: different particle sizes and
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42 aspect ratios [15], stress distribution on the manganese oxide particle due to the phase transition
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44 [16], and the resistive heat generated by considering particle shape [17]. However, both Li-ion
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46 diffusion processes in the electrolyte and the interaction through the surface of the active particles
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48 are strongly dependent on microstructure geometric connectivity. To represent the microstructural
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50 particle network at the cell-scale, tortuosity is usually employed [18], and the effective properties
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52 based on tortuosity are used in the simulations [19, 20]. Still, this approach cannot account for the
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54 local microscopic particle network.
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5 Some efforts to study the microstructural effect have been made; these include coupling between
6 measurement and modeling. Tomography data were used both to produce the 3D microstructure of
7 a cathode electrode as well as to calibrate electrochemical properties from inhomogeneous
8 cathode particles [21]. A set of 3D full cells with details of microscopic active materials, conductive
9 additives, and electrolytes were used to predict microstructural parameter effects on discharge
10 capacity in [22, 23]. Such models are capable of introducing realistic electrode geometries and of
11 investigating their structural effects on cell performance. However, these models are generally
12 computationally expensive due to the fact that they require a full mesh of the system; they are
13 therefore not feasible for parameter studies or optimizations for improving battery performance.
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26 In order to include the microstructural effect in the Li-ion battery model, a multi-scale framework
27 was established based on a homogenization approach and surrogate-based scale bridging [24].
28 Homogenization resulted in a micro/macro formulation for lithium batteries that was derived by
29 employing a generalized Poisson-Nernst-Planck (PNP) equation set [25]. Wang and co-workers [26,
30 27] used volume-averaged equations and a parabolic profile approximation for solid-phase
31 concentration. This helped reduce the solid-phase partial differential equation to two differential
32 algebraic equations. Nevertheless, an appropriate multi-scale method has not been introduced in
33 the battery field, while fluid mechanics, ceramic matrix composites, heat transfer, and many other
34 areas have successfully adopted macro/micro coupled multi-scale approaches. Generally, the
35 scale-bridging between scales of different lengths using the homogenization approach is based on
36 an assumption that the micro length scale is much smaller than the macro-scale; thus it is assumed
37 that the micro-scale is at a steady state [28]. The Li-ion battery system is investigated using an
38 asymptotic multi-scale model based on the assumption that the length scale is very different
39 between macro and micro [29]. However, the steady state assumption is not applicable in the Li-ion
40 battery system because the length of the electrode is generally several hundreds of micrometers,
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and microscopic active particle aggregation is several tens of micrometers [30]. Therefore, the microscopic particle aggregations cannot be assumed as a point in the cell-scale.

In this study, we adopted the variational multi-scale enrichment method, which is effectively applicable to the multi-scale study of the Li-ion battery system. Unlike conventional multi-scale approaches based on the homogenization method, this method can decompose the scales without assuming scale separation. Also, the transient phenomenon at the micro-scale can be included. Initially, the multi-scale variational formulation was developed in order to find detailed solutions that were missing in the general finite element approximation [31, 32, 33]. Independently, a similar multi-scale framework was developed for the advective-diffusive model as well as for the linearized compressible Navier-Stokes equations; these methods have been shown to stabilize numerical simulations by implementing bubble functions [34, 35]. The approach has been extended to solve incompressible Navier-Stokes equations [36, 37, 38] and has been applied to solid and fluid systems combined with other numerical methods: mesh-free [39, 40], x-FEM and level set [41], and adaptive FEM [42]. By employing the variational multi-scale approach, this paper presents the general procedure of multi-scale modeling, followed by the application to a Li-ion battery system. For verification of the approach, a direct numerical simulation model is developed, and the results are compared with those from the multi-scale model. Numerical simulation results include detailed electrochemical behaviors at the particle scale and microscopic geometric effects on the battery cell performance. Finally, discussions and conclusions related to the numerical model and simulation results are offered.

2. Methods

2.1. Electrochemical Li-ion battery system

The governing equations representing the electrochemical Li-ion battery system are given below:

$$\text{Li-ion mass conservation in solid: } \frac{\partial c_s}{\partial t} + \nabla \cdot \mathbf{q}_s = 0 \quad (1)$$

$$\text{Li-ion mass conservation in liquid: } \frac{\partial c_e}{\partial t} + \nabla \cdot \mathbf{q}_e = 0 \quad (2)$$

$$\text{electronic charge balance: } \nabla \cdot \mathbf{\Gamma}_s = 0 \quad (3)$$

$$\text{ionic charge balance: } \nabla \cdot \mathbf{\Gamma}_e = 0 \quad (4)$$

where subscripts s and e denote the solid phase and the electrolyte phase, respectively. Eq. (1) represents mass balance in the solid phase, and Li-ion flux can be written in terms of the diffusivity tensor ($\mathbf{D}_s$) and the Li-ion concentration (c_s) as:

$$\mathbf{q}_s = -\mathbf{D}_s \nabla c_s \quad (5)$$

In the electrolyte, the Li-ion flow is given in the equation below:

$$\mathbf{q}_e = -\mathbf{D}_e \nabla c_e - \frac{\mathbf{i}_e (1-t_+)}{F} \quad (6)$$

where c_e is the Li-ion concentration, F is Faraday's constant, and t_+ is the transference number.

In the equation, the Li-ion flux is driven by the concentration gradient proportional to the diffusion coefficient ($\mathbf{D}_e$), and charged Li-ion particles can move freely in the liquid phase. The flow due to this particle's mobility is called species migration, which is derived based on the concentrated solution and binary electrolytes. The current in the electrolytic solution ($\mathbf{i}_e$) and in the solid ($\mathbf{i}_s$) are given based on Ohm's law as:

$$\mathbf{\Gamma}_s = \mathbf{i}_s = -\mathbf{K}_s \nabla \phi_s \quad (7)$$

$$\mathbf{\Gamma}_e = \mathbf{i}_e = -\mathbf{K}_e \nabla \phi_e + \frac{2RT}{F} (1-t_+) \mathbf{K}_e \nabla (\ln c_e) \quad (8)$$

in which R is the gas constant, and T is the temperature. The measures of the potential in both the solid and electrolyte are represented by ϕ_s and ϕ_e , respectively. Due to the potential gradients, electrons and ions flow through the conductive media; this conduction is characterized by the conductivities ($\mathbf{K}_s$ and $\mathbf{K}_e$), which are dependent on the materials composing the electrode. In addition to the ionic conduction in the electrolyte, Li-ion particles carry the current as described in Eq. (6). The current can be computed when the transference number (t_+) is known.

On the interface between the solid particle and electrolyte (S^I), the Li-ion (de-) intercalation rate can be defined as:

$$\mathbf{J} \cdot \mathbf{n}^I = j \quad (9)$$

where $\mathbf{n}^I$ is the normal vector on the particle surface, and j is calculated using the Butler–Volmer equation:

$$j = i_0 \left\{ \exp\left(\frac{\alpha_a \eta F}{RT}\right) - \exp\left(-\frac{\alpha_c \eta F}{RT}\right) \right\} \quad (10)$$

in which η is the overpotential, and i_0 is the exchange current density. The overpotential is dependent on the equilibrium potential, E_0 , which is an empirical quantity carried out experimentally and written as:

$$\eta = \phi_s - \phi_e - E_0 \quad (11)$$

The exchange current density is a function of Li-ion concentrations at solid phase C_s , electrolyte phase C_e , and maximum solid phase Li-ion concentration C_t :

$$i_0 = k c_e^{\alpha_a} (c_t - c_s)^{\alpha_a} c_s^{\alpha_c} \quad (12)$$

where k , α_a , and α_c are reaction constants, and their values are dependent on materials.

