

Letter

Evaluation of the Effect of Multiparticle on Lithium-Ion Battery Performance Using an Electrochemical Model

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Dear editor,

This letter focuses on modeling the electrode heterogeneity by extending the pseudo-two-dimensional model (P2D) with actual particle-size distributions (PSD). The effects of different particle characterization techniques, including the area-weighted, volume-weighted, and number-based methods on cell dynamics are compared. The model with number-based PSD achieves better rate capability (maximum 2.0% improvement in capacity, maximum 2.6% increase in energy). Besides, the effectiveness of the multiparticle (MP) model is evaluated against the single-particle model (SPME) and P2D model under fast charging conditions. Results show that the PSD generates greater heterogeneities of cell internal states at higher C-rates current.

Related work: Understanding the microstructural properties of batteries is of considerable significance to cell design in order to optimize the performance of lithium-ion batteries [1]–[3]. Both positive and negative electrodes have complex porous structures composed of electroactive particles of various sizes. This yields a highly heterogeneous system. The multiparticle electrodes have an impact on the cell rate capability [4], mechanical stress [5], and resistive heating [6]. Electrochemical models are effective tools to predict the electrochemical performances of lithium-ion batteries [7]. Incorporating microstructure into battery models can provide design criteria for enhanced battery performance. The PSD can quantify the many-particle effects. In this work, a two-dimensional microstructural model is presented to analyze the impact of PSD on performance.

The Doyle-Fuller-Newman (DFN) model is a classic multi-scale electrode particle to a single cell [8]. The cell-scale electrochemical states, including the potentials and electrolyte lithium concentrations, are coupled across the electrodes to the particle-scale for surface concentration predictions. However, the heterogeneous electrode features consisting of various-sized particles is usually neglected. The PSD of an electrode can be characterized experimentally in different ways concerning the weighting of individual particles. The weighting mechanism depends on the measuring principle being used [9]. A frequency or cumulative distribution curve is commonly used to represent the distribution. Generally, there are three different weighted methods: number-weighted distributions, volume-weighted distributions, and area-weighted distributions [10]. The number weighted distribution is a counting technique where each particle is given equal weighting irrespective of its size. The contribution of each particle in the area and volume-weighted distribution is related to the area and volume of each particle, respectively. Although it is well known that the smaller particles could provide better performances, the influences of the different PSD characterization methods are not investigated.

The PSD of the active material is a fundamental property in Li-ion batteries. However, the impact of different PSD quantification methods on cell performance is scarcely addressed in current research. Hence, in this letter, we aim to use a multiparticle model that considers the PSD of the active material to analyze the performance of cell electrodes. In detail, the negative and positive electrodes are

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described with distributed particle sizes of the active material. The PSD is characterized by three methods: number-weighted, volume-weighted, and area-weighted distributions. The effects of the size of these distributions on the electrode performance were investigated. In addition, the multiparticle model is compared with the single-particle model and P2D model under fast charging protocols to evaluate the advantages of the PSD. Furthermore, the effects of PSD on the surface concentration and current density are explored. This work makes the following contributions:

1) A two-dimensional MP model is presented considering the PSD at two electrodes. The effect of the spread of PSD on the cell rate capability and the electrode dynamics is investigated.

2) The numerical solutions of the MP model for different PSDs, including the number-based, volume-weighted, and area-based methods are presented.

3) A comparative study is carried out between the MP model, single-particle model, and P2D model. The model performances under fast charging are examined.

Problem statement: Usually, the P2D model assumes that the electrodes are macro-homogeneous. The non-uniform distribution of particles leads to an inhomogeneous microstructure within the electrodes. The particle heterogeneity appears on μm length scale. The PSD has different approximation functions. The choice of PSD expressions dramatically impacts the results of local current density distribution. Including the microscale structures would increase the computational cost of the model inevitably. Therefore, selecting the appropriate PSD functions and accounting for the contribution of microstructural heterogeneity in battery macro-homogeneous models is challenging.

Basic concepts: The Newman-type P2D model is extended to include a distribution of active particle sizes. The schematic of the multiscale model is shown in Fig.1. The macroscale geometry of the model is in the cross-section direction of the electrode and denoted as x . The macroscale electrode contains three regions: the negative electrode, separator, and positive electrode, respectively. The thickness of the negative electrode, separator, and the positive electrode is L_n , L_{sep} , and L_p , respectively. The electrolyte-phase variables in three regions are electrolyte potential φ_e , electrolyte concentration c_e . The solid-phase variables are potential φ_s , and current densities i_s . At each macroscale location of the electrodes, a microscale domain consists of solid active material spherical particles. The radius of each particle is denoted as R_k ($R_{k,\min} \leq R_k \leq R_{k,\max}$). The range of particle radius R_k is considered as continuum media. The fraction density of particles with a given radius R_k is defined as particle-size distribution $f(R_k)$, satisfying $\int_0^\infty f_i(R) dR = 1$. $i \in \{n, \text{number-based}; a, \text{area-weighted}; v, \text{volume-based}\}$. $f(R_k)$ represents the probability density function of a particle having radius R_k . It is assumed that the particles of a given size at a given location have the same dynamic response. The internal domain of the particle is $0 \leq r_k \leq R_k$. The particle interfacial current density and lithium-ion concentration are denoted as j_s and c_s , respectively.