At the electrode boundary, prescribed cell potential and electronic flux are given as:

$$\phi_s = \phi_s^D \text{ on } \partial\Omega_D \quad (13)$$

$$\mathbf{\Gamma}_s \cdot \mathbf{n} = -i_{\text{apply}} \text{ on } \partial\Omega_N \quad (14)$$

in which subscriptions D and N denote Dirichlet and Neumann boundary conditions, respectively, and $\partial\Omega$ denotes the boundary of domain Ω . Since the electrolyte is physically insulated by the current collector, no ionic Li-ion flux and ionic current flow are assumed:

$$\mathbf{q}_e \cdot \mathbf{n} = 0 \text{ on } \partial\Omega_N \quad (15)$$

$$\mathbf{\Gamma}_e \cdot \mathbf{n} = 0 \text{ on } \partial\Omega_N \quad (16)$$

2.2. Variational multi-scale enrichment for the Li-ion battery

In this section, the following procedure shows how to derive a variational multi-scale model from the governing equations (Eqs. (1)-(4)). First, applying the variational principle leads to weak integral equations, such as:

$$\int_{\Omega} w \frac{\partial c_s}{\partial t} d\Omega - \int_{\Omega} \nabla w \cdot \mathbf{q}_s d\Omega = - \int_{S'} w \frac{1-t_+}{F} j dS' \quad (17)$$

$$\int_{\Omega} w \frac{\partial c_e}{\partial t} d\Omega - \int_{\Omega} \nabla w \cdot \mathbf{q}_e d\Omega = \int_{S'} w \frac{1-t_+}{F} j dS' \quad (18)$$

$$\int_{\Omega} \nabla w \cdot \mathbf{\Gamma}_s d\Omega = - \int_{S'} w j dS' \quad (19)$$

$$\int_{\Omega} \nabla w \cdot \mathbf{\Gamma}_e d\Omega = \int_{S'} w j dS' \quad (20)$$

where field variables (c_s, c_e, ϕ_s , and ϕ_e) and a weight function, w , reside in the functional spaces

$\mathbf{S}$ and $\mathbf{V}$, respectively. These spaces are defined with respect to Hilbert spaces (H^1) as:

$$\mathbf{S}([\cdot]) = \left\{ [\cdot] \in H^1(\Omega) \mid [\cdot] = [\cdot]^D \text{ on } \partial\Omega_D \right\} \quad (21)$$

$$\mathbf{V} = \left\{ w \in H^1(\Omega) \mid w = 0 \text{ on } \partial\Omega_D \right\}$$

in which $[\cdot]$ can be c_s , c_e , ϕ_s , and, ϕ_e . The weak form equation can be rewritten by introducing

abstract notation such as:

$$\langle w, \dot{c}_s \rangle_{\Omega} + a(w, \mathbf{q}_s)_{\Omega} = \left\langle w, -\frac{1-t_+}{F} j \right\rangle_{S'} \quad (22)$$

$$\langle w, \dot{c}_e \rangle_{\Omega} + a(w, \mathbf{q}_e)_{\Omega} = \left\langle w, \frac{1-t_+}{F} j \right\rangle_{S'} \quad (23)$$

$$a(w, \mathbf{\Gamma}_s)_{\Omega} = \langle w, -j \rangle_{S'} \quad (24)$$

$$a(w, \Gamma_e)_\Omega = \langle w, j \rangle_{S^t} \quad (25)$$

where the abovementioned symbol dot denotes the time derivative. The abstract equations above can be defined as:

$$\langle w, f \rangle_{[\cdot]} = \int_{[\cdot]} w f d[\cdot] \quad (26)$$

$$a(w, \Gamma)_{[\cdot]} = - \int_{[\cdot]} \nabla w \cdot (\Gamma) d[\cdot] \quad (27)$$

Next, we introduce a domain accompanying the physics. In order to model details of the microscopic geometry, the domain is partitioned into coarse and fine domains as:

$$\Omega = \bar{\Omega} \oplus \tilde{\Omega} \quad (28)$$

where the over-line denotes the coarse domain, and the over-tilde refers to the fine domain. Figure 1 (a) shows a 2D schematic illustration of the decomposition. The engineering viewpoint investigation will take place at the coarse scale while microscopic heterogeneous phenomena can be represented at the fine scale so that the micro domain is composed of different materials with different volumes (Figure 1 (b)):

$$\tilde{\Omega} = V^s \cup V^e \cup \dots \quad (29)$$

In this approach, it is noted that the fine domain is not assumed to be a point in the coarse domain; instead, it is a portion of the coarse domain so that the multi-scaled portion of the coarse domain exactly coincides with its counterpart microscopic model.

Because the domain is decomposed, the field variable is also decomposed into coarse and fine quantities:

$$\bar{c}_e, \bar{\phi}_s, \bar{\phi}_e : \text{macro solution at } \bar{\Omega} \quad (30)$$

$\tilde{c}_s, \tilde{c}_e, \tilde{\phi}_s, \tilde{\phi}_e$: micro solution at $\tilde{\Omega}$

such that

$$c_s = \tilde{c}_s \quad (31)$$

$$c_e = \bar{c}_e + \tilde{c}_e \quad (32)$$

$$\phi_s = \bar{\phi}_s + \tilde{\phi}_s \quad (33)$$

$$\phi_e = \bar{\phi}_e + \tilde{\phi}_e \quad (34)$$

Since the solid phase Li-ion concentration remains in the fine domain, the c_s does not need to be multi-scaled. Plugging the decomposed variables into weak equations leads to:

$$\langle \tilde{w}, \dot{\tilde{c}}_s \rangle_{\Omega} + a(\tilde{w}, \mathbf{q}_s)_{\Omega} = \left\langle \tilde{w}, -\frac{1-t_+}{F} j \right\rangle_{S^I} \quad (35)$$

$$\langle \bar{w} + \tilde{w}, \dot{\bar{c}}_e + \dot{\tilde{c}}_e \rangle_{\Omega} + a(\bar{w} + \tilde{w}, \mathbf{q}_e)_{\Omega} = \left\langle \bar{w} + \tilde{w}, \frac{1-t_+}{F} j \right\rangle_{S^I} \quad (36)$$

$$a(\bar{w} + \tilde{w}, \mathbf{\Gamma}_s)_{\Omega} = \langle \bar{w} + \tilde{w}, -j \rangle_{S^I} \quad (37)$$

$$a(\bar{w} + \tilde{w}, \mathbf{\Gamma}_e)_{\Omega} = \langle \bar{w} + \tilde{w}, j \rangle_{S^I} \quad (38)$$

where it is assumed that flux terms $\mathbf{q}$ and $\mathbf{\Gamma}$ are non-linear for the generic applications. Since the weak equation is bilinear, the equation can be separated into equations corresponding to the coarse and fine domains as:

$$\langle \tilde{w}, \dot{\tilde{c}}_s \rangle_{\tilde{\Omega}} + a(\tilde{w}, \mathbf{q}_s)_{\tilde{\Omega}} = \left\langle \tilde{w}, -\frac{1-t_+}{F} j \right\rangle_{\tilde{S}^I} \quad (39)$$

$$\langle \bar{w}, \dot{\bar{c}}_e \rangle_{\bar{\Omega}} + a(\bar{w}, \mathbf{q}_e)_{\bar{\Omega}} = \left\langle \bar{w}, \frac{1-t_+}{F} j \right\rangle_{\bar{S}^I} - \langle \bar{w}, \dot{\bar{c}}_e \rangle_{\bar{\Omega}} \quad (40)$$

$$\langle \tilde{w}, \dot{\tilde{c}}_e \rangle_{\tilde{\Omega}} + a(\tilde{w}, \mathbf{q}_e)_{\tilde{\Omega}} = \left\langle \tilde{w}, \frac{1-t_+}{F} j \right\rangle_{\tilde{S}^I} - \langle \tilde{w}, \dot{\tilde{c}}_e \rangle_{\tilde{\Omega}} \quad (41)$$

$$a(\bar{w}, \Gamma_s)_{\bar{\Omega}} = \langle \bar{w}, -j \rangle_{\bar{S}^I} \quad (42)$$

$$a(\tilde{w}, \Gamma_s)_{\tilde{\Omega}} = \langle \tilde{w}, -j \rangle_{\tilde{S}^I} \quad (43)$$

$$a(\bar{w}, \Gamma_e)_{\bar{\Omega}} = \langle \bar{w}, j \rangle_{\bar{S}^I} \quad (44)$$

$$a(\tilde{w}, \Gamma_e)_{\tilde{\Omega}} = \langle \tilde{w}, j \rangle_{\tilde{S}^I} \quad (45)$$

In the decomposed equations, coupled variables from the coarse and fine domains appear in the last term in Eqs. (40) and (41). These force terms involve corrections of the physics coming from the counterpart domain; because the domain is decomposed, each domain is complementary via those two terms.