Model implementation and computation time: The MP model is implemented by discretizing the spatial dimensions using the finite volume method to convert the system of partial-differential-equations (PDEs) into a system of differential-algebraic equations (DAEs). The separator, negative electrode, positive electrode, and particle radius are discretized with N points. This turns the variables in the model into a state vector, and replaces spatial operators with matrix-vector multiplications, ready to be passed to a time-stepping algorithm. Finally, a solver is used to solve the problem. The model is simulated using Python on a workstation with Intel(R) Xeon(R) Silver 4214R CPU @ 2.40GHz and 16GB RAM. Increasing the number of points in the mesh could obtain more accurate solutions but need longer computational time. For real-time automation applications, it is desirable to solve with an acceptable degree of accuracy but in a shorter computational time. A pure C++ implementation of the models would increase the speed of model simulations. In Table 1, we compare the solutions of the MP model with 5, 10, 20, 30, 40, and 50 points in each domain (negative electrode, separator, positive electrode, negative particle, and positive particle) across the 1C discharge test. The RMS voltage error is calculated with respect to the MP model solution with 100 points in each domain. The key obser-

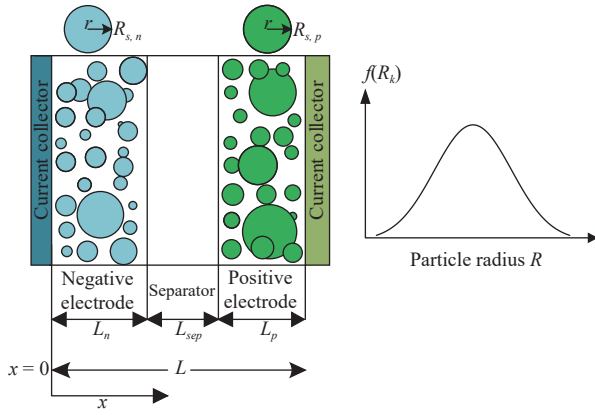


Fig. 1. The structure of multiparticle model (left) and particle radius distribution (right).

Table 1. RMS Voltage Error Relative to the MP Model With 100 x-Grid Points in Each of the Domains: Negative Electrode, Separator, and Positive Electrode; as well as 100 r-Grid Points in the Particles

Number of mesh points	Computation time (ms)	RMS voltage error (mV)
5	561.978	0.2404
10	582.265	0.0566
20	634.321	0.0149
30	681.693	0.0083
40	748.063	0.005
50	827.331	0.0031

vation from Table 1 is that for a relatively small increase in RMS voltage error, a pronounced decrease in computation time is achieved. Further, it is noted that the 30 mesh points increase the MP model's accuracy by an order of magnitude while maintaining a similar computation time compared with 20 mesh points. Therefore, achieving an accurate and fast solution of the MP model for real-time automation applications is feasible by carefully choosing an appropriate partial discretization method and the number of mesh points.

Effects of PSD methods on rate capability: Different means and variances can be defined depending on how the PSD is collected and analyzed. The three most commonly used methods for particle sizing, including the area-weighted, volume-weighted, and number-based are described below. Each particle is given equal weighting for number weighted distributions, irrespective of size. Volume weighted distributions is related to the volume of that particle. Area weighted distribution means that each particle is counted according to its surface area. The particles are assumed to be spherical. The experimental measurements of the PSDs of positive and negative electrode particles are summarized. The lognormal PSDs with the area-weighted, number-based, and volume-based are calculated. Table 2 summarizes the mean and variance of the particle radius with these methods. It can be observed that the volume-based method produces the largest mean particle radius compared with area-weighted and number-based methods. The number-based mean radius is the smallest. The results may differ from the specific electrode design. The effects of different PSD quantification methods on cell rate capability and output energy are studied in Fig. 2. The cell is discharged from 100% SOC to a terminal voltage of 3.1V. As it can be seen in Fig. 2(a), the number-based radius generates the most discharge capacity since the number-based mean particle is smaller. In Fig. 2(b), the number-based mean particle could achieve the best output energy. To evaluate the local current densities across the electrodes for different PSDs, the interfacial current density in the positive electrode j_p and negative electrode j_n for a 1C discharge process are depicted in Fig. 3. The large PSDs current density is almost constant across the positive electrode. However, the current density can be considerably smaller than for larger ones for smaller number-based PSD. This implies that small-scale PSDs show lower internal resistance and provide a higher electrode capacity and energy. The MP model provides insights into the porous structure and PSD, benefiting the design and optimization of micro-structure for electrodes. Therefore, the electrode structures with better cell rate capability could be selected with the help of the MP model, which could improve the dynamic performances of electric vehicles.