At the fine scale, the domain is composed of the solid phase of active particles and the liquid phase of the electrolyte. However, the coarse scale is assumed to be homogenized from the fine scale. In order to observe this homogenized response, a volume-averaging scheme is applied to the equations at the coarse scale. Based on the macro equations derived in [24], Eqs. (40), (42), and (44) can be converted as:

$$\langle \bar{w}, \dot{\bar{c}}_e \rangle_{\bar{\Omega}} + a(\bar{w}, \bar{\mathbf{q}}_e)_{\bar{\Omega}} = \left\langle \bar{w}, \frac{1-t_+}{F} \bar{j} \right\rangle_{\bar{\Omega}} - \langle \bar{w}, \dot{\bar{c}}_e \rangle_{\bar{\Omega}} \quad (46)$$

$$a(\bar{w}, \bar{\Gamma}_s)_{\bar{\Omega}} = \langle \bar{w}, -\bar{j} \rangle_{\bar{\Omega}} \quad (47)$$

$$a(\bar{w}, \bar{\Gamma}_e)_{\bar{\Omega}} = \langle \bar{w}, \bar{j} \rangle_{\bar{\Omega}} \quad (48)$$

where $\bar{\mathbf{q}}_e$, $\bar{\Gamma}_s$, and $\bar{\Gamma}_e$ calibrate the macroscopic electrolyte phase Li-ion mass flux, electronic charge current, and ionic charge current in terms of the effective transport parameters as shown below:

$$\bar{\mathbf{q}}_e = -\bar{\mathbf{D}}_e \nabla c_e - \frac{\bar{\Gamma}_e (1-t_+)}{F} \quad (49)$$

$$\bar{\Gamma}_s = -\bar{\mathbf{K}}_s \nabla \phi_s \quad (50)$$

$$\bar{\Gamma}_e = -\bar{\mathbf{K}}_e \nabla \phi_e + \frac{2RT}{F} (1-t_+) \bar{\mathbf{K}}_e \nabla (\ln c_e) \quad (51)$$

In the study of Li-ion batteries, the effective diffusivity and conductivity for each phase is used by introducing Bruggeman's relations based on the material porosity (ϵ) as:

$$\bar{\mathbf{D}}_i = \epsilon_i^n \mathbf{D}_i \quad (52)$$

$$\bar{\mathbf{K}}_i = \epsilon_i^n \mathbf{K}_i \quad (53)$$

where i can be s or e for the solid phase and electrolyte phase, respectively. The use of this simplified relationship generally cannot account for the microstructural particle network effects on the species transports when the microstructures have the same porosity and different structures. However, the macro equations are coupled with micro models via force terms as derived in Eqs. 40 to 41. The macro solution can be corrected, and the multi-scale model is still applicable to the study of Li-ion batteries regarding microscopic phenomena.

Weak equations at the coarse scale include the source of the flux due to the Li-ion intercalations, which is volume-averaged from the micro model in Eqs. (49), (50), and (51). In general, by assuming that active material aggregates in the electrode are composed of spherical particles and are distributed uniformly, the genuine Li-ion flux on the particle surface is computed by multiplying a modification factor named specific surface area S_a :

$$\bar{j} = S_a j \quad (54)$$

where S_a is defined as the surface area divided by the particle volume such that the specific surface area as a function of porosity (ϵ_s) can be written as:

$$S_a = \frac{3\epsilon_s}{r} \quad (55)$$

where r is the particle radius. However, the microstructure includes convex and concave geometries even though the aggregation of the active particles is composed of spherical particles, and even though the generalization of the specific surface area as a function of porosity cannot capture uncertainty due to the microstructural percolation. Therefore, in order to insure the mass conservation from micro to macro, a volume-averaging scheme is used to obtain S_a :

$$S_a = \frac{1}{V} \int_{\tilde{S}^I} 1 d\tilde{S}^I \quad (56)$$

Considering the domain decomposition as well as solving micro problems, the idea of the residual free bubbles is used to set up the micro-scale boundary conditions because of the discontinuities across the enriched domain boundaries. At the micro-scale, homogeneous zero values of the Dirichlet boundary condition are enforced at the boundary overlapping with coarse mesh ($\bar{\Omega}_D$) in order to ensure the field variable continuity as:

$$\tilde{c}_e = 0 \text{ on } \partial\tilde{\Omega}_D \quad (57)$$

$$\tilde{\phi}_s = 0 \text{ on } \partial\tilde{\Omega}_D \quad (58)$$

$$\tilde{\phi}_e = 0 \text{ on } \partial\tilde{\Omega}_D \quad (59)$$

In this study, the COMSOL Multiphysics software package is used to implement the equations and simulate the Li-ion battery system. Readers interested in a detailed derivation of the discretized variation multi-scale model for the Li-ion battery system are referred to Appendix A.

2.3. Numerical model for a Li-ion battery system

In this work, the microstructure of active particles is generated randomly. The radius of the particles is 8 μm , and the size of the aggregate is $37.6 \times 37.6 \times 37.6 \mu\text{m}^3$. The number of the particles is varied according to the set of the volume fraction, which is in the range of 0.2 and 0.7. As the position of each particle is determined, 3D geometry is generated using Autodesk Inventor 9.0. Finally, the mesh is generated using Patran 2008 R2. It is essential to examine the effect of mesh size on convergence because the multi-scale simulation result is quite dependent on the quality of the micro-scale mesh. In order to investigate mesh-dependent convergence, the effective diffusion coefficient is evaluated by changing the mesh quality on the same geometry. Based on the homogenization approach [43], the effective diffusion coefficient is evaluated at the steady state. Flux change ($\delta\bar{\mathbf{q}}$) corresponding to a perturbation of the concentration gradient ($\delta\nabla c$) can be expressed as:

$$\delta\bar{\mathbf{q}} = \bar{\mathbf{D}}\delta\nabla c \quad (60)$$

From this relationship, the effective diffusion coefficient ($\bar{\mathbf{D}}$) can be calculated. It can then be used to examine a convergence, which is defined as:

$$\text{convergence} = -\frac{\bar{\mathbf{D}} - \bar{\mathbf{D}}(\text{finer mesh})}{\bar{\mathbf{D}}(\text{finer mesh})} \times 100 \quad (61)$$

Figure 2 (a) shows the convergence of the effective diffusivity with a different number of elements. Since the microscopic geometry involves the convex and concave structures, the material interface cannot be represented exactly by finite grids. As a result, the effective diffusivity can oscillate with different mesh sizes. As the mesh becomes finer, however, the variation of the effective properties becomes smaller. It is found that at least 37,000 elements are required to generate accurate results with a convergence of less than 1%. The same mesh resolution was used for all cases.

In order to verify the VMS model result, a direct numerical simulation (DNS) model is developed. In this model, the whole domain (including active materials and electrolytes) is meshed with the same resolution as the micro-scale VMS model, as shown in Figure 2 (b). In this model, Eq. (1) and Eq. (3) are solved in the solid domain, and Eq. (2) and Eq. (4) are solved in the liquid domain without any assumption. The boundary condition at the interface is given by Eq. (6). Even though the DNS approach is very expensive in terms of computational cost, it solves the governing equations directly, thus providing a good avenue for verifying the developed VMS model. Figure 2 (b) shows the geometry used in the verification, which is composed of one particle cluster of each electrode.

The DNS model has a limitation of being a relatively small scale system due to the full mesh of the system. On the other hand, the VMS approach is quite flexible in selecting the region of fine mesh. In this study, VMS is applied to the cathode electrode while the P2D approach is applied to the anode electrode. As seen in Figure 2 (d), the responses of microstructures are coupled with each corresponding 1D cell level behavior. For mapping between two scales, a scale bridging between the 3D microstructure and the 1D continuous cell (Eq. (62) is for 3D to 2D and Eq. (63) is for 2D to 1D) is introduced as:

$$u(x, y) = \frac{\int_0^{L_z} u(x, y, z) \gamma(x, y, z) dz}{\int_0^{L_z} \gamma(x, y, z) dz} \quad (62)$$

$$u(x) = \frac{\int_0^{L_y} u(x, y) \gamma(x, y) dy}{\int_0^{L_y} \gamma(x, y) dy} \quad (63)$$

where u is the variable that needs to be integrated from 3D to 1D, and L_y and L_z are the bounds of the 3D micro model in the y and z directions, respectively. Because the micro model includes two different material phases (solid and liquid), γ is used to distinguish the phases.

3. Results

For the numerical simulation, we considered the below system:

The material properties and parameters used in the simulations can be found in reference [8].

3.1. Verification and comparison

VMS results are verified by comparing the results from DNS. The geometries used for verification are shown in Figure 2 (b) for DNS and (c) for VMS. The microstructures for the anode and cathode are identically constructed for the sake of convenience. Figure 3 (a) shows the voltage responses corresponding to a 1 C-rate discharge from VMS and DNS. The results from both models are almost identical. In addition to the cell-scale results, the micro-scale Li-ion concentration profile on the particle surface from the VMS is very close to that from the DNS, as shown in Figure 3 (b). Even though the number of elements in the VMS model (74,984 elements) is smaller than the number in the DNS model (82,375 elements), the predicted behavior at the cell-scale and particle scale are in good agreement. For the computing time, DNS and VMS took 1,595 seconds and 894 seconds, respectively, when 1 C-rate was used. This comparison demonstrates that the developed

VMS model can precisely predict battery performance, including detailed microstructure with a reduced computational cost.

The results from the VMS model are also compared with the results from the P2D model. The effective properties for the P2D model are extracted from the microstructures used in the VMS model. In the P2D model, the complexity of mass transport in the porous network is reduced to only one effective geometric parameter: tortuosity. The tortuosity of the microstructure is used to obtain the effective properties. In a porous medium, the flow rate (q) can be expressed by

$$\mathbf{q} = -\phi^A(\epsilon) \mathbf{D} \nabla c \quad (64)$$

where D is the diffusion coefficient, ∇c is the concentration gradient, and ϕ^A is the areal porosity [19,20,44]. Here, the areal porosity can be assumed to be a function of volumetric porosity (ϵ) and the tortuosity factor (κ) as:

$$\phi^A = \frac{\epsilon}{\kappa} \quad (65)$$

where the tortuosity factor is computed from the tortuosity:

$$\kappa = \tau^2 \quad (66)$$

From Eqs. (64), (65), and (66), the tortuosity can be calculated by measuring the flux change corresponding to the concentration change.

In [19], tortuosity is given as a function of porosity for the spherical particle packing system as:

$$\tau = \frac{1}{\epsilon^m} \quad (67)$$

Afterward, areal porosity can be expressed in terms of porosity as:

$$\varphi^A = \varepsilon^{1+2m} = \varepsilon^n \quad (68)$$

This equation is generally used in the porous electrode system known as the Bruggeman equations when $n = 1.5$. Based on the above equations, the relationship between tortuosity and n can be found with respect to porosity as:

$$\tau = \sqrt{\varepsilon^{1-n}} \quad (69)$$

Table 1: Effective material properties achieved from the micro model for the 1D-pseudo 2D model simulation

parameter	Unit	Value
solid phase volume fraction	-	0.4104
specific surface area	1/m	1.26×10^5
solid phase tortuosity	-	1.2803
electrolyte phase tortuosity	-	1.2307
ionic diffusivity	m^2/s	1.2307×10^{-11}
electronic conductivity	S/m	0.9514

Table 1 shows the calculated effective properties corresponding to the geometry shown in Figure 2 (d). These values are used in the calculation, which uses the P2D model. The geometry of the target cell is shown in Figure 2 (d). In order to observe clear differences in the response, the only cathode region includes microscopic features.

Figure 4 (a) and (b) show the comparison between the VMS and P2D model in terms of the voltage response (Figure 4 (a)) and Li-ion concentration in the electrolyte (Figure 4 (b)) when the cell is discharged at a rate of 1C (1 C-rate). Although the material properties in the P2D model were extracted from the same geometry as in the VMS model, the resulting responses (the voltage and the Li-ion concentration) are different from two different approaches. Figure 4 (b) shows the time-

dependent Li-ion concentration in the electrolyte. As time goes on, the gap from the two models becomes larger—especially in the cathode region (cell dimension $x \geq 150 \text{ um}$) where microstructures are embedded. This implies that the microscopic feature of the electrode materials plays an important role in determining the battery performance. The local concentration profile in the particle, which cannot be expressed in the P2D model, results in a variation of redox flux at the interface; therefore, the whole battery response changes. Further, the differences between VMS and P2D indicate that one simple value representing the complexity of a microscopic feature in a porous structure, generally expressed by tortuosity, cannot effectively capture microscopic features in Li-ion batteries.

3.2 Microscopic geometry effects on battery performance

The common electrode materials for Li-ion batteries are fabricated by a random mixing of the constituent materials. As a result, the effect of the microstructure on battery performance must be evaluated through a stochastic approach using a set number of microstructures. Figure 5 (a) explores the effects of microstructures with different porosities. As shown, the P2D model overestimates cell capacity even though the pseudo 2D particles update transport properties via volume averaging scheme (as described above). The only parameter representing microscopic features in the P2D model is tortuosity. It is a function of the volume fraction; as a result, the capacity increases monotonously and converges to 15.8 Ah/m^2 , as shown in Figure 5 (b). However, the results from VMS vary more dynamically. Also, capacity decreases when the volume fraction is larger than 0.5. It is thought that a larger volume fraction may lose the inherent advantage of a porous electrode because of a decrease in the interfacial area in which the redox occurs. This is also observed from the difference in the voltage response of the two approaches, as shown in Figure 5 (b). Although two cells have similar volume fractions of 0.54 and 0.55 respectively, the cells show a different discharge curve, and the resultant capacity difference is about 10%.

In order to identify the effects of microstructure on individual effective properties, all of the properties are calculated as a function of the volume fraction of the active material. These values are compared with the effective properties that are calculated from the empirical relationship as:

$$D^{\text{eff}} = \varepsilon^n D \quad (70)$$

where D^{eff} is the effective property, and D is the intrinsic property of the material. This is the common way to calculate the effective properties in the P2D model; $n = 1.5$ is widely used for the porous electrode battery system.

In Figure 5 (c)-(f), each plot includes the effective properties using Eq. (83) where n is obtained from the micro model bounding upper and lower limits. Comparing n from each property, solid diffusivity has a wider range of n , from 0.48 to 1.46, while the electrolyte phase diffusivity and conductivity are in a smaller range from 1.17 to 1.32. It is worth noting that most of the estimated values from the simulations, except for the case of solid phase conductivity, are out-ranged from $n = 1.5$, which is the conventional value. This indicates that the conventional 1.5 value may underestimate the transport properties. It is also observed that the variation of the effective properties in the solid phase is greater than that of the liquid phase. This is probably due to the difference in connectivity.

As the volume fraction increases, solid phase diffusivity and conductivity also increase, while the diffusivity and conductivity of the liquid phase decrease. Therefore, an increase of the active material volume fraction enhances the transport of Li-ions and electrons in the solid phase, but hinders the transport in the electrolyte phase. This competition between the charge and Li-ion transport in these different material phases determines the overall electrochemical behavior in porous electrodes, and eventually the battery cell capacity.

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5 The specific surface area is also a function of the volume fraction. The specific surface area used in
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7 the conventional P2D model is linear with the volume fraction, as shown in Figure 6 (a). The
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9 surface area obtained from the 3D microstructure, however, shows an asymptotic behavior at a
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11 volume fraction of around 0.5. For this reason, as already shown in Figure 5 (a), battery capacity
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13 decreases above a volume fraction of 0.48. Initially, more capacity can be achieved by adding
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15 active material because it can enhance Li-ion diffusion and electron conduction. However, the
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17 increased solid material impedes the transport of ions in the electrolyte; as a result, the contribution
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19 of this addition to the Li-ion redox rate can be saturated (Figure 6 (b)).
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24 Particle isolation is an important issue in terms of energy density and power performance. Particles
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26 can be isolated during the manufacturing process or during cycling, due to mechanical loads. The
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28 approaches based on homogenization cannot capture the local isolation of particles. The
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30 developed VMS can easily be extended to predict this isolation problem. The solid phase Li-ion
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32 diffusion and electronic conduction are set to have no periodic boundary conditions when particles
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34 are connected to particle aggregation with geometrical periodicity. This numerical setting ensures
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36 that the isolated particle model has the same conditions except for particle connectivity. The results
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38 shown in Figure 6 (c) and (d) are from the case of 0.41 volume fraction of the active particle, while
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40 the non-connected particle's volume fraction is 0.03; Figure 6 (c) shows the cell potential during the
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42 1C discharge, and Figure 6 (d) shows the available capacity for Li-ion intercalation into active
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44 materials in the cathode electrode. A small portion of isolated particles results in a slight capacity
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46 drop mainly because the utilization of active material decays due to the lack of available host space
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48 in which Li-ion can be intercalated from the electrolyte during discharging.
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54 Detailed happenings at the particle level can be observed in Figure 7, which shows potential and
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56 Li-ion concentration distribution at the surface of the particles after 2,420 seconds with a 1C
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58 discharge rate. In these 3D microscopic contours, gray-colored areas denote initial states; the initial
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Li-ion concentration is 3900 mol/m^3 , and the solid phase potential is 4.22V except for isolated particles in which potential is not determined. As shown in Figure 7 (a), isolated particles maintain their initial state and do not contribute to the Li-ion redox process since these particles are physically disconnected from the electronic conductions, as shown in Figure 7 (c). As a result, the overall usage of active particles for Li-ion intercalation declines in comparison to the cell without an isolated particle (Figure 7 (b) and (d)).