Particle parameter	Positive electrode		Negative electrode	
	Mean radius \bar{R} (μm)	Particle variance σ_R (μm)	Mean radius \bar{R} (μm)	Particle variance σ_R (μm)
Area-weighted	5.22	1.74	5.85	1.55
Number-weighted	4.39	1.48	4.93	1.32
Volume-weighted	5.68	1.88	6.37	1.68

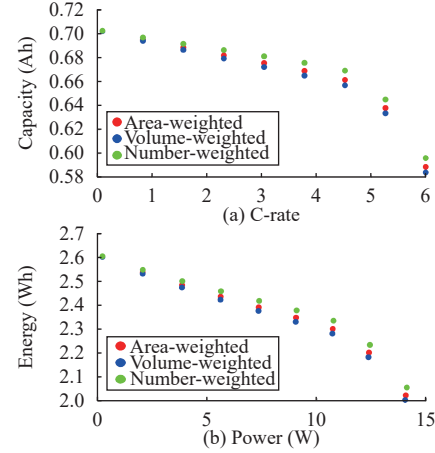


Fig. 2. Cell discharge capacity versus current C-rates with area-weighted, volume-weighted, and number-weighted PSD quantification methods (a). The output energy versus power with area-weighted, volume-weighted, and number-weighted PSD quantification methods (b).

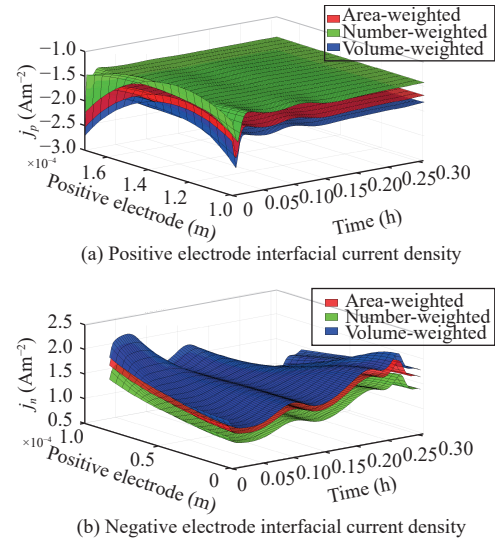


Fig. 3. Interfacial current density across electrodes throughout a 1C discharge test with area-weighted, number-based, and volume-weighted PSD quantification methods. (a) Positive electrode; (b) Negative electrode.

Comparative study between MP, P2D, and SPME models on fast charging: Fast charging for lithium-ion batteries is a critical challenge for the widespread adoption of electric vehicles. The MP, P2D, and SPME models are simulated under fast charging conditions to provide insight into the physical process during fast charging. The performances of these models with fast charging are compared. The experiments are carried out by charging the cell from 0% SOC to 4.2 V with 5C constant-current-constant voltage (CCCV). The positive and negative electrode interfacial current density at the end of charge are depicted in Figs. 4(a) and 4(b), respectively. Not surprisingly, the current density of SPME is constant throughout this CCCV charge process. This is because the SPME is based on the assumption of average current. The P2D and MP models produce nonlinear distributions of the interfacial current density. The distribu-

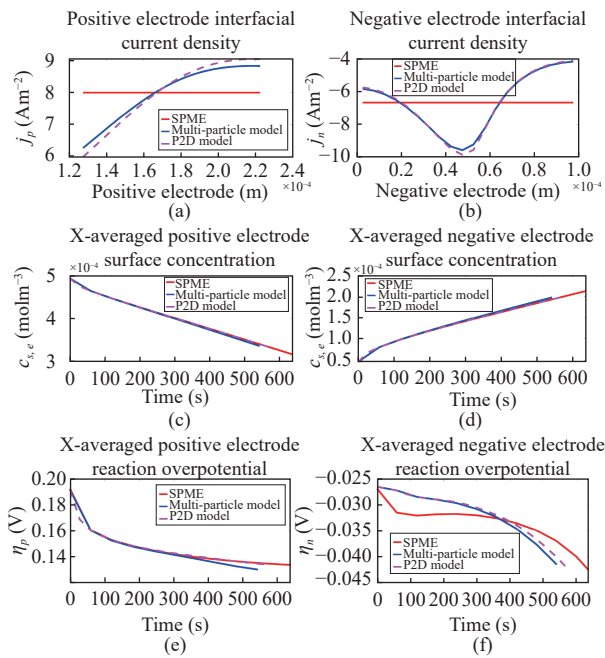


Fig. 4. Solid-phase electrochemical states across 5C CCCV charge test with single particle model with electrolyte (SPME), multiparticle model, and P2D model. (a) Positive electrode interfacial current density at the end of charge; (b) Negative electrode interfacial current density at the end of charge; (c) X-averaged positive electrode surface concentration; (d) X-averaged negative electrode surface concentration; (e) X-averaged positive electrode reaction overpotential; (f) X-averaged negative electrode reaction overpotential.