In this study, it is observed that more of a Li-ion concentration gradient is developed in a cell without isolated particles than in a cell with isolated particles (Figure 7 (b) vs. (a)). This is because Li-ion flows in order to fill more available space since a cell without isolated particles has more room in which Li-ion can be intercalated, as shown in Figure 7 (d). Although a small portion of the particles was disconnected from the particle network, the Li-ion diffusion process was influenced and resulted in a different electrochemical performance. Furthermore, even though the capacity drop is small (as a result of less isolation), the isolation can be increased as batteries are cycled; also, the conductive particles could be isolated due to external load and intercalation-induced stress [45,46,15]. Therefore, the existence of isolated particles can strongly impact the electrochemical performance of the Li-ion battery, and needs to be included in the numerical study in order to properly predict battery cell performance.

4. Discussion

In this work, a stochastic approach is employed in which several random aggregates of particles are used. As studied in [21], the microstructure can be reconstructed from real electrode materials. However, this work also requires repeated measurements to obtain an average value of the random structures. At the micro models, conductive additives are not included, due to an increase in the mesh cost. As much finer mesh grid resolution is required for the conductive additives, a simple overlapping of the particle is done instead of modeling the conductive additives. This

enables us to minimize computational expenses as well as meshing difficulties. This simplification may introduce additional Li-ion flux between particles. However, its effect is not significant because the flux from the outside is much larger than from the neighboring particles. This is verified from a comparison with the P2D model, as shown in Figure 4 (a).

The developed model is based on the multi-scale enrichment approach by adding a micro-scale 3D microstructure into the continuum 1D model. This requires mapping between the 1D and 3D models. To accomplish this, a mean value of the micro quantity in the y and z directions (parallel to current collector) is used in the mapping process. This may reduce the local gradient, especially at a high C rate. However, this would not degrade the model's performance because the gradient in the x direction is the most important factor at high C rates. It can also be verified, as shown in Figure 8 (a and b). Up to 4C, the differences (0.17%) between VMS and DNS are almost negligible.

As described earlier, the conventional effective-value-based approach (such as Bruggeman's relationship) turned out to be inadequate for modeling the microscopic features in battery electrodes. One single value cannot capture the complexity of porous structures. As shown in Figures 4 (a, b), although the effective properties in the P2D model were extracted from the same geometry as the VMS model, the voltage responses and Li-ion concentration were different in each of the two approaches. In order to understand this difference, effective material properties were evaluated as a function of time based on the method described in the method section. Figure 8 (c and d) shows that the effective properties are time dependent, which means it is a function of SOC (state of charge). In particular, the solid phase transport properties are more sensitive to the SOC than to those of the electrolyte phase. It is found that the variation of the effective properties (diffusivity and conductivity) is small in the electrolyte (Figure 8c). However, the variation in the solid phase (Figure 8d) is not negligible; the effective diffusivity and conductivity show 17.9% and 8.5% changes in the values, respectively. This SOC-dependency did not result from the

thermodynamics of mixing the solution, but from microscopic features such as volume fraction (porosity), tortuosity, and specific surface area. In general, the diffusion coefficients for lithium ion battery materials are SOC-dependent. Fick's law relates the diffusive Li flux to the Li concentration gradient through a proportional constant called the Li chemical diffusion coefficient D . This chemical diffusion coefficient indicates the macroscopic Li-ion mobility within the active material. This chemical diffusion coefficient can be decomposed by $D=D^*H$, where D^* is the tracer diffusion coefficient and H is the thermodynamic factor. The trace diffusion coefficient represents a stochastic random walk of Li-ion without thermodynamic influences. The thermodynamic factor describes the deviation from the ideal mixing behavior. Existence of this factor indicated that the diffusivity of the Li-ion can be altered by the thermodynamics of mixing of the solution in a chemical concentration gradient. However, in the current work, a constant chemical diffusion coefficient was used in the VMS model (SOC-dependent values can be used in the model). This clearly indicates that the microscopic feature has a significant impact on material transport. To determine the validity of the material properties of different structures, further investigation is required for so-called uncertainty quantification. The proposed model in this paper allows this type of study that will show uncertainties of the microstructures.

As mentioned in the introduction section, in the multi-scale simulations, the upscaling scheme is critical for correctly solving the related PDEs. If a computational homogenization method was used, based on the homogeneity condition, it is assumed that the difference between scales would be very large (several orders of magnitude). If this assumption is valid, it would be possible to formulate micro scale PDEs at a steady state. However, the scale difference between the cell scale and particle packs is less than 10 times, which means that a computational homogenization cannot be used in the study of the Li-ion battery. On the one hand, the variational multi-scale simulation that can solve two-scale equations concurrently includes transient terms. If the varied multi-scale scheme is used, any microscopic geometry can be used because this method makes connections

between length scales as well as time scales, rather than geometries. Indeed, geometric effects are connected to the physics. Here, the demonstration of DNS is conducted just to verify the proposed VMS model. Including all of the constituent materials in a cell microstructure is not effective and computationally efficient. For instance, there is on the order of 10^{12} microscale particles in a 15-Ah pouch cell. A DNS model has limitations in constructing full geometry and in meshing the constructed geometry. This limitation can be overcome via the developed methodology here, in which a detailed microstructure can be attached to a continuum-based model, as needed, so that microstructural behaviors are evident in battery responses. The size of the microstructure and spatial and temporal management can be adjusted (available in any size, for any location, and at any time). This flexibility will enable us to adjust numerical loading, and to include key micromechanisms that determine cell scale behavior, such as capacity and power performance.

5. Conclusion

Natural microstructure elements such as tortuosity, conductivity, diffusivity, and a specific surface area are key factors in determining battery performance. The conventional approach based on homogenization cannot capture the details of the nature of the microstructure. In this work, a multi-scale simulation tool for Li-ion battery systems is developed by adopting the variational multi-scale principle. This model is capable of evaluating the effects of microscopic features of the electrodes. The developed model was verified by comparing a direct numerical model without any assumption. Next, the results from the multi-scale model are compared with the conventional pseudo-2D model. This reveals several important characteristics related to the microstructures in the electrodes. It is found that the local concentration gradient in the electrode structure plays an important role in the transport of the species. There is a competition between the charge and Li-ion transport in the different material phases, which determines overall battery performance. Also, the exposed

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5 interfacial area between the particle and electrolyte, which is significantly important for estimating
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7 the reaction rate, is not linearly related with respect to the volume fraction of the active material—
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9 which is one of the main assumptions of the conventional approach. Furthermore, this model can
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11 capture the effect of particles' local isolation, which is one of the main mechanical degradation
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13 mechanisms. The existence of isolated active particles from the network affects the transport
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15 process of the species in the solid phase as well as the electrolyte phase. This limits the utilization
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17 of active materials and degrades battery performance.
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Appendix A. Finite element implementation of variational multi-scale model for Li-ion battery

From Eqs. (39) to (48), the coupled weak equations based on the variational multi-scale approach can be solved using the finite element method. Based on Galerkin's formulation, the weak equation is discretized using the following solution approximation:

$$\bar{w}^h = \bar{\mathbf{N}}^T \bar{\mathbf{w}} \in \bar{\mathbf{V}}^h \subset \bar{\mathbf{V}}, \tilde{w}^h = \tilde{\mathbf{N}}^T \tilde{\mathbf{w}} \in \tilde{\mathbf{V}}^h \subset \tilde{\mathbf{V}} \quad [\text{A.1}]$$

$$\tilde{c}_s^h = \tilde{\mathbf{N}}^T \tilde{\mathbf{C}}_s \in \tilde{\mathbf{S}}^h \subset \tilde{\mathbf{S}} \quad [\text{A.2}]$$

$$\bar{c}_e^h = \bar{\mathbf{N}}^T \bar{\mathbf{C}}_e \in \bar{\mathbf{S}}^h \subset \bar{\mathbf{S}}, \tilde{c}_e^h = \tilde{\mathbf{N}}^T \tilde{\mathbf{C}}_e \in \tilde{\mathbf{S}}^h \subset \tilde{\mathbf{S}} \quad [\text{A.3}]$$

$$\bar{\phi}_s^h = \bar{\mathbf{N}}^T \bar{\mathbf{\Phi}}_s \in \bar{\mathbf{S}}^h \subset \bar{\mathbf{S}}, \tilde{\phi}_s^h = \tilde{\mathbf{N}}^T \tilde{\mathbf{\Phi}}_s \in \tilde{\mathbf{S}}^h \subset \tilde{\mathbf{S}} \quad [\text{A.4}]$$

$$\bar{\phi}_e^h = \bar{\mathbf{N}}^T \bar{\mathbf{\Phi}}_e \in \bar{\mathbf{S}}^h \subset \bar{\mathbf{S}}, \tilde{\phi}_e^h = \tilde{\mathbf{N}}^T \tilde{\mathbf{\Phi}}_e \in \tilde{\mathbf{S}}^h \subset \tilde{\mathbf{S}} \quad [\text{A.5}]$$

The vector component of the above equation is defined below:

$$\bar{\mathbf{N}} = \bar{\Psi}(N), \tilde{\mathbf{N}} = \tilde{\Psi}(N), \bar{\mathbf{w}} = \bar{\Psi}(w), \tilde{\mathbf{w}} = \tilde{\Psi}(w) \quad [\text{A.6}]$$

$$\bar{\mathbf{C}}_e = \bar{\Psi}(c_e), \tilde{\mathbf{C}}_e = \tilde{\Psi}(c_e), \tilde{\mathbf{C}}_s = \tilde{\Psi}(c_s) \quad [\text{A.7}]$$

$$\bar{\mathbf{\Phi}}_s = \bar{\Psi}(\phi_s), \tilde{\mathbf{\Phi}}_s = \tilde{\Psi}(\phi_s), \bar{\mathbf{\Phi}}_e = \bar{\Psi}(\phi_e), \tilde{\mathbf{\Phi}}_e = \tilde{\Psi}(\phi_e) \quad [\text{A.8}]$$

and

$$\bar{\Psi}([\cdot]) = \left\{ \begin{bmatrix} \bar{[\cdot]}_1^h \\ \bar{[\cdot]}_2^h \\ \vdots \\ \bar{[\cdot]}_n^h \end{bmatrix} \right\}, \tilde{\Psi}([\cdot]) = \left\{ \begin{bmatrix} \tilde{[\cdot]}_1^h \\ \tilde{[\cdot]}_2^h \\ \vdots \\ \tilde{[\cdot]}_n^h \end{bmatrix} \right\} \quad [\text{A.9}]$$

where N is the piecewise continuous finite element basis function, and n is the number of the node of the finite element grid. The superscript h denotes discretized solutions lying on corresponding nodal points in the finite element grids. The matrix form of the discretized weak equation can be constructed in terms of the approximated solutions as:

$$\tilde{\mathbf{w}}^T \tilde{\boldsymbol{\tau}} \left(\dot{\tilde{\mathbf{C}}}_s \right) = \tilde{\mathbf{w}}^T \tilde{\mathbf{K}}^{CS} + \tilde{\mathbf{w}}^T \tilde{\mathbf{b}}^{CS} \quad [\text{A.10}]$$

$$\overline{\mathbf{w}}^T \overline{\boldsymbol{\tau}} \left(\dot{\overline{\mathbf{C}}}_e \right) = \overline{\mathbf{w}}^T \overline{\mathbf{K}}^{CE} + \overline{\mathbf{w}}^T \overline{\mathbf{b}}^{CE}$$

$$\tilde{\mathbf{w}}^T \tilde{\boldsymbol{\tau}} \left(\dot{\tilde{\mathbf{C}}}_e \right) = \tilde{\mathbf{w}}^T \tilde{\mathbf{K}}^{CE} + \tilde{\mathbf{w}}^T \tilde{\mathbf{b}}^{CE}$$

$$0 = \overline{\mathbf{w}}^T \overline{\mathbf{K}}^{\phi S} + \overline{\mathbf{w}}^T \overline{\mathbf{b}}^{\phi S}$$

$$0 = \tilde{\mathbf{w}}^T \tilde{\mathbf{K}}^{\Phi S} + \tilde{\mathbf{w}}^T \tilde{\mathbf{b}}^{\Phi S}$$

$$0 = \overline{\mathbf{w}}^T \overline{\mathbf{K}}^{\phi E} + \overline{\mathbf{w}}^T \overline{\mathbf{b}}^{\phi E}$$

$$0 = \tilde{\mathbf{w}}^T \tilde{\mathbf{K}}^{\Phi E} + \tilde{\mathbf{w}}^T \tilde{\mathbf{b}}^{\Phi E}$$

where

$$[\dot{\cdot}] = \frac{d}{dt}([\cdot]) \quad [\text{A.11}]$$

and

$$\bar{\tau}_i([\cdot]) = \int_{\bar{\Omega}} \bar{N}_i[\cdot]^h d\bar{\Omega}, \tilde{\tau}_i([\cdot]) = \int_{\tilde{\Omega}} \tilde{N}_i[\cdot]^h d\tilde{\Omega} \quad [\text{A.12}]$$

$$\tilde{K}_i^{CS} = \int_{\tilde{\Omega}} \nabla \tilde{N}_i \cdot \tilde{\mathbf{q}}_s d\tilde{\Omega}, \tilde{b}_i^{CS} = \int_{S^I} \tilde{N}_i \frac{1-t_+}{F} (-j) dS^I$$

$$\bar{K}_i^{CE} = \int_{\bar{\Omega}} \nabla \bar{N}_i \cdot \bar{\mathbf{q}}_e d\bar{\Omega}, \bar{b}_i^{CE} = \int_{\bar{\Omega}} \bar{N}_i \left(\frac{1-t_+}{F} \bar{j} - \dot{\bar{c}}_e^h \right) d\bar{\Omega}$$

$$\tilde{K}_i^{CE} = \int_{\tilde{\Omega}} \nabla \tilde{N}_i \cdot \tilde{\mathbf{q}}_e d\tilde{\Omega}, \tilde{b}_i^{CE} = \int_{S^I} \tilde{N}_i \frac{1-t_+}{F} j dS^I - \int_{\tilde{\Omega}} \tilde{N}_i \dot{\bar{c}}_e^h d\tilde{\Omega}$$

$$\bar{K}_i^{\phi S} = \int_{\bar{\Omega}} \nabla \bar{N}_i \cdot \bar{\Gamma}_s d\bar{\Omega}, \bar{b}_i^{\phi S} = \int_{\bar{\Omega}} \bar{N}_i (-\bar{j}) d\bar{\Omega}$$

$$\tilde{K}_i^{\phi S} = \int_{\tilde{\Omega}} \nabla \tilde{N}_i \cdot \tilde{\Gamma}_s d\tilde{\Omega}, \tilde{b}_i^{\phi S} = \int_{S^I} \tilde{N}_i (-j) dS^I$$

$$\bar{K}_i^{\phi E} = \int_{\bar{\Omega}} \nabla \bar{N}_i \cdot \bar{\Gamma}_e d\bar{\Omega}, \bar{b}_i^{\phi E} = \int_{\bar{\Omega}} \bar{N}_i (\bar{j}) d\bar{\Omega}$$

$$\tilde{K}_i^{\phi E} = \int_{\tilde{\Omega}} \nabla \tilde{N}_i \cdot \tilde{\Gamma}_e d\tilde{\Omega}, \tilde{b}_i^{\phi E} = \int_{S^I} \tilde{N}_i (j) dS^I$$