tion of particle radius and diffusion timescales shows that the MP model with a greater scope of internal heterogeneities has a more moderating interfacial current density compared with the DFN model. The differences between these three models for the solid-phase lithium-ion surface concentration are observed as shown in Figs. 4(c) and 4(d). This is attributed to the variation of interfacial current density with these models. The solid overpotential results are shown in Figs. 4(e) and 4(f). η_p decreases significantly in three models. Compared with SPME and P2D model, η_p in the MP model decreases more significantly as depicted in Fig. 4(e). Similarly, η_n in the MP model increases more significantly as shown in Fig. 4(f). It is implied that a more significant non-uniformity of ion concentration is developed inside positive and negative electrode particles in MP model. As the MP model considers the particle size distribution while the P2D and SPME models neglect it, large particles exist in the MP model, where a significant concentration gradient in electroactive

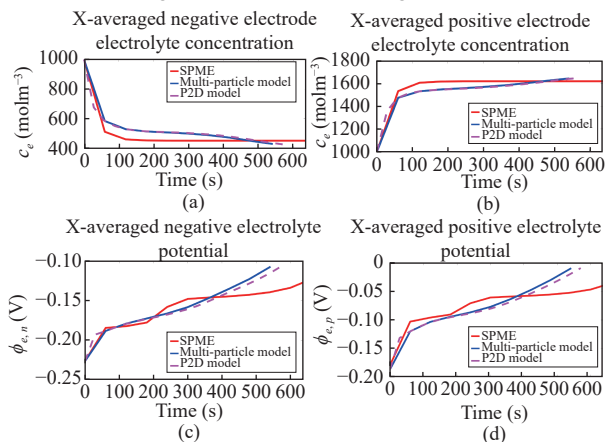


Fig. 5. Electrolyte-phase electrochemical states across 5C CCCV charge test with single particle model with electrolyte (SPME), multiparticle model, and P2D model. (a) Electrolyte current density; (b) X-averaged separator electrolyte concentration; (c) X-averaged negative electrode electrolyte concentration; (d) X-averaged positive electrode electrolyte concentration.

particles in positive and negative electrode is developed.

On the other hand, more considerable variation of overpotential in the MP model than the SPME and P2D models is resulted from PSD of electroactive particles in positive and negative electrodes in the MP model. The PSD could lead to the different specific electroactive surface area. The specific surface area in the P2D model is calculated as $a_s = \epsilon_s \times 6/D_{50}$, while in the MP model, $a_s = \epsilon_s \times 6/D_{area}$. Since the area-averaged diameter is larger than the number average particle diameter D_{50} , so the specific electroactive surface area is smaller in the MP model and produces the larger overpotential variation in the MP model. For electrolyte-phase variables depicted in Fig. 5, similar behaviors could be observed. The SPME model has a flat electrolyte distribution due to the local linearization assumption as shown in Figs. 5(a) and 5(b). The difference between the MP and DFN model is clear. As shown in Figs. 5(c) and 5(d), $\phi_{e,n}$ and $\phi_{e,p}$ predicted by three models decrease rapidly. Comparatively, $\phi_{e,n}$ and $\phi_{e,p}$ in the P2D and SPME models are significantly lower than the MP model. This result indicates that the ion transport in the electrolyte is hindered due to PSD in the MP model compared with P2D and SPME models. Hence, it is critical to reduce the polarization composition for cells with thick electrodes in order to improve the rate performance.

Based on the comparison results, the PSD of electroactive particles leads to different model performances between P2D and SPME models. Since the particle size is assumed as uniform in the P2D and SPME models, the deviation of the simulated power capability is observed when the particle size is largely distributed.

Conclusions: This paper presents an electrochemical model considering the PSDs. Three PSDs quantification methods are evaluated: area-based, number-based, and volume-weighted algorithms. The results show that the number-based method could produce a smaller mean particle radius and PSD. It is found that small-scale PSD leads to lower internal resistance and local interfacial current density. This illustrates that a small particle size could achieve a higher electrode capacity. Comparative studies between the SPME, multiparticle model, and P2D model show that the inclusion of PSD would cause variations of solid-phase local interfacial density compared with the SPME and P2D model.

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