In the above equations, the index i ranges from 1 to $\bar{n}$ or n , for each domain, respectively. In order to satisfy the equality of Eq. (10) for an arbitrary weight function, the equations are simplified as:

$$\boldsymbol{\tau} \left(\dot{\bar{\mathbf{C}}}_s \right) = \tilde{\mathbf{K}}^{CS} + \tilde{\mathbf{b}}^{CS} \quad [\text{A.13}]$$

$$\bar{\boldsymbol{\tau}} \left(\dot{\bar{\mathbf{C}}}_e \right) = \bar{\mathbf{K}}^{CE} + \bar{\mathbf{b}}^{CE}$$

$$\boldsymbol{\tau} \left(\dot{\tilde{\mathbf{C}}}_e \right) = \tilde{\mathbf{K}}^{CE} + \tilde{\mathbf{b}}^{CE}$$

$$0 = \bar{\mathbf{K}}^{\phi S} + \bar{\mathbf{b}}^{\phi S}$$

$$0 = \tilde{\mathbf{K}}^{\phi S} + \tilde{\mathbf{b}}^{\phi S}$$

$$0 = \overline{\mathbf{K}}^{\phi E} + \overline{\mathbf{b}}^{\phi E}$$

$$0 = \tilde{\mathbf{K}}^{\phi E} + \tilde{\mathbf{b}}^{\phi E}$$

While solving the multi-scale problem, each domain's quantities are called from the counterpart domain because of the coupled complementary terms in Eqs. (39)-(48), and it is needed to communicate two different domain variables concurrently. In order to use values from the counterpart domain, a scale bridging scheme between the two domains is proposed using the linear mapping method. The linear mapping method is defined to map a value from a source domain to a destination domain as a function of positions in micro and macro domains as revealed below:

$$\text{from macro to micro: } \tilde{\overline{[\cdot]}}^h(\mathbf{x}) = \overline{[\cdot]}_{ref}^h + \nabla \overline{[\cdot]}^h \cdot (\mathbf{x} - \mathbf{x}_{ref}) \quad [\text{A.14}]$$

$$\text{from micro to macro: } \overline{[\cdot]}^h(\mathbf{x}) = \sum_{i=1}^n \tilde{N}_i(\mathbf{x}) \tilde{[\cdot]}_i^h$$

where $\tilde{\overline{[\cdot]}}^h$ is the available macroscopic field variable at the micro-scale transferred from the macro-scale, and $\tilde{[\cdot]}$ replaces $\overline{[\cdot]}$ at the micro-scale and vice versa for the usage of $\overline{[\cdot]}^h$ at the macro-scale. The coordinates $\overline{\mathbf{x}}$ and $\tilde{\mathbf{x}}$ represent a point in the macro- and micro-scale, respectively, and subscript *ref* denotes the reference point at the micro-scale. In this study, the macro mesh lies on the boundary of the micro mesh because of the enrichment modeling, as shown in Figure 1(b), and it is assumed that the quantities from the macro are linearly expended onto the micro destination mesh. However, the value bridging from the micro to the macro is accomplished using a linear interpolation of the quantities in an element at the micro-scale.

For the transient Li-ion mass in the solid and electrolyte $\ddot{\mathbf{C}}_s$, $\ddot{\mathbf{C}}_e$, and $\ddot{\mathbf{C}}_e$, the backward Euler method is applied, and constructing a function form of equations leads to:

$$\bar{\mathbf{F}} = \frac{1}{\Delta t} \begin{Bmatrix} \bar{\boldsymbol{\tau}}(\bar{\mathbf{C}}_e^{t+1} - \bar{\mathbf{C}}_e^t) \\ 0 \\ 0 \end{Bmatrix} - \begin{Bmatrix} \bar{\mathbf{K}}^{CE}(\bar{\mathbf{C}}_e^{t+1}, \bar{\mathbf{C}}_e^t, \bar{\boldsymbol{\Phi}}_e^{t+1}, \bar{\boldsymbol{\Phi}}_e^t) \\ \bar{\mathbf{K}}^{\Phi S}(\bar{\boldsymbol{\Phi}}_s^{t+1}, \bar{\boldsymbol{\Phi}}_s^t) \\ \bar{\mathbf{K}}^{\Phi E}(\bar{\mathbf{C}}_e^{t+1}, \bar{\mathbf{C}}_e^t, \bar{\boldsymbol{\Phi}}_e^{t+1}, \bar{\boldsymbol{\Phi}}_e^t) \end{Bmatrix} - \begin{Bmatrix} \bar{\mathbf{b}}^{CE}(\bar{j}, \bar{\mathbf{C}}_e^{t+1}, \bar{\mathbf{C}}_e^t) \\ \bar{\mathbf{b}}^{\Phi S}(\bar{j}) \\ \bar{\mathbf{b}}^{\Phi E}(\bar{j}) \end{Bmatrix} \quad [\text{A.15}]$$

$$\bar{\mathbf{F}} = \frac{1}{\Delta t} \begin{Bmatrix} \tilde{\boldsymbol{\tau}}(\tilde{\mathbf{C}}_s^{t+1} - \tilde{\mathbf{C}}_s^t) \\ \tilde{\boldsymbol{\tau}}(\tilde{\mathbf{C}}_e^{t+1} - \tilde{\mathbf{C}}_e^t) \\ 0 \\ 0 \end{Bmatrix} - \begin{Bmatrix} \tilde{\mathbf{K}}^{CS}(\tilde{\mathbf{C}}_s^{t+1}, \tilde{\mathbf{C}}_s^t) \\ \tilde{\mathbf{K}}^{CE}(\tilde{\mathbf{C}}_s^{t+1}, \tilde{\mathbf{C}}_s^t, \tilde{\boldsymbol{\Phi}}_e^{t+1}, \tilde{\boldsymbol{\Phi}}_e^t) \\ \tilde{\mathbf{K}}^{\Phi S}(\tilde{\boldsymbol{\Phi}}_s^{t+1}, \tilde{\boldsymbol{\Phi}}_s^t) \\ \tilde{\mathbf{K}}^{\Phi E}(\tilde{\mathbf{C}}_s^{t+1}, \tilde{\mathbf{C}}_s^t, \tilde{\boldsymbol{\Phi}}_e^{t+1}, \tilde{\boldsymbol{\Phi}}_e^t) \end{Bmatrix} - \begin{Bmatrix} \tilde{\mathbf{b}}^{CS}(j) \\ \tilde{\mathbf{b}}^{CE}(j, \tilde{\mathbf{C}}_e^{t+1}, \tilde{\mathbf{C}}_e^t) \\ \tilde{\mathbf{b}}^{\Phi S}(j) \\ \tilde{\mathbf{b}}^{\Phi E}(j) \end{Bmatrix} \quad [\text{A.16}]$$

where Δt is the time step size, and $t+1$ and t refer to the time steps such that the problem statement is now finding:

$$\bar{\mathbf{u}} = \langle \bar{\mathbf{C}}_e^{t+1}, \bar{\boldsymbol{\Phi}}_s^{t+1}, \bar{\boldsymbol{\Phi}}_e^{t+1} \rangle^T \quad [\text{A.17}]$$

$$\tilde{\mathbf{u}} = \langle \tilde{\mathbf{C}}_s^{t+1}, \tilde{\mathbf{C}}_e^{t+1}, \tilde{\boldsymbol{\Phi}}_s^{t+1}, \tilde{\boldsymbol{\Phi}}_e^{t+1} \rangle^T \quad [\text{A.18}]$$

satisfying $\mathbf{F} = \langle \bar{\mathbf{F}}, \tilde{\mathbf{F}} \rangle^T = 0$. In order to solve the algebraic non-linear equations, the Newton–Raphson iteration is considered. To find the slope of $\mathbf{F}$ with respect to $\mathbf{u} = \langle \bar{\mathbf{u}}, \tilde{\mathbf{u}} \rangle^T$ at time $t+1$, the Jacobian matrix is constructed as:

$$\mathbf{J} = \begin{bmatrix} \bar{\mathbf{J}} & 0 \\ 0 & \tilde{\mathbf{J}} \end{bmatrix} = \begin{bmatrix} \frac{\partial \bar{\mathbf{F}}}{\partial \bar{\mathbf{u}}} & 0 \\ 0 & \frac{\partial \tilde{\mathbf{F}}}{\partial \tilde{\mathbf{u}}} \end{bmatrix} \quad [\text{A.19}]$$

$$\bar{\mathbf{J}} = \begin{bmatrix} \bar{\mathbf{J}}^{11} & 0 & \bar{\mathbf{J}}^{13} \\ 0 & \bar{\mathbf{J}}^{22} & 0 \\ \bar{\mathbf{J}}^{31} & 0 & \bar{\mathbf{J}}^{33} \end{bmatrix}, \quad \tilde{\mathbf{J}} = \begin{bmatrix} \tilde{\mathbf{J}}^{11} & 0 & 0 & 0 \\ 0 & \tilde{\mathbf{J}}^{22} & 0 & \tilde{\mathbf{J}}^{24} \\ 0 & 0 & \tilde{\mathbf{J}}^{33} & 0 \\ 0 & \tilde{\mathbf{J}}^{42} & 0 & \tilde{\mathbf{J}}^{44} \end{bmatrix}$$

$$\bar{J}_{ij}^{11} = \frac{1}{\Delta t} \int_{\bar{\Omega}} \bar{N}_i \bar{N}_j d\bar{\Omega} - \int_{\bar{\Omega}} \frac{d\bar{N}_i}{d\bar{x}_p} \bar{D}_e^{pq} \frac{d\bar{N}_i}{d\bar{x}_q} d\bar{\Omega} - \frac{(1-t_+)}{F} \bar{J}_{ij}^{31} \quad [\text{A.20}]$$

$$\bar{J}_{ij}^{13} = -\frac{(1-t_+)}{F} \bar{J}_{ij}^{33}$$

$$\bar{J}_{ij}^{22} = -\int_{\bar{\Omega}} \frac{d\bar{N}_i}{d\bar{x}_p} \bar{K}_s^{pq} \frac{d\bar{N}_i}{d\bar{x}_q} d\bar{\Omega}$$

$$\bar{J}_{ij}^{31} = \int_{\bar{\Omega}} \frac{d\bar{N}_i}{d\bar{x}_p} \frac{(1-t_+)}{F} \left\{ -\bar{K}_e^{pq} \frac{d(\bar{c}_e^h + \bar{c}_e^h)}{d\bar{x}_q} \frac{\bar{N}_j}{(\bar{c}_e^h + \bar{c}_e^h)^2} + \frac{\bar{K}_e^{pq}}{c} \frac{d\bar{N}_i}{d\bar{x}_q} \right\} d\bar{\Omega}$$

$$\bar{J}_{ij}^{33} = -\int_{\bar{\Omega}} \frac{d\bar{N}_i}{d\bar{x}_p} \bar{K}_e^{pq} \frac{d\bar{N}_i}{d\bar{x}_q} d\bar{\Omega}$$

$$\tilde{J}_{ij}^{11} = \frac{1}{\Delta t} \int_{\tilde{\Omega}} \tilde{N}_i \tilde{N}_j d\tilde{\Omega} - \int_{\tilde{\Omega}} \frac{d\tilde{N}_i}{d\tilde{x}_p} \tilde{D}_s^{pq} \frac{d\tilde{N}_i}{d\tilde{x}_q} d\tilde{\Omega}$$

$$\tilde{J}_{ij}^{22} = \frac{1}{\Delta t} \int_{\tilde{\Omega}} \tilde{N}_i \tilde{N}_j d\tilde{\Omega} - \int_{\tilde{\Omega}} \frac{d\tilde{N}_i}{d\tilde{x}_p} \tilde{D}_s^{pq} \frac{d\tilde{N}_i}{d\tilde{x}_q} d\tilde{\Omega} - \frac{(1-t_+)}{F} \tilde{J}_{ij}^{42}$$

$$\tilde{J}_{ij}^{24} = -\frac{(1-t_+)}{F} \tilde{J}_{ij}^{44}$$

$$\tilde{J}_{ij}^{33} = -\int_{\bar{\Omega}} \frac{d\bar{N}_i}{d\tilde{x}_p} \tilde{K}_s^{pq} \frac{d\bar{N}_i}{d\tilde{x}_q} d\bar{\Omega}$$

$$\tilde{J}_{ij}^{42} = \int_{\bar{\Omega}} \frac{d\tilde{N}_i}{d\tilde{x}_p} \frac{(1-t_+)}{F} \left\{ -\tilde{K}_e^{pq} \frac{d\left(\tilde{c}_e^h + \tilde{c}_e^h\right)}{d\tilde{x}_q} \frac{\tilde{N}_j}{\left(\tilde{c}_e^h + \tilde{c}_e^h\right)^2} + \frac{\tilde{K}_e^{pq}}{c} \frac{d\tilde{N}_i}{d\tilde{x}_q} \right\} d\tilde{\Omega}$$

$$\tilde{J}_{ij}^{44} = -\int_{\bar{\Omega}} \frac{d\tilde{N}_i}{d\tilde{x}_p} \tilde{K}_e^{pq} \frac{d\tilde{N}_i}{d\tilde{x}_q} d\tilde{\Omega}$$

where $\tilde{D}_s^{pq}$, $\tilde{D}_e^{pq}$, $\tilde{K}_s^{pq}$, and $\tilde{K}_e^{pq}$ are the intrinsic microscopic material properties, and index p and q range from 1 to nsd (number of space dimensions). Since the macroscopic material properties are dependent on the micro model, a volume-averaging scheme is employed to derive effective transport properties $\bar{\chi}_{pq}$ as:

$$\bar{\chi}_{pq} = \frac{1}{V} \int_{\bar{\Omega}} \tilde{\chi}_{pq} d\tilde{\Omega} \quad [\text{A.21}]$$

In this approach, variables in the coarse domain, $\bar{[\cdot]}_{t+1}$, and in the fine domain, $\tilde{[\cdot]}_{t+1}$, are assumed to be independent of one another so that

$$\frac{d\bar{[\cdot]}_{t+1}}{d\tilde{[\cdot]}_{t+1}} = 0 \text{ and } \frac{d\tilde{[\cdot]}_{t+1}}{d\bar{[\cdot]}_{t+1}} = 0 \quad [\text{A.22}]$$

Introducing the iteration step $l+1$ and l for 'next' and 'current', respectively, the iteration will be started from the initial guess of the solution, $\mathbf{u}_0$, and a new solution can be updated using the below equation:

$$\mathbf{u}_{l+1} = \mathbf{u}_l - \mathbf{J}^{-1}(\mathbf{u}_l) \mathbf{F}(\mathbf{u}_l) \quad [\text{A.23}]$$

Here, while the residual ($\mathbf{J}^{-1}\mathbf{F}$) approaches the prescribed criterion, this iteration is repeated.

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Figure Captions

Figure 1: (a) Domain and (b) grid decomposition into coarse and fine scales

Figure 2: (a) Micro mesh convergence as number of element increases, percent change of effective diffusivity decreases due to the mesh variations; Numerical simulation model for (b) direct numerical simulation (DNS) and (c) variational multi-scale simulation (VMS); (d) Variational multi-scale enrichment for the Li-ion battery cell simulation - 1D cathode electrode is coupled with 3D micro models

Figure 3: Comparisons of the 1C-discharge simulation results at the cell-scale and micro-scale: (a) cell potential and (b) li-ion concentration (mol/m^3) in solid phase

Figure 4: (a) cell potential (cut off voltage = 3.0V) obtained from VMS (solid line) and 1D-pseudo 2D model (dotted line); and (b) Li-ion concentration in the electrolyte phase obtained from VMS (lines) and 1D-pseudo 2D model (symbols)

Figure 5: Comparisons of the 1C-discharge simulation results: (a) cell potential vs time and (b) capacity vs active material volume fraction; Microscopic particle network effects on effective parameters: (c)-(f) diffusion and conductivity

Figure 6: (a) Specific surface area of active material exposed to the electrolyte, (b) utilization of active material in cathode electrode at the end of discharge; Comparison between cell with isolated particle and without particles (c) cell potential (V), (d) available capacity where Li-ion can be intercalated

Figure 7: Comparison of Li-ion concentration (initial is 3900 mol/m^3) and electronic charge (initial is 4.22V) between 3D micro model in which the gray-colored area denotes isolated particles; (a) and (c) are modeled with isolated particles, (b) and (d) are modeled without isolated particles respectively

Figure 8: (a) Discharge curves with different c-rates (b) percent capacity differences between VMS and DNS with varying c-rate, (c) normalized effective properties in solid phase, and (d) normalized effective properties in electrolyte phase

Figure 1_a

coarse/macro mesh

fine/micro mesh

Figure 1_b

Figure 2_a

Figure 2_b

Figure 2_c

Figure 2_d

Figure 3_a

Figure 3_b

Figure 4_a

Figure 4_b

Figure 5_a

Figure 5_b

Figure 5_c

Figure 5_d

Figure 5_e

Figure 5_f

Figure 6_a

Figure 6_b

Figure 6_c

Figure 6_d

Figure 7_a

Figure 7_b

Figure 7_c

Figure 7_d

Figure 8_a

Figure 8_b

Figure 8_c

Figure 8_